

**Multiscale Simulation of Viscoelastic Flows:
Applications to Kinetic Theory Models of Polymer Melts
and Liquid Crystalline Polymers**

by

Jason Ka-Chun Suen
B.S. Chemical Engineering
University of Wisconsin at Madison, 1996

Submitted to the Department of Chemical Engineering in
Partial Fulfillment of the Requirements for the Degree of

Doctorate of Philosophy in Chemical Engineering

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 2002

[February 2003]

© 2002 Massachusetts Institute of Technology. All Rights Reserved.

Author

Department of Chemical Engineering
September 18, 2002

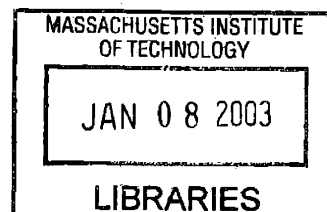
Certified by

Robert C. Armstrong
Professor of Chemical Engineering
Thesis Supervisor

Accepted by

Daniel E. Blankschtein
Professor of Chemical Engineering
Chairman, Committee for Graduate Students

ARCHIVES



V.1

Multiscale Simulation of Viscoelastic Flows: Application to Kinetic Theory Models of Liquid Crystalline Polymers and Polymer Melts

Jason K.C. Suen

Submitted to the Department of Chemical Engineering on September 1, 2002 in partial fulfillment of the requirements for the Degree of Doctorate of Philosophy in Chemical Engineering

Abstract

Knowing and understanding the dynamics and molecular configurations of polymer molecules is important for efficient process design and novel product development. Much research has been focused on combining molecular simulations and traditional fluid mechanics computations to simulate the behavior of polymeric liquids in a fabrication process. These simulation approaches require solution of the coupled set of the equations of change, the governing equations from kinetic theory, and the flux expressions that map molecular configurations to macroscopic quantities. Most complex flow simulations so far make use of a mixed finite element method to calculate the velocity field, with stress tensor evaluated by using a stochastic simulation method. This so-called CONNFESSIT approach suffers from both a large memory requirement and stochastic noise. This thesis focuses on the development and application of a *fully deterministic* numerical approach for computing viscoelastic flows with constitutive descriptions based directly on diffusion equations from kinetic theory. The numerical approach is based on an operator splitting time integration method that decouples the calculation of microstructure by solution of a hyperbolic diffusion equation from the velocity and pressure field evolution, which is obtained by solution of a generalized Stokes problem. The generalized Stokes problem is written in the DEVSS-G formulation, where a direct interpolation of the components of the velocity gradient tensor is introduced.

The efficiency and robustness of this numerical method is demonstrated through calculating the viscoelastic flows of a modified Doi model for liquid crystalline polymer and a number of reptation models for polymer melts in different flow geometries. Simulations of the original Doi model with the Maier-Saupe potential in a pressure-driven channel flow by Nayak showed disclination formation due to the shear-rate-dependent frequencies of the tumbling/wagging states of the Doi model in a shear or mixed shear flow. The lack of an intrinsic length scale in the model leads to an infinitesimal structure refinement that eventually causes numerical instabilities. In this thesis, the effect of concentration variation is incorporated to develop a modified Doi model for introducing an intrinsic length scale through translational diffusion. This changes the mathematical characteristics of the spatial variation of the underlying diffusion equation from that of a hyperbolic equation to that of an elliptic equation. The resulting elliptic diffusion equation is then solved by using a local discontinuous Galerkin method, where an auxiliary variable is introduced to rewrite the elliptic diffusion equation into a pair of formal, hyperbolic equations, which in turn is solved by the standard discontinuous Galerkin method. Unlike the original Doi model, a steady state is reached for a variety of De . Although there is structure variation across the channel width, the director profiles point uniformly along the flow direction. The lack of

disclination formation may be rectified by introducing Frank elasticity into the modified Doi model. However, the imprecise mathematical characteristic of the resulting diffusion equation makes the application of the mixed wavelet-Galerkin/finite-element method difficult.

Reptation is one of the most useful physical pictures for describing the dynamics of an entangled polymer system. Early implementations of reptation into a constitutive equation (such as the Doi-Edwards or Curtiss-Bird models) neglect some important non-reptative relaxation mechanism and hence fails to describe a number of important rheological properties. Although various advanced reptation models developed in the past decade can predict quantitative features of most homogeneous flows, the complicated mathematical structure of the resulting diffusion equations makes complex flow calculations difficult. In this thesis, an extension of the wavelet-Galerkin/finite-element method is used to simulate two different reptation models, a double reptation model and a thermodynamically admissible reptation model. The dynamics of these models in flow around an isolated cylinder confined in a planar channel is calculated to benchmark the numerical algorithm and the dynamics of the reptation models. Both serial and parallel computation strategies are implemented. For the double reptation model, the efficiency of the deterministic approach is compared with a stochastic approach based on the Brownian configuration fields (BCF) method. Although the speed of the BCF method is in general comparable to the fully deterministic approach, the very large memory requirement for the stochastic approach limits the size of the problem that can be solved. Furthermore, the stochastic noise of the BCF method may lead to difficulties in a quantitative analysis such as a stability calculation. The flow kinematics resulting from the double reptation model show minimal effects of memory due to the lack of some essential non-reptative mechanism such as chain-stretching and constraint release. Furthermore, the drag force exerted on the cylinder surface decreases monotonically with increasing Deborah number De .

To test whether or not the advanced reptation models will show stronger memory effects as compared to the double reptation model, a thermodynamically admissible reptation (TAR) model developed by Fang et al. is simulated with the mixed finite-Fourier/wavelet-Galerkin/finite-element method. This model incorporates a number of non-reptative effects including chain-stretching, convective constraint release, and alignment-coupling. We first examine the material functions in simple, homogeneous flows to test the usefulness of the finite-Fourier/wavelet-Galerkin method for the configuration space of the TAR model. The simulations of the flow around an isolated cylinder confined in a channel show significant changes in the flow kinematics even at low De . This is in contrast with the predictions of most constitutive equations, for which limited modifications of the flow kinematics are observed. Although rich dynamics in the kinematics are observed, the drag force acting on the cylinder surface still decreases monotonically with increasing De . To verify the usefulness of this TAR model for describing the rheology of an entangled polymer systems, comparisons with experimental data for the benchmark, complex flow geometries of entangled polymer systems are needed.

Thesis Supervisor: Robert C. Armstrong
Title: Professor of Chemical Engineering

Acknowledgments¹

No word can describe how grateful I am for the support from those who help me to overcome so many huddles and eventually leads to this thesis. First and foremost, I must thank my advisor, Bob Armstrong, for his guidance and support. His continuous confident in believing in my ability to develop my own research interests is extremely important for my professional growth. He has also provided a shelter for me to do research that I believe in, despite disagreements from other researchers in the field. I always know that he is a great mentor but until now, I can truly understand how excellent he really is.

I would also like to thank my thesis committee, Professors Bob Brown, Daniel Blank-schtein and Greg Rutledge for their input to my project, attending the various committee meeting, reading through this thesis, and providing valuable comments and suggestions. Bob's insight on numerical method and his challenging on the feasibility of my approaches leads to various break-through in this thesis. My insights on rheology and engineering research have been expanded tremendously by the "rheology family" at MIT (Professors Gareth McKinley, Ken Beers, and Pat Doyle).

It is hard for me to imagine where I would be now if I had not learnt from Professors Bird and de Pablo of the University of Wisconsin during my undergraduate studies. Their trainings and guidance are an integrated part of my current vision on engineering research. Professor Bird introduced me to the field of rheology and the application of kinetic theory. His over-whelming recommendation on this group makes coming to MIT and joining this group a easy decision. Professor de Pablo expanded my understanding on nonequilibrium

1. This work was supported in part by the ERC Program of the National Science Foundation under Award Number EEC-9731680

statistical mechanics beyond the kinetic theory level. This provided me with the intuition and insights on the molecular modeling at multiscale levels, which is necessary for my success in graduate school, as well as getting myself ready for future research.

The learning curve in graduate school is long and difficult. No single graduate student could get through it without assistance from other members of the group. I am fortunate to meet and work with a number of highly intelligent and successful graduate students (Indranil, Yong, Mark, Radha, Garrent, Howard, Tony, Junsuo, Alice, Lars, Zhihong, Wei, Yoo, Talid, Tatsuo, Aleksei, Scott, Irina, Arvind, Michelle, Christine, Nina, David, Fred). Indranil, the first person I know from MIT, helped me tremendously in enlarging my vision on engineering science and showed me various ways that I could apply my knowledge into areas of practical interests. Yong sets a great example of how a good postdoc should be. He is a very focused individual who worked closely with nearly everyone in the group and helped each other through various issues. I hope I could follow his footsteps and become an efficient postdoc researcher and a distinguished faculty member in a prestige school.

Because of Bob's administrative duties, a lot of weekly meetings have to be rearranged to fit his extremely tight schedule. To this end, I owe a great debt to all Bob's assistants, Arline, Molly, Emmi, and Keryx. I would also like to thank Carol Phillips for relentlessly emailing me back and forth to set up time for committee meeting with Bob Brown, as well as Elaine, Janet, Anne, and Suzanne for taking care of many of the paper works for me.

Having a "life" is essential for a graduate student to balance out the stress and frustrations from various research activities in graduate school. I am glad to meet and become long-lasting friends with people both from the professional cycle and outside of the pro-

fessional cycles (Teddy, Peter, Siu, SM, Vivian, Vicky, Karen(s), Dorothy, Lisa, Alex, Thomas, Phillip, Brenda). I thank them for their supports over all these years.

I would also like to thank my parents and my sister for their continuous support and encouragement. Without them, I do not think I would have studied in the states for my undergraduate degree. I thank my dad and mom for arranging all the decent schools since kindergarten. Their continuous push me to study hard was the main reason that I was able to study at the University of Wisconsin for undergraduate and MIT for graduate school.

With my degree being expected, the best thing I get from my graduate life is my girlfriend, Catherine Suen. Her presence brightens my life in many different ways. I thank her for staying with me to give love, understanding and support. She scarifies a lot of career opportunities and takes a much more difficult career path just for me. Boston is never as enjoyable before she comes to stay with me. We explored so many different places of Boston since she came to Boston. She also takes good care of nearly every aspects of my life and let me focus on my research. Now I am moving to San Diego, I thank her for staying with me and I hope we will walk together through all the uncertainties in our future.

Table of Content

1	Introduction.....	23
1.1	Motivation.....	23
1.2	Analysis of viscoelastic flow.....	25
1.3	Constitutive modeling of polymeric liquid.....	28
1.4	Numerical analysis of viscoelastic flow phenomena.....	30
1.5	Goal and outline of the thesis.....	33
2	Microstructural Modeling of Macromolecules.....	39
2.1	Introduction.....	39
2.2	Micromechanical models.....	40
2.3	The Geometry and Coordinate Systems used for Chain-like Molecules.....	47
2.3.1	Generalized coordinates.....	48
2.3.2	Constrained coordinates.....	51
2.4	Kinetic Theory.....	53
2.4.1	Polymer Singlet Distribution Function.....	56
2.4.2	Equation of Continuity.....	66
2.4.3	Equation of Motion.....	68
2.5	Nonequilibrium thermodynamics.....	71
2.6	Issue of coarse-graining and mapping evolution equations of different micromechanical models for representing the same polymer species.....	76
2.6.1	Model development through parameter mapping.....	77
2.6.2	Formal projection operator method for developing dynamic equations.....	80
2.6.3	Hybrid method between parameter mapping and projection operator methods: the adaptive description method.....	83
3	Numerical Analysis of Molecular Orientation in Rheological Experiments.....	89
3.1	Introduction.....	89
3.2	Direct Simulation of the Fokker-Planck Equation.....	89
3.2.1	Theory and computation using scaling function expansions.....	92
3.2.2	Applications of direct simulation of Fokker-Planck equation.....	96
3.3	Stochastic Simulations.....	98
3.3.1	Fundamentals of stochastic differential equations.....	99
3.3.2	Application of Brownian dynamics for rheological calculations.....	103
3.3.3	Brownian dynamics simulations of wall effects on molecular conformations.....	103
3.3.4	Brownian dynamics simulation of more realistic molecular models.....	105
4	Numerical Algorithm for Computing Rheological Dynamics of Microstructural Models.....	111
4.1	Introduction.....	111
4.2	Continuum Simulation Methods.....	113
4.2.1	Mixed finite element analysis for the Stokes problem.....	113
4.2.2	Mathematical formulation of a viscoelastic flow calculation.....	117

4.2.3	Development of a fully implicit, element-by-element decomposition algorithm for continuum calculations.	121
4.2.4	Topological sort	123
4.2.5	Simulation of Integral Constitutive Models	127
4.3	Hybrid Simulations using Brownian Dynamics	129
4.3.1	Lagrangian CONNFFESSIT Method	131
4.3.2	Eulerian CONNFFESSIT method	132
4.4	Hybrid Simulations using Direct Solution of the Fokker-Planck Equation...	133
4.5	Use of Distributed Computing Environment for Multiscale Simulation	136
5	Survey of rheological modeling of liquid crystalline polymers and polymer melts	139
5.1	Introduction.....	139
5.2	Kinetic theory for liquid crystalline polymers.....	141
5.2.1	Model description	141
5.2.2	The intermolecular potential	143
5.2.3	The kinetic theory of liquid crystalline polymers	149
5.2.4	Linear stability analysis around the isotropic state	154
5.3	Reptation models for concentrated polymer solutions and melts	158
5.3.1	Doi-Edwards model with independent alignment	159
5.3.2	Application of kinetic theory in modeling reptation dynamics of polymer melts	162
5.3.3	Advanced physics and non-repetative relaxation mechanisms	163
6	A wavelet-Galerkin method for simulating the Doi model with orientation dependent rotational diffusivity	173
6.1	Introduction.....	173
6.2	Kinetic theory of liquids of rigid rod-like polymers.....	178
6.2.1	Intermolecular interaction potential	180
6.2.2	Structure tensor and structure parameters	182
6.3	Numerical methods	184
6.3.1	Trial and test functions	185
6.3.2	Time integration method	189
6.3.3	Solution method for the linear algebra problem and computational issues	191
6.4	Convergence study.....	193
6.4.1	Steady state simulations with $De = 0$	194
6.4.2	Convergence studies for time-dependent simulations	202
6.5	Nonlinear dynamics of the exact Doi model	206
6.5.1	Dynamics at low De	206
6.5.2	Dynamics at high De	212
6.5.3	Nonlinear stability analysis for the exact Doi model during transitions between in-plane states	215
6.6	Conclusions.....	220
7	Complex flow simulations of Doi model.....	223
7.1	Introduction.....	223

7.2	Governing Equations	227
7.2.1	Equation of change	227
7.2.2	Doi model with concentration fluctuation	228
7.3	Numerical method.....	230
7.3.1	Finite element approximation to the equations of change	231
7.3.2	Wavelet-Galerkin/Finite element method	231
7.3.3	Local discontinuous Galerkin method	232
7.3.4	Time integration algorithm	233
7.3.5	Solution strategy for solving for the nodal values of the distribution function	235
7.4	Simulation Results for a Planar Pressure-driven Channel Flow	237
7.4.1	Doi model	237
7.4.2	Effect of spatial concentration nonuniformities	244
7.5	Conclusion	248
8	A Mixed Finite-Element/Wavelet-Galerkin Method for Multiscale Simulations of Viscoelastic Flows with Reptation Models for Concentrated Polymer solutions and Melts	251
8.1	Introduction.....	251
8.2	Mathematical formulation.....	255
8.2.1	Generalized Double Reptation model	256
8.3	Numerical method.....	258
8.3.1	Discretization of the diffusion equation	258
8.3.2	Solution strategy for the diffusion equation	261
8.3.3	Time integration algorithm	263
8.3.4	Brownian configuration fields method	265
8.3.5	Other computational issues	267
8.4	Sample calculation for flow around an isolated cylinder in a channel	268
8.4.1	Convergence study	270
8.4.2	Parallel efficiency of the wavelet-Galerkin/Finite Element method ..	278
8.4.3	Comparison with Brownian configuration fields calculations	283
8.4.4	Effect of different viscous stress expressions on the complex flow behavior at $De = 1$	286
8.4.5	Effect of different De on the structure formation	287
8.5	Conclusion	289
9	Viscoelastic Flow Simulations of an Advanced Reptation Model by a Coupled Wavelet-Galerkin/Finite-Element Method.....	293
9.1	Introduction.....	293
9.2	Governing equations.....	297
9.2.1	Mathematical formulation	297
9.2.2	Thermodynamically admissible reptation model for fast flows of entangled polymers	298
9.3	Numerical method.....	303
9.3.1	Spatial discretization	303
9.3.2	Time integration algorithm	307

9.3.3	Solution strategy	310
9.4	Review of numerical results for simple, homogeneous flows	312
9.4.1	Simple shear flow	313
9.4.2	Planar Elongational flow	320
9.5	Simulation of complex flows	322
9.5.1	Mesh Convergence	324
9.5.2	Predictions of the TAR model	326
9.5.3	Drag force calculation	332
9.6	Conclusion	334
10	Conclusion	337
10.1	Summary	339
10.1.1	General numerical approach for multiscale simulation of viscoelastic flows	339
10.1.2	Modeling and simulation of kinetic theory models for liquid crystalline polymers	341
10.1.3	Numerical simulation of confined flow around a cylinder in a planar channel for reptation models	344
10.2	Suggested future work	346
Bibliography		351

List of Figures

Figure 1.1: Striking flow phenomena exhibited by viscoelastic liquids. (a) Elastic recoil [19]. When pouring a polymer solution into a container, a cut in midstream leads to the liquid above the cut springs back to the beaker and the lower portion falls to the container; (b) Rod-climbing or Weissenberg effect [19]. Polymer solution climbs the rotating rod in a fixed cylinder; (c) Drag reduction [19]. Friction factor of dilute polymer solution is smaller than that of the solvent in the turbulent regime; (d) Die (or extrudate)-swell [19]. Polymer solution shows a dramatic increase in diameter as it flows downward out of the tube. .25

Figure 2.1: A schematic representation of various micromechanical models and their interconnections used in studying polymer properties. ℓ_p is the Khun segment length or the persistence length as defined by Equation (2.1). 41

Figure 2.2: Concept of persistence length, ℓ_p 43

Figure 2.3: Comparison of different force-extension relationships for three spring laws: Inverse Langevin force law (solid line), FENE force law (dash line), and Hookean force law (dotted line). The dashed line at $Q/Q_0 = 1$ corresponds to the maximum possible extension for inverse Langevin and FENE force law at which both of these force laws will diverge. 45

Figure 2.4: Equations of change and the flux expressions obtained from the general equation of change (Eqn. 2.19) and how the five main assumptions are used to get expressions for the fluxes for a specific molecular model. Here, $\delta(x)$ is the Dirac delta function. 56

Figure 2.5: Linear viscoelastic properties for the 6-bead Rouse chain, the mapping between a 6-bead Rouse chain and a Hookean dumbbell model based on nkT and λ , and the new mapping (Eqn. 2.79) strategy based on the viscosity and first normal stress coefficient.79

Figure 2.6: Start-up of steady elongational flow behavior for the 6-bead Rouse chain, the traditional mapping between a 6-bead Rouse chain and a Hookean dumbbell model, and the new mapping (Eqn. 2.79) strategy 80

Figure 2.7: Comparison of the ALS model and a FENE chain model representation of an equilibrium coil, a polymer stretched to small strains in a rapid extensional flow, and a fully stretched polymer. $Q_{\max}$ is the maximum (contour) length of the molecule, and Q_0 is the maximum length of a segment. 85

Figure 2.8: Total drag on a cylinder in flow past a linear array of cylinders confined in a channel. Predictions of the Oldroyd-B, FENE-P, ALS-C (closed version of the adaptive length scale model) models as a function of We are shown. Experimental data for the drag on the cylinder are also presented. Cylinder spacing $L = 6R$, where R is the radius of the cylinders. Figure reproduced from Joo et al. [89].....87

Figure 2.9: Asymmetric structure of the perturbation of $\mathbf{u}$ in a stability analysis of a flow around a cylinder confined in a planar channel with the ALS-C model.....87

Figure 3.1: Contour plots for the rigid rod distribution function in shear flow at $De = 10$. The figure on the left is reproduced from Stewart and Sørensen [204]; the figure on

the right is the calculation by the wavelet-Galerkin method with a 32×64 Daubechies 6 scaling function expansion. The peak of the function lies at $\theta = 13^\circ$ 91

Figure 3.2: Snapshots from a sample trajectory of a 20-bead Kramers chain in steady shear flow with. One end of the chain has been tagged by a filled bead. The dimensionless time shown is . Here, ζ is the drag coefficient for a bead and a is the length of the rod connecting the beads. Reproduced from Liu [140]......106

Figure 4.1: Illustration of the index one set of DAEs for a typical viscoelastic problem leading to a set of ODEs, which in turn may be solved by time integration methods such as the θ method or standard fourth order Runge-Kutta method. Developed based on Smith [199]. 120

Figure 4.2: A graph of numbers that represents order of elements in a streamline direction. The flow occurs according the the blue arrows 124

Figure 4.3: Comparison between Lagrangian and Eulerian implementation of multiscale calculation with stochastic simulation. (a) Lagrangian implementation where the location of each molecule is continuous in the computational domain; (b) Eulerian implementation where spatially, highly correlated Brownian force leads to favorable variance reduction. 131

Figure 5.1: The rigid dumbell model 142

Figure 5.2: Dispersion relationship for the three most dangerous modes for the exact Onsager model with $U = 12$ 156

Figure 5.3: Comparison between the dispersion relationship for the second-order approximate model (diamonds), Maccurri and Greco potential (upper triangle), and the exact Onsager model (empty circles) at small (upper figure) and large wavenumbers (lower figure). 158

Figure 6.1: Typical Daubechies scaling functions in physical space and their power spectra. (a) First-order Daubechies scaling function with four coefficients in h_0 ; (b) power spectrum of the first-order Daubechies scaling function; (c) fourth-order Daubechies scaling function with 10 coefficients in h_0 ; (d) power spectrum of the fourth-order Daubechies scaling function (e) 7th-order Daubechies scaling function and wavelets with 16 coefficients in h_0 ; (f) power spectrum of the 7th-order Daubechies scaling function... 188

Figure 6.2: Convergence properties of the discretization error for various scaling functions. Discretization error is defined as the L_2 norm of the difference between the nodal value of Onsager's trial function with $\alpha = 14.2$ and the nodal value of the same function calculated from the projection of the scaling function expansion. The convergence rates for various Daubechies scaling functions are (from top to bottom): 2.95 for D4, 3.85 for D6, 6.05 for D10, and 7.48 for D14. 196

Figure 6.3: Convergence properties of the approximation error in representing S_2 of Onsager's trial function with $\alpha = 14.2$ by using various Daubechies scaling functions, D4, D6, D10, and D14. The reference value of S_2 is calculated from Eq. 6.23. 197

Figure 6.4: Effect of mesh refinement on the computation of the distribution function in the equilibrium problem with $U = 10.67$ and the director pointing along the x_3 direction. D10 scaling functions are used as the basis functions. Successive meshes correspond to 16, 32, and 64 basis functions per interval of π	200
Figure 6.5: Effect of h-refinement on the convergence of a time-periodic state of the Doi model ($De = 30$, $U = 12$); $\Delta t = 0.01$. D10 scaling functions are used as basis functions. Successive meshes correspond to 16, 32, and 64 basis functions per interval of π	203
Figure 6.6: Effect of p-refinement on the convergence of a time-periodic state of the Doi model ($De = 30$, $U = 12$); $\Delta t = 0.01$. 32 basis functions are used per interval of π . D6, D10, D14, and D16 scaling functions are used in the simulation.....	204
Figure 6.7: Convergence study for the time integration scheme with different Δt by simulating the time-periodic state of the Doi model at ($De = 30$, $U = 12$). 32 D10 basis functions are used per interval of π . The four values of Δt used in the simulations are 0.03, 0.01, 0.005, and 0.001. Except for $\Delta t = 0.03$, all of the simulation results superpose.	205
Figure 6.8: Convergence study for the time integration scheme with different Δt and different interpolates (x^* in Eq. 6.17). The circle symbols correspond to the simulation results for a second-order interpolate and the diamond symbols correspond to the simulation results for a third-order interpolate. The reference point is the structure parameter at dimensionless time equal to 2 during the start-up of simple shear flow from an isotropic initial distribution function of the Doi model with $De = 30$, $U = 12$. 32 D10 basis functions are used per interval of π . The convergence rate for the second-order interpolate is 2, and the convergence rate for the third-order interpolate is 3.5.....	206
Figure 6.9: Effect of initial director orientation on the dynamics of (a) $S_{22} - S_{33}$ and (b) S_3 for $U = 10.67$ and $De = 7$. The simulations employ 32 ¥ 64 D10 scaling functions with $\Delta t = 0.01$. The initial director angle is calculated from Onsager's trial function. The initial director angles from bottom to top are 0° , 15° , 30° , 50° , 65° , and 90° in part (a).....	208
Figure 6.10: Dynamics of the distribution function of the Doi model for tumbling motion with $U = 10.67$ and $De = 7$. The simulations employ 32 ¥ 64 D10 scaling functions with $\Delta t = 0.01$. Time is made dimensionless by λ . The period of this tumbling state at $De = 7$ is 1.8. The location of minimum contour is denoted by "×" and the increment of each contour line is 0.1 with the first contour line value equal to 0.1. The location and magnitude of the peak of the distribution function as well as its breadth depend on time. This suggests that the dynamics of the distribution function is much more complicated than the description given by director or structure tensor theories.	210
Figure 6.11: Dynamics of a distribution function of the Doi model for kayaking motion with $U = 10.67$ and $De = 7$. The simulations employ 32 ¥ 64 D10 scaling functions with $\Delta t = 0.01$. Time is made dimensionless by λ . The period of this kayaking state at $De = 7$ is 1.8. As in Fig. 6.10, the location of minimum contour is denoted by "×"; and the increment between each contour line is 0.1, with the value of the first contour line equal to 0.1. The location and the magnitude of the peak, breadth, and even the skewness of the distribution function all depend on time.	211

Figure 6.12: Effect of initial director orientation on the dynamics of (a) $S_{22} - S_{33}$ and (b) S_3 for $U = 10.67$ and $De = 12$. The simulations employ 32 $\times$ 64 D10 scaling functions with $\Delta t = 0.01$. The initial director angle is set by using Onsager's trial function. The initial director angles from bottom to top are 0° , 30° , and 90° in part (a). 213

Figure 6.13: Dynamics of the distribution function of the Doi model in a wagging motion with $U = 10.67$ and $De = 12$. The simulations employ 32 $\times$ 64 D10 scaling functions with $\Delta t = 0.01$. Time is made dimensionless by λ . The period of the wagging state at $De = 12$ is 0.90. As in Fig. 6.10 the location of minimum contour is denoted by " $\times$ "; and the increment of each contour line is 0.1, with the value for the first contour line set to 0.1. The location, peak magnitude, and breadth of the distribution function all depend on time..... 214

Figure 6.14: The amplitude, A , of the periodic, in-plane motion of S_3 for $U = 10.67$ and various De . The simulations employ 32 $\times$ 64 D10 scaling functions with $\Delta t = 0.01$. The maximum at $De = 7.5$ corresponds to the transition between the tumbling state and the wagging state. 215

Figure 6.15: The amplitude plot for $U = 10.67$. The simulations employ 32 $\times$ 64 D10 scaling functions with $\Delta t = 0.01$. Numerical data are fit to the equation, $A = A_0(De_c - De)^\alpha$; and α and De_c are found to be 0.5 and 13.52, respectively. The insert provides the definition for A in the time-periodic state.....217

Figure 6.16: Disturbance plots for $U = 10.67$. The simulations employ 32 $\times$ 64 D10 scaling functions with $\Delta t = 0.01$. The measure of the disturbance is the L_2 norm of the deviation of the distribution function from the steady-state distribution function. The curves ranging from the bottom to top in the figure correspond to $De = 13.8, 13.6, 13.5, 13.4, 13.25$, and 13.0 . The insert shows the interpolation for the critical De from the growth rates of the disturbance plots. The curve fit is given by $\sigma = 2.429 - 0.1797De$. The critical De , which corresponds to $\sigma = 0$, is 13.52. 218

Figure 6.17: Phase diagram of the critical De in the wagging to flow aligning state transition for the Doi model with (a) the Onsager potential with anisotropic drag (circular symbols) and (b) the Maier-Saupe potential with isotropic drag (triangular symbols). The data for (b) are from Nayak [161]......220

Figure 7.1: Time evolution of centerline velocity for pressure driven channel flow of the Doi model with $U = 6$. Blue solid line corresponds to the calculation with $De = 1$, and the red solid line corresponds to the calculation with $De = 5$ 238

Figure 7.2: Time evolution of the cross-stream structure profile in pressure-driven channel flow at $U = 6$. Mesh contains of 60 elements cross-stream. Results are shown at dimensional times of (a) 0, (b) 5, (c) 15, (d) 25, (e) 35, (f) 45 relaxation times.....240

Figure 7.3: Time evolution of the cross-stream structure profile in pressure-driven channel flow at $De = 5$ and $U = 6$. Mesh contains of 60 elements cross-stream. Results are shown at dimensional times of (a) 0, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100 relaxation times. 243

Figure 7.4: Time evolution of centerline velocity for pressure driven channel flow for the liquid

crystalline model that allows for spatially varying concentration. We take $U = 6$, $\sigma = 1$ and $D_{tr} = 0.04$ 245

Figure 7.5: Time evolution of the cross-stream structure profile in pressure-driven channel flow at $De = 1$ and $U = 6$. Mesh contains 60 elements in the cross-stream. Results are shown at dimensional times of (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, and (f) 60 relaxation times. A steady structure profile is achieved after 40 relaxation times.....246

Figure 7.6: Time evolution of the cross-stream structure profile in pressure-driven channel flow at $De = 5$ and $U = 6$. Mesh contains 60 elements in the cross-stream direction. Results are shown at dimensional times of (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, (f) 30 relaxation times. A steady state structure profile is achieved after 20 relaxation times.....247

Figure 7.7: Steady state profiles of the structure parameter and the number density for two different values of De 248

Figure 8.1: Finite element mesh M2 for calculation of the viscoelastic flow of a double reptation model past an isolated cylinder in a channel with $H = 2$ 270

Figure 8.2: Distribution of velocity and pressure fields calculated with the wavelet-Galerkin/Finite-Element method for the Doi-Edwards model for $De = 1$ 272

Figure 8.3: Dimensionless velocity profile in the gap between the cylinder and the wall. The three results shown for the Doi-Edwards model corresponds to the calculations with M1 (square symbol), M2 (cycle symbol), and M3 (triangle symbol). The Newtonian flow field is shown as a dashed-line for comparison. 273

Figure 8.4: Microstructure $\kappa\mu\mu\lambda_{yx}$ profile in the gap between the cylinder and the wall. The three results shown for the Doi-Edwards model correspond to calculations with by M1 (triangle symbols), M2 (square symbols), and M3 (circular symbols).....274

Figure 8.5: Dimensionless velocity gradient (G_{yx}) profile in the gap between the cylinder and the wall. The two results shown for the Doi-Edwards model correspond to calculations with different resolutions of the wavelet-Galerkin method: Circular symbols correspond to the calculation with a 16×32 D6 scaling function expansion; triangular symbols correspond to the calculation with a 32×64 D6 scaling function expansion. The Newtonian flow field is shown as a dashed-line for comparison. 275

Figure 8.6: Microstructure profile in the gap between the cylinder and the wall. The two results shown for the Doi-Edwards model correspond to the calculation by different resolutions of the wavelet-Galerkin method: Circular symbols correspond to the calculation with a 16×32 D6 scaling function expansion; triangular symbols correspond to the calculation with a 32×64 D6 scaling function expansion. 275

Figure 8.7: Dimensionless velocity profile in the gap between the cylinder and the wall. The three results shown for the Doi-Edwards model correspond to the calculations with different number of Fourier modes: Circular symbols correspond to one Fourier mode; triangles correspond to five Fourier modes, and squares correspond to 10 Fourier modes. The Newtonian flow field is shown as adashed-line for comparison. 277

Figure 8.8: Microstructure profile in the gap between the cylinder and the wall. The three

results shown for the Doi-Edwards model correspond to the calculations by with one (square symbol), five (circular symbol), and 10 (triangular symbol) Fourier modes. The small insert corresponds to same results enlarged for $y \in [1, 1.2]$ 277

Figure 8.9: Parallel computing strategy for the multiscale simulation of viscoelastic flows with diffusion equations. Communications required at each time step for the computation are in dashed boxes. 280

Figure 8.10: Parallel efficiency for the solution of the Fokker-Planck equation for the Doi-Edwards model by the use of wavelet-Galerkin method. The filled symbols corresponds to the speed-up for a fixed problem size using an increasing number of processors for the solution; the empty symbols correspond to speed-up evaluated for a series of progressively refined meshes (larger problems) designed so that the load per processor remains constant. 283

Figure 8.11: Simulation result for the drag force exerted on the cylinder for the Doi-Edwards model at $De = 1$. All calculations are performed with mesh M1. The black solid line corresponds to the wavelet-Galerkin/finite element calculation with 5 Fourier mode and 16×32 D6 scaling function expansions. The three fluctuating curves on top of the black solid line corresponds to the Brownian configuration fields calculations with different number of trajectories: blue solid line corresponds to 4,000 trajectories; the green dotted line corresponds to 64,000 trajectories, and the red dashed line corresponds to 112,000 trajectories. 285

Figure 8.12: Statistical error for Brownian configuration fields calculations of the Doi-Edwards model with mesh M1. Solid symbols corresponds to the statistical error measured by the fluctuation of the drag force at steady state. The correlation equation of the solid line is . Empty symbols corresponds to the error measures represented by the accuracy of the drag force calculation from a reference drag force, $\langle \rangle$. The correlation equation for the dashed line is . The reference drag force is chosen to be 96.2086, which is the value computed by using the wavelet-Galerkin/Finite-Element method with 5 Fourier modes and a Daubechies 6 scaling function expansion. 286

Figure 8.13: Comparison between the values of xx component of the stress tensor for the double reptation model with different stress tensor expressions, Eqns 8.5 and 8.6. in Eqn. 8.5 = in Eqn. 8.6 = 0.03. The red solid line corresponds to the calculation by Eqn. 8.5 and blue dash line corresponds to the calculation by Eqn. 8.6. 287

Figure 8.14: The evolution of the xx component of the stress tensor for the Doi-Edwards model along the downstream centerline. Red rectangles correspond to $De = 0.1$; green triangles correspond to $De = 0.25$; blue cycles correspond to $De = 0.5$; yellow diamonds correspond to $De = 1.0$; and "X" corresponds to $De = 1.25$ 288

Figure 8.15: Effect of double reptation and viscous stress on the prediction of the drag force acting on the cylinder. Empty square symbols correspond to the prediction of the Doi-Edwards model; red squares correspond to the prediction of the Curtiss-Bird model with ; yellow circles correspond to the prediction of the double reptation model without viscous stress; blue triangles correspond to the stress tensor expression evaluated with Eqn. 8.5 with ; cyan diamonds correspond to the stress tensor expression evaluated with

Eqn. 8.5 with ; “X” corresponds to the stress tensor expression evaluated with Eqn 8.6 with .289

Figure 9.1: Material functions in a steady-state shear flow for the TAR model with independent alignment assumption predicted by the wavelet-Galerkin method (solid symbols) and Brownian dynamics simulation (empty symbols): (a) shear stress, (b) viscosity, (c) first normal stress coefficient, (d) second normal stress coefficient, (e) Stretch, (f) recoverable shear and ratio of normal stress coefficients. For (a) to (d) the solid blue line corresponds to predictions by the Doi-Edwards model and dashed lines to the power law fit; (f) dashed lines are the predictions of the Doi-Edwards model.....316

Figure 9.2: Transient material functions predicted by the TAR model during the start-up of steady simple shear flow calculated by the wavelet-Galerkin method: (a) viscosity; (b) stretch function; (c) first normal stress coefficient; (d) second normal stress coefficient.. 317

Figure 9.3: Effect of the Rouse time scale on the viscometric properties, stretch ratio, and the stress ratios for the TAR model. 319

Figure 9.4: Steady state elongation viscosity (and) and stretching function λ for the TAR model. 321

Figure 9.5: Transient elongational viscosity and the stretch function during the start up of planar elongation flow for the TAR model.....322

Figure 9.6: Central part of the finite element mesh for calculation of the viscoelastic flow of the TAR model past an isolated cylinder in a channel with $H = 2$ 323

Figure 9.7: Contours for the Newtonian flow field in flow around an isolated cylinder confined in a channel. (a) v_x , (b) v_y , (c) p 324

Figure 9.8: Dimensionless velocity profile in the gap between the cylinder and the wall. The three results shown for the Doi-Edwards model corresponds to the calculations with M1 (square symbol), M2 (cycle symbol), and M3 (triangle symbol). The Newtonian flow field is shown as a dashed-line for comparison. 325

Figure 9.9: Predictions of v_x by the TAR model for $De = 0.5, 1.5, 3$ for (a) overall velocity field in the computation domain; (b) cross-section velocity profile at $x = -2$; (c) cross-sectional velocity profile at $x = 0$; and (d) cross-sectional velocity profile at $x = 2$; (e) velocity profile along the centerline. On these figures, the dashed line corresponds to the Newtonian velocity profile. 328

Figure 9.10: Predictions of τ_{xx} by the TAR model for $De = 0.5, 1.5$, and 3 for (a) the overall stress field in the computational domain; (b) cross-sectional profile at $x = -2$; (c) cross-sectional profile at $x = 0$; and (d) cross-sectional profile at $x = 2$; (e) and axial profile along the centerline of $y = 0$ 329

Figure 9.11: Predictions of τ_{yx} by the TAR model for $De = 0.5, 1.5$, and 3 for (a) the overall stress field in the computational domain; (b) cross-sectional profile at $x = -2$; (c) cross-sectional profile at $x = 0$; and (d) cross-sectional profile at $x = 2$ 330

Figure 9.12: Predictions of λ by the TAR model for $De = 0.5, 1.5$, and 3 for (a) the overall stretch field in the computational domain; (b) cross-sectional profile at $x = -2$; (c) cross-sectional profile at $x = 0$; and (d) cross-sectional profile at $x = 2$; (e) and axial profile along the centerline of $y = 0$ 332

Figure 9.13: Time evolution of the drag force acting on the cylinder surface for $De = 0.5, 1.5$, and 3 for the TAR model. 333

Figure 9.14: Comparison of viscoelastic drag enhancement for the TAR model with the Doi-Edwards and Giesekus models. The two different values of τ_d/τ_R for the TAR model used are 1 and 10 334

List of Tables

Table 2.1: Notation and symbols used in describing generalized coordinates	48
Table 3.1: Comparison of numerical accuracy of various methods for solving the Fokker-Planck equation for a dilute suspension of rigid dumbbells in a steady, simple shear flow. In each cell, the first entry is the viscosity and the second entry is the first normal stress coefficient. The numerical results for the spherical harmonics approach are from the work by Stewart and Sørensen [204]	91
Table 4.1: Dependence list for graph in Figure 4.2	124
Table 4.2: Dependence list for graph in Figure 4.2 after step 2.....	125
Table 4.3: Sorted list after each execution of step 2 of the algorithm	126
Table 6.1: Values of in the linearly extrapolated Crank-Nicholson method for a given order of accuracy.	191
Table 6.2: Convergence study for the structure parameter S_2 at equilibrium ($De = 0$) for various U with the nematic director taken to point in the x_1 direction. Because of under resolution, no converged results were obtained for entries represented by dashes.	198
Table 6.3: Convergence study of the structure parameter S_2 at equilibrium for $U=10.67$ with the director pointing along the x_3 direction. Error is defined as	199
Table 6.4: Effect of anisotropic σ on the accuracy of the numerical solution of the equilibrium problem.....	201
Table 8.1: Comparison of the computation requirement between the wavelet-Galerkin method and the Brownian configuration field method	267
Table 8.2: Mesh dimension and number of unknowns for meshes (M1, M2, M3) for the calculation of the viscoelastic flow past an isolated cylinder confined in a planar channel with . The drag force of viscoelastic flow at $De=1$ is calculated by using one Fourier mode and D6 scaling expansion for the Doi-Edwards model.	270
Table 8.3: Comparison of the values of the drag force and the wall shear rate computed with the three different meshes M1, M2, and M3. Daubechies 6 scaling functions and one Fourier mode are used to resolve the configuration space of the Doi-Edwards model.	273
Table 8.4: Comparison between the values of the drag force and the wall shear rate with the two different Daubechies 6 scaling functions resolutions for the configuration space of u . One Fourier mode is used for the configuration space of σ and mesh M2 is used to resolve the physical space.	276

Table 8.5: Comparison between the values of the drag force and the wall shear rate with different number of Fourier modes for the σ -space: 1, 5, and 10. Daubechies 6 scaling functions are used to resolve the u -space at each node, and mesh M2 is used to resolve the physical space..... 278

Table 9.1: Characteristic of the meshes used in the calculation for a flow around an isolated cylinder confined by a channel 323

Table 9.2: Comparison of the values of the drag force and the wall shear rate computed with the three different meshes M1, M2, and M3. Daubechies 6 scaling functions and one Fourier mode are used to resolve the configuration space of the Doi-Edwards model. 326

Chapter 1

Introduction

1.1 Motivation

Polymers are very large molecules made by thousands, or millions of repeated units known as monomers. Each monomer unit may be a simple molecule (such as ethylene) or contain tens or thousands of atoms (such as amino or fatty acids). Two or even more types of monomers can be used to form polymer chains known as copolymers. Polymer molecules can have the simple topology of linear chains or more complex architectures such as branches, rings, helices, combs, stars, or large networks. Non-covalent interaction between different monomer units can lead to unique local structure (such as the helix conformation of protein molecules), as well as complex, global morphology (such as those found in thermoplastic olefins). Because of the wide variety complex architecture and chemical constituents, there is a huge potential in developing polymers tailored to provide specific, desirable properties in terms of toughness, tensile strength, lightness, moldability, and transparency. The unique properties of engineering polymers or plastics lead to a wide variety of applications such as shatter-resistant containers for peanut butter and mouthwash, automobile tires, light-emitting diodes and optical switches in the electric and electronics information industry, and drug delivery agents in biomedical engineering.

The long chain architecture of polymeric fluids also leads to striking differences with respect to Newtonian fluids in a variety of flow situations. For example, the viscosity of many polymeric liquids depend strongly on the velocity gradients, and in addition, these fluids may display pronounced “elastic effects”. These properties lead to a variety of interesting phenomena and some of these are summarized in Figure 1.1: (a) elastic recoil occurs when pouring a viscoelastic fluid into a container, a cut in midstream leads to the

spring-back of the upper portion into the beaker and only the lower portion falls to the container; (b) rod-climbing that occurs when a rotating cylinder is placed in a beaker of viscoelastic fluid; (c) drag reduction, when a dilute polymer solution undergoes turbulent tube flow, pressure drop in a extremely dilute polymer solution is significantly smaller than that of the pure solvent; (d) extrudate swell that is observed when a viscoelastic fluid is extruded from an orifice. Other phenomena such as secondary flow, jet break-up, elastic recoil, and other elastic instabilities have been summarized pictorially [19][24]. Knowing and understanding these phenomena in terms of the underlying molecular or microstructural features of the viscoelastic fluid and their interactions with macroscopic transport phenomena is essential for efficient process design and control to arrange polymer molecules for the optimal mechanical and optical properties. Due to the lack of computational tools that relate the process variables to the molecular conformations and their subsequent relationship to the product properties, engineers rely on years of experience to design process equipment and fine-tune process variables, such as extruder screw speed and die temperature. When a new polymer product emerges, the applicability of this practical experience is often inadequate. One of the goals of studying viscoelastic flows is to describe and to predict the interaction between conserved quantities (such as velocity fields for an incompressible fluid) and the configuration of the polymer molecules. The ability to do so would allow engineers reduce the number of process design iterations and to enhance the efficiency of developing the optimal design that controls the degree of molecular orientation for the desirable material properties.

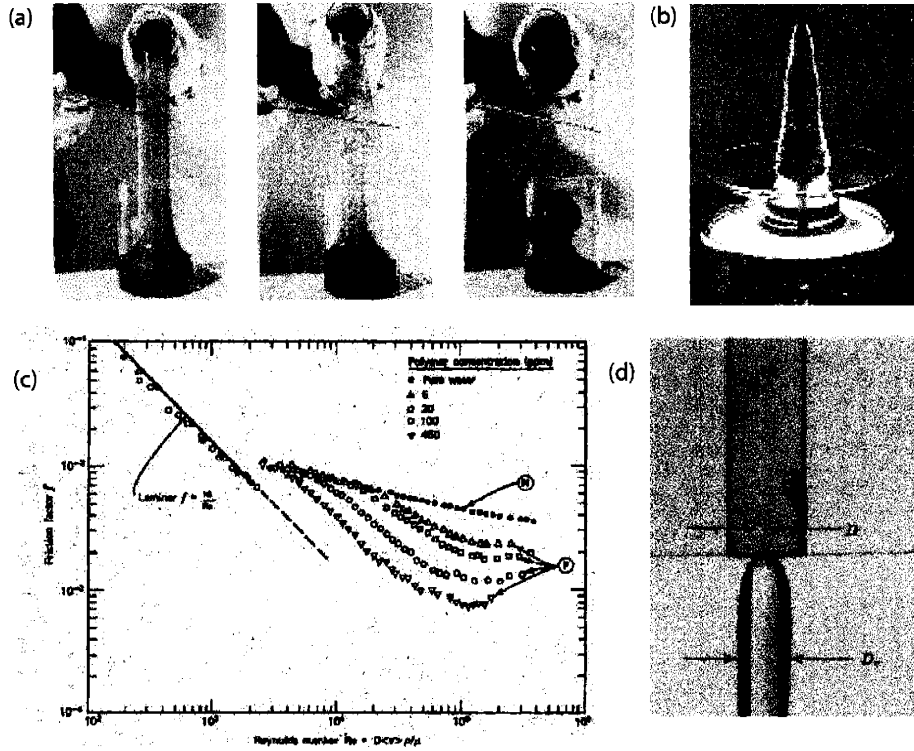


Figure 1.1: Striking flow phenomena exhibited by viscoelastic liquids. (a) Elastic recoil [19]. When pouring a polymer solution into a container, a cut in midstream leads to the liquid above the cut springs back to the beaker and the lower portion falls to the container; (b) Rod-climbing or Weissenberg effect [19]. Polymer solution climbs the rotating rod in a fixed cylinder; (c) Drag reduction [19]. Friction factor of dilute polymer solution is smaller than that of the solvent in the turbulent regime; (d) Die (or extrudate)-swell [19]. Polymer solution shows a dramatic increase in diameter as it flows downward out of the tube.

1.2 Analysis of viscoelastic flow

The traditional approach of studying viscoelastic fluid mechanics is to solve the continuum equations of change. These conservation equations for mass, momentum, and energy derived from continuum mechanics are solved for the concentration, velocity, and temperature fields with the constitutive description for the polymer behavior embedded in the mass flux vector (j_p), stress tensor (τ_p), heat flux vector (q_p), and internal energy (U_p). The fundamental challenge is then deriving appropriate constitutive equations in terms of the conserved variables for the various flux expressions in the equations of change. The development of constitutive equation is aided by experimental data from certain benchmark

experiments such as rheometric experiments and a number of nontrivial flow benchmark experiments. Rheometric experiments are carefully designed such that the equations of change are trivially satisfied. Various material functions, which characterize the response of a polymeric liquid to a specific rheometric experiment, can be extracted and then be compared with the predictions of a proposed constitutive equation. For example, in a steady state shear flow between two parallel planes, $v_x = \dot{\gamma}y$, one may measure a shear stress τ_{yx} and two normal stress difference $\tau_{xx} - \tau_{yy}$ and $\tau_{yy} - \tau_{zz}$; three material functions are then defined by

$$\begin{aligned}\tau_{yx} &= -\eta\dot{\gamma} \\ \tau_{xx} - \tau_{yy} &= -\Psi_1\dot{\gamma}^2 \\ \tau_{yy} - \tau_{zz} &= -\Psi_2\dot{\gamma}^2\end{aligned}\tag{1.1}$$

The viscosity η is positive and, for most polymer solutions, monotonically decreasing with shear rate $\dot{\gamma}$; The first normal stress coefficient, Ψ_1 , is positive for most polymeric liquids but can be negative for liquid crystalline polymers. It normally decreases much faster than the viscosity with shear rate; The second normal stress coefficient, Ψ_2 , is normally negative and small in magnitude. The small magnitude makes its measurement extremely difficult, and sometimes controversial results are reported [19]. Some other rheometric experiments include various types stress-strain response of a polymeric fluid under both steady state or transient simple, homogeneous shear and shear-free flows [19,153,223]. Additional experimental techniques used for a deeper understanding and characterization of the rheology and conformations of polymers and other complex fluid systems include optical methods such as birefringence [26,83,87,178,179] and light scattering [26,41,131,132] that provide information about the mean orientation and conformations of the molecules, nuclear magnetic resonance (NMR) [32,38,116,136] and neutron scattering [143,160] methods that provide detailed information about the conformational

distribution function, and fluorescence video microscopy [173,177,197,198] that provides direct observations of molecular conformational changes in flow.

Dimensional analysis allows condensation of a wide array of experimental data for comparison and characterization. In viscoelastic flows, the important dimensionless groups used to characterize the flow strength are Reynolds number, *Deborah number* (De), and *Weissenburg number* (We). The high viscosity of typical polymeric liquids makes inertia negligible and hence $Re \approx 0$. The Deborah number¹ [183] is defined as the ratio of a characteristic relaxation time scale of the polymeric fluid λ and an observation time scale T , i.e.

$$De = \frac{\lambda}{T} \quad (1.2)$$

The observation time scale is normally taken as the residence time of a polymer molecule in the flow process. Two limiting values of the De can be identified with classical mechanics: (1) $De \ll 1$. Thermal motion keeps polymer molecules around equilibrium configuration and hence the polymer solution behaves like Newtonian solution; (2) $De \rightarrow \infty$. The extremely fast flow process gives no chance for polymer molecules to change their configuration and hence the solution behaves like a Hookean elastic solid.

The Weissenburg number is defined as the product of the relaxation time scale of the polymer fluid λ and a characteristic strain rate κ , i.e. $We = \lambda \kappa$. In many cases, De and We are used interchangeably because the characteristic strain rate is often the same as the reciprocal of a characteristic time for the flow. An example of a flow in which there is a significant difference between De and We can be found in the calculation of flow around a linear array of cylinders [139], where the observation time scale (T) is defined as the time

1. De is named after the prophetess Deborah (Deborah's Song, Judges, 5:5) who said "The mountains flowed before Lord". This emphasizes the relative importance between the observation time scale and relaxation time scale.

it takes for the fluid to traverse from one cylinder to the next and the characteristic strain rate (κ) is the average strain rate for the flow in the narrow gap between the cylinder and the confining wall. At the limit of single cylinder in the channel, there is no interaction between neighboring cylinders ($De \rightarrow 0$) and the flow is characterized completely by We .

1.3 Constitutive modeling of polymeric liquid

Traditional approaches for deriving constitutive equations involve combining simple mechanical models (such as found in the derivation of Maxwell or Jeffery models), as well as utilizing engineering correlations (such as the power law model and Criminale-Ericksen-Filbey model) or mathematical expansion (such as the retarded-motion or memory integral expansion models). Most of these models are only applicable for the specific flow systems they are designed for and will otherwise provide erroneous results such as frame variance. Continuum mechanics imposes “admissibility conditions” such as frame invariance or rheological invariance[163] that can only serve as guidelines for constructing a constitutive equation but lack molecular information.

In the study of viscoelastic flows, considerable important information and insights can be gained through the use of molecular theory. Ultimately, a molecular theory can provide a description of effects such as chain architecture, polydispersity, and polymer-wall and polymer-solvent interaction on various rheological properties, as well as a precise relationship between rheological properties and other physicochemical properties such as thermodynamic, optical and electric properties[21].

Constitutive equations derived from molecular theory consist of an evolution equation for the molecular orientation and a set of flux expressions. While mathematical manipulation could result a single constitutive equation, the advantage of using a pair of equations

for the molecular evolution and flux expression could be tremendous. For example, in the constitutive equation for a suspension of FENE-P molecules in a Newtonian solvent (For more information, see Chapter 2), the evolution of the average conformation $\langle \mathbf{Q}\mathbf{Q} \rangle$ and the corresponding dimensionless stress tensor expression are given by Equation 1.3:

$$\begin{aligned} \text{De} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} &= \boldsymbol{\delta} - \frac{\langle \mathbf{Q}\mathbf{Q} \rangle}{1 - \text{tr} \langle \mathbf{Q}\mathbf{Q} \rangle / b} \\ \boldsymbol{\tau}_p &= \boldsymbol{\delta} - \frac{\langle \mathbf{Q}\mathbf{Q} \rangle}{1 - \text{tr} \langle \mathbf{Q}\mathbf{Q} \rangle / b} \end{aligned} \quad (1.3)$$

where b is the dimensionless parameter for the maximum extensibility of the elastic dumb-bell and $\boldsymbol{\tau}_p$ is scaled with nkT with n being the number density of the polymer. $\langle \mathbf{B} \rangle_{(1)}$ is the upper convected derivative. For symmetric tensor $\boldsymbol{\Lambda}$, the upper convected derivative is defined as $\boldsymbol{\Lambda}_{(1)} = \frac{\partial \boldsymbol{\Lambda}}{\partial t} + \mathbf{v} \cdot \nabla \boldsymbol{\Lambda} - \{ \boldsymbol{\Lambda} \cdot \nabla \mathbf{v} + (\boldsymbol{\Lambda} \cdot \nabla \mathbf{v})^T \}$. The corresponding single constitutive equation for the stress tensor is shown in Equation 1.4.

$$Z \boldsymbol{\tau}_p + \text{De} \boldsymbol{\tau}_{p(1)} - \text{De} (\boldsymbol{\tau}_p - \boldsymbol{\delta}) \frac{D \ln Z}{Dt} = -\text{De} \dot{\boldsymbol{\gamma}} \quad (1.4)$$

where $Z \equiv 1 + 3/b - \text{tr} \boldsymbol{\tau}_p / b$, and $\dot{\boldsymbol{\gamma}} \equiv \nabla \mathbf{v} + \nabla \mathbf{v}^T$. The presence of the extra variable Z , nonlinear coupling of the various components of the stress tensor, and the substantial derivative of $(\ln Z)$ makes numerical simulation difficult and demonstrates the relative ease of implementation and use of the evolution equation and stress tensor expression pair.

In addition to the simplicity afforded by this pair of equations, the molecular orientation is solved directly and no mapping from the stress tensor to the molecular orientation is required. The effects of various molecular processes on the flow calculation are thus clearly shown in the evolution equation; and, hence, a systematic investigation is possible. More importantly, effects of closure approximations for reducing the number of unknowns in a flow calculation can be tested easily by the application of a different closure approxi-

mation or by directly solving the underlying PDE for the probability density or the equivalent stochastic differential equation.

Polymer physicists and theoretical chemists have distinct interests in deriving constitutive equation by using molecular theory. Most polymer physicists are interested in the derivation of a specific mathematical expression for the relaxation time for a molecular process. The underlying equations for the evolution of molecular orientation and the stress tensor expressions are assumed to be of specific simple forms. This approach is adequate for describing macroscopic process but the assumption that all topological information (such as that found in branched polymers) can be condensed into mathematical expressions for the relaxation time makes it doubtful whether these models can represent the polymer chain behavior at a molecular level. Theoretical chemists address the derivation of the evolution equations for the molecular orientation and flux expressions through the application of phase space kinetic theory to a specific underlying micromechanical model. As a result, all the molecular processes are described through the force or torque acting on the beads of the micromechanical model. Projected polymer descriptions such as those found in the reptation model are derived through systematically introducing coarse-graining assumptions. This allows a systematic test to determine the physics and topological information necessary to describe the molecular behavior and rheological properties. The expressions for various flux contributions in the equations of change are summarized as residuals from the projection of a microscopic equations of change (such as the Liouville equation) to a macroscopic equations of change (such as the equation of motion).

1.4 Numerical analysis of viscoelastic flow phenomena

Given a constitutive equation, the task of solving for variables such as velocity is still very difficult. Some specific difficulties include the increase in the number of variables

and hence the degrees-of-freedom in a single calculation, nonlinearity and strong coupling between the constitutive equation and the conservation equations, and the change of mathematical type with increasing importance of elasticity [114]. The state of the art in finite element formulations for solving viscoelastic flow problems is based on several paradigms that have emerged in the last decade [213]. These include:

1. Synthesis of an operator splitting that decouples the calculation of polymer stress contribution by solution of a hyperbolic constitutive equation from the velocity and pressure field evolution, which is obtained by solution of a generalized Stokes problem.
2. Reformulation of the equation of motion to enhance explicit the elliptic character of this equation with respect to the velocity field. Various formulations of rewriting the equation of motion include EEME (**E**xplicitly **E**lliptic **M**omentum **E**quation) [117], EVSS (**E**lastic-**V**iscous **S**plit-**S**tress) [180], and DEVSS (**D**iscrete **E**lastic-**V**iscous **S**plit-**S**tress) [94].
3. Developing and applying numerically stable and accurate methods for solution of hyperbolic equations to approximate well the complex boundary layer structure that seems inherent in the solution of these problems at moderate and high Deborah numbers. Some of these methods include SI (**S**treamline **I**ntegration) , SU (**S**treamwise **U**pwind) for linear finite elements, SUPG (**S**treamline **U**pwind **P**etrov-**G**alerkin) method, and the DG (**D**iscontinuous **G**alerkin) method.
4. Introduction of accurate, smooth interpolation of velocity gradient tensor for additional numerical stability in the solution of the constitutive equation, as demonstrated by Brown, et.al. [28] and Szady et al. [216] in the EVSS-G formulation.

In the development of a molecular-based approach for viscoelastic flow calculations, the first paradigm allows and ensures the possibility of including various forms and types of constitutive equations in a viscoelastic flow calculation. The constitutive equation can be explicitly written as a partial differential equation or an integral expression for the stress tensor in terms of the time history of a finite strain tensor. Alternatively, the constitutive descriptions can consist of an expression for the stress tensor in terms of the underlying microstructural arrangements coupled with a description of the evolution of the microstructure. This microstructure evolution can be described in turn by (1) diffusion equation, a partial differential equation for the evolution of probability density of polymer molecules; (2) a stochastic differential equation for the evolution of molecular trajectories; or (3) a moment equations with an appropriate closure approximation. The use of the diffusion equation or the stochastic differential equation in the constitutive description for a viscoelastic flow simulation is often known as the multiscale or micro-macro calculation. This approach allows direct assessment of the usefulness of a molecular model in a complex flow simulations through comparing the model prediction with experimental observations and identifying whether the discrepancies between theory and experimental observations are due to closure approximations or constitutive equation deficiency. Therefore, this approach has been extremely popular over the last decade despite its unfavorable computational demands as compared with the use of moment equations. The focus of this thesis is to synthesize several of the advances in the components of these algorithms to create a computationally accurate and robust method for solving viscoelastic flow problem with constitutive description derived directly from the diffusion equation of kinetic theory. Comparison of this approach to the application of a stochastic differential equation or moment equations is examined carefully in various chapters of the thesis.

1.5 Goal and outline of the thesis

The goal of this thesis is to develop and to evaluate robust, powerful numerical approaches for simulating viscoelastic flows with constitutive descriptions derived directly from kinetic theory or nonequilibrium statistical mechanics. Three distinct research directions have been carried out:

1. Development of a comprehensive numerical package of solving viscoelastic flow problem with constitutive descriptions derived directly from the Fokker-Planck equation. This package should be compatible and easily incorporated into various numerical simulation approaches at MIT and elsewhere, for example, time-dependent, free surface calculation methods and a parallel iterative solver for the ν - p - G problem with B-CLAM preconditioner [33].
2. Application of the numerical package on the study of liquid crystalline polymers.
3. Application of the numerical package on the study of concentrated polymer solutions and melts.

Prior to describing the achievements in these three research direction, the fundamental and background knowledge relevant to the work is summarized in Chapters 2 to 5. Chapter 2 introduces and reviews the microstructural modeling of polymers. This chapter begins by introducing the various micromechanical models used in kinetic theory and the notation or language that is used to describe their conformations in the physical or configurational space. Then formal phase space kinetic theory will be presented with the focus on the systematic development of the diffusion equation and the various constitutive equations that arise in the continuum equations of change. Chapter 3 introduces and compares the various numerical methods used for simulating constitutive equations. This chapter is devoted to the simulation methods used in calculating the rheological properties of a

kinetic theory model under fixed, homogeneous flow kinematics. Such homogeneous flow kinematics are the result of carefully designed experiments for extracting material properties, such as viscosity and normal stress coefficients. The relative merits between stochastic simulation and deterministic calculation are compared. Chapter 4 focuses on the coupling of constitutive equation calculation with flow kinematics calculation by the finite element method. After first reviewing some features and deriving some numerical techniques (such as the application of topological sorting to calculate the stress tensor in the order of the streamline flow direction) that will be used throughout this thesis, concepts of multiscale calculation will be introduced. The limitations of the previous implementation of the wavelet-Galerkin/finite-element approach [161] will be explored and a novel two stage, node-by-node decomposition (TSND) is introduced. TSND exploits the fact that the basis functions of the discontinuous Galerkin finite element analysis and wavelet-Galerkin method are tensorial products of each other in order to improve the algorithm. By factorizing the mass matrix and part of the stiffness matrix, TSND allows a node-by-node decomposition in the wavelet-Galerkin/finite element method. This leads to a four-fold speed up in comparison with existing numerical algorithms. It also provides a path for solving problems. These include, for example, spatially dependent Jacobian for the mass matrix for quadrilateral elements or involve coordinate systems other than Cartesian coordinates that can not be solved by the existing implementation. Chapter 5 focuses on the specific physics introduced in the study of concentrated solution and melts of liquid crystalline polymers and flexible polymers. In particular, the need of self-consistency in developing the diffusion equation and the stress tensor expression is emphasized.

Chapters 6 to 9 constitute the most of the numerical results in this thesis. Each chapter is resulted from separate articles. This leads to overlap and recurrence in the description of the numerical methods between these chapters. In Chapters 6 and 7, the focus is on the

simulation of liquid crystalline polymers. One of the major uses of the rigid-rod model for polymers is to provide a micromechanical model that is suitable for describing rheological phenomena of rod-like macromolecules such as liquid crystalline polymers. Chapter 6 focuses on the development of the wavelet-Galerkin method to simulate diffusion equations with a complicated mean-field, intermolecular potentials and orientation-dependent rotational diffusivity. In particular, the behavior of the Doi model with Onsager potential and orientation-dependent rotational diffusivity in a homogeneous shear flow is simulated for various flow and intermolecular interaction strengths. The complicated expression of the Onsager potential and the orientation-dependent rotational diffusivity have made the simulation of the Doi model extremely difficult. The orientation-dependent rotational diffusivity excludes the possibility of using spherical harmonics as basis functions for solving for the distribution function; both the Onsager potential and the orientational dependent rotational diffusivity contain nonlinear couplings between the molecular trajectory and the mean-field environment, which makes stochastic simulation expensive. This is because the molecular potential has to be evaluated for each trajectory for every time step; thus the operation count scale as N^2 , where N is the number of the trajectories used in the simulation. Although there is an advanced numerical algorithm that reduces the operation count to order N [9], the error or noise present in the orientation-dependent rotational diffusivity calculation amplifies the stochastic force and hence makes stochastic simulation unreliable for the calculation. The wavelet-Galerkin method resolves both problems and becomes one of the few methods capable of simulating this version of the Doi model. This is first shown by a rigorous convergence study for both steady-state and time-periodic state calculations. Nonlinear dynamics of the Doi model are then explored both qualitatively and quantitatively. The existence of the time-periodic solution is traced to a supercritical Hopf bifurcation point at $De = De_{\text{Hopf}}$, where the value of De_{Hopf} scales

with $(U - U_c)^\alpha$, and U is the strength of the intermolecular potential. The exponent in this correlation, α , depends on the form of the mean-field intermolecular potential and can be used to characterize the anisotropic environment experienced by the polymer molecules.

Chapter 7 presents the calculation of a simplified Doi model in an inhomogeneous flow environment. The wavelet-Galerkin method is coupled with a finite element technique that allow spatial decoupling of the complex flow problem, while eliminating the restriction to the use of triangular elements. The deficiency of the homogenous Doi model in an inhomogeneous flow is explored through the simulation of a planar, pressure-driven flow geometry. Then, an *ad hoc* diffusion equation that incorporates the effect of concentration fluctuation is used to simulate the same flow geometry. The constraint that couples all the variations in the orientation and physical space in the distribution function is solved by introducing an additional equation for the local number density. This decouples the solution of the number density from the variation of the diffusion equation with constraint to be the local number density. The goal here is of two folds. First, on a physics level, we test whether the postulate that the presence of an intrinsic length scale would stabilize the structure refinement observed by the monodomain Doi model in an inhomogeneous flow. Second, on a numerical level, the incorporation of the concentration fluctuation effects results in an elliptic diffusion equation. This elliptic characteristic of the diffusion equation is common for various modifications of the Doi model as attempts to include the Frank elasticity and the distortional stress contribution. Therefore, strategies for simulating the Doi model with concentration fluctuation can eventually lead to efficient numerical methods that can simulate the various diffusion equations with the Frank elasticity. In this chapter, the physical space variation of the elliptic diffusion equation is discretized by using the local discontinuous Galerkin method through introducing an auxiliary variable

for the distribution function flux. The pair of equations is then formally rewritten as a pair of hyperbolic equation which are solved by the standard discontinuous Galerkin method.

In Chapters 8 and 9, the focus is shifted from rodlike polymers to flexible polymers. In particular, our interest lies on the concentrated polymer solutions and melts, where polymer entanglement is significant. The goal of Chapter 8 is to introduce the use of wavelet-Galerkin/finite-element-analysis to the simulation of a higher dimensional kinetic theory model. In particular, a generalized double reptation model [20] is simulated in both homogeneous flow and complex flow environments. This generalized reptation model reduces to both Doi-Edwards model and the Curtiss-Bird model in certain parameter regions of the model. Flow around an isolated cylinder in a channel is used in this chapter as an illustrative complex flow problem. Mesh convergence and the performance in a distributed computing environment are demonstrated. Comparison with the Brownian configuration fields method reveals the robustness and accuracy of the wavelet-Galerkin/finite-element method. Because of the lack of a chain stretching mechanism, the generalized double reptation model shows a monotonically decreasing drag force on the cylinder with Weissenburg number (We).

To circumvent some of the deficiencies of the double reptation model, a reptation model with chain-stretching, double reptation, and convective constraint effects is simulated and the numerical results are presented in Chapter 9. The reptation model is developed by Fang et al. by using the guidance by the nonequilibrium thermodynamics. We call this model as the TAR (Thermodynamically Admissible Reptation) model. The response of the TAR model is first simulated in simple flows such as shear and elongational flows. Calculations obtained by a wavelet-Galerkin method is compared with the predictions of a Brownian dynamics simulation. This explores the usefulness of the wavelet-Galerkin method in solving the TAR model. Then, the complex flow calculation is per-

formed for the flow around an isolated cylinder confined in a channel. The same geometry is simulated in Chapter 8. The complex interaction between the flow field, the reptative and non-reptative mechanism in the TAR model leads to a substantial modification of the velocity field. Noticably, an upstream shift of the centerline axial velocity, as well as a long strand of normal stress which increases with increase in De are observed in the calculation. While the flow field is very different from the Newtonian or the various double reptation models, the drag force calculated by using the TAR model is monotonically decreasing with increase in De . This is owing to the small values of the chain stretching function. Experimental results is desperately required to verify the difference between the prediction of the TAR model and the general expectation on the viscoelastic drag enhancement owing to the observations from viscoelastic flows for dilute polymer solutions.

A large variety of molecular models are simulated with the wavelet-Galerkin method through various extensions of the numerical approach. Chapter 10 will summarize some of the important contributions in this thesis to the field of viscoelastic flow calculation with molecular models. Future works that can be developed from the advances of this thesis are outlined. From a numerical point of view, the central problem of searching an accurate set of basis functions is a long-standing issue that is unlikely to be resolved in any near future. Furthermore, numerical method for calculating the coefficients in the expansion (Galerkin, collocation, tau, or other mixed methods) is essential for utilizing the advanced of various basis functions for different systems. From a physical point of view, the development of advanced model with well-defined mathematical characteristics is needed. More important, quantitative experimental interpretations that provide meaningful output functionals for the comparison with theoretical model is essential.

Chapter 2

Microstructural Modeling of Macromolecules

2.1 Introduction

The increasing awareness of the importance of the structure-property relationship and the influence of transport phenomena on the microstructure of polymers promotes the desire for a multiscale understanding of polymer processes. Two important contributions include the development of experimental techniques that capture microscale morphology and dynamics and the derivation of microstructural theory for studying complex fluids such as polymer melts and solutions, copolymer systems and polymer mixtures. Both local chemical composition and long chain architecture of polymers contribute to the unique properties and behavior of polymers. One of the goals of this thesis is to explore the rheological dynamics of polymers based on the long chain architecture of polymers, which is represented by generic micromechanical models such as bead-rod-spring chains. Depending on the time resolution, different molecular theories and simulation techniques may be used to describe the configurational changes. For example, molecular dynamics simulations based on the nonequilibrium statistical mechanics have to be used when polymer-solvent collisions are important for a process; on the other hand, when only the changes in molecular conformation is important (such as in the case of studying the fluid mechanics of polymers), time-smoothed nonequilibrium statistical mechanics, or kinetic theory may be used in the place of nonequilibrium statistical mechanics. It is the focus of this chapter to review the various methods in deriving models for describing the macromolecular mechanics of polymer molecules by coarse-grained models.

Constitutive expression for various flux expressions in the equations of change have to be derived before a molecular model is of any use in a viscoelastic flow calculation. These

expressions, such as the stress tensor, can be obtained based on physical arguments, thermodynamics arguments, or a rigorous derivation from kinetic theory. While both physical and thermodynamics arguments are common in a large body of literature, the use of rigorous kinetic theory derivations is relatively uncommon. Therefore, one of the goals in this chapter is to review some of the derivations based on kinetic theory and to list some of the crucial assumptions that lead to limitations or inconsistency in extending kinetic theory to inhomogeneous systems such as found in liquid crystalline polymers or polymer blends.

In this chapter, the general phase space kinetic theory for deriving equations for the molecular motion and the constitutive expression for various flux expressions will first be reviewed. Notation for describing the internal configuration of a polymer molecule will first be presented, followed by a discussion on the use of kinetic theory to derive a Fokker-Planck equation for the evolution of the probability density of these molecules and various flux expression for the equation of continuity and the equation of motion. The application of non-equilibrium thermodynamics will then be reviewed and some important applications will be discussed. This chapter will conclude with a discussion of the various mapping strategies for two micromechanical models used to study rheology of polymers.

2.2 Micromechanical models

The heart of all molecular theories is the choice of a micromechanical model for representing the configuration of a polymer molecule. Because computing the electronic structure of each atom within a polymer molecule through the use of *ab initio* molecular dynamics is impractical for calculating thermodynamic and transport properties, most micromechanical models are constructed by using classical mechanics. These micromechanical models can be generally divided into two types: (1) particle-based (discrete) models, and (2) field-theoretical (continuous) models. An illustration of some of the popu-

lar models is shown in Fig. 2.1

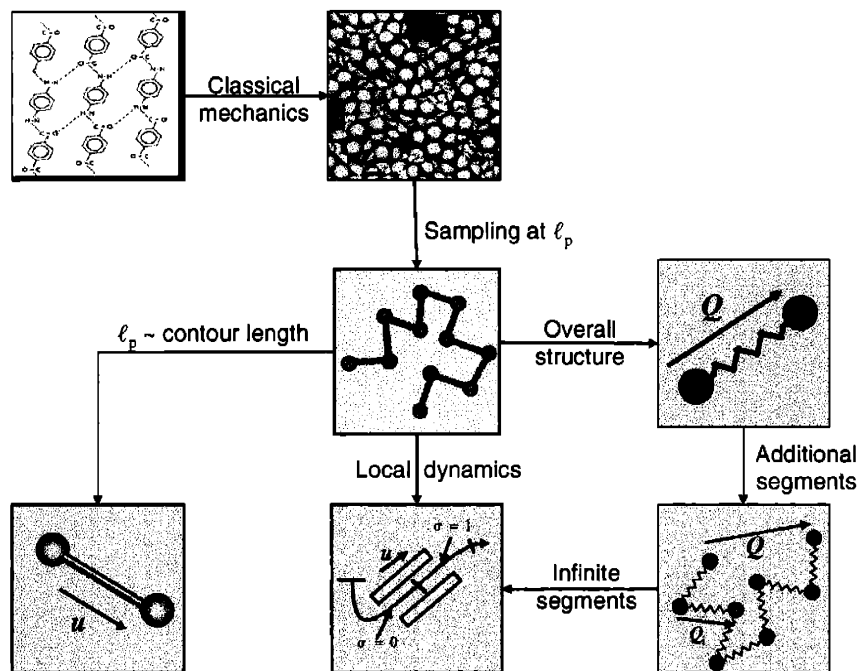


Figure 2.1: A schematic representation of various micromechanical models and their interconnections used in studying polymer properties. ℓ_p is the Khun segment length or the persistence length as defined by Equation (2.1).

Particle-based micromechanical models generally consist of collections of beads joined together by elastic springs or rigid rods. Depending on the time and length scale resolution of a model, each bead may have different representation for a small portion (ranging from individual atom, monomer, or even a group of monomers) of the molecule and arbitrary multi-bead intermolecular forces can be incorporated into the model. For example, at the atomistic level, each bead in the molecule corresponds to an atom or a monomer in a polymer molecule. Bonded or non-bonded interaction can be parametrized with two (stretching), three (bending) or/and four (torsional) body potentials. Ideally, the functional form and the parameters of these potential can be obtained through experimental data or through *ab initio* (first principle) molecular dynamic calculations [108].

While micromechanical models at the atomistic level can be used to elucidate macroscopic information such as elastic constants, they are intractable for dynamical calculation, because the extremely long equilibration time for a sufficiently large systems of polymers at realistic densities for structural and thermodynamical information is computationally exhaustive. Furthermore, dynamic and rheological behavior of polymers depends mostly on universal properties (such as overall shape of the polymer molecule) associated with the configurational properties and long chain architecture of polymer molecules. Resolution at an atomistic level is not necessary and coarse graining or simplification of atomistic models is both justified and necessary.

Coarse-graining from the atomistic description can be carried out at a number of different levels. The most important concept underlying coarse-graining is the local equilibrium or the time-smoothing assumption. For example, the assumption that molecular motion within a monomer is much faster than that of the overall chain motion leads to the united atom model, where each bead corresponds to one monomer unit, instead of an atom in the system. Another very useful coarse-grained model for predicting solid-state properties, the rotational isomeric state (RIS) model [82], results from the assumption that torsional motions are much slower than stretching or bending motions. This model has a fixed bond length and bond angle, but the torsional angle is variable with a probability given by a molecular potential. Both the united atom model and rotational isomeric state model have proven to be extremely useful in describing both solid state and dilute solution properties. However, these models still contain too many degrees-of-freedom to be useful in a fluid mechanics calculations. Further coarse-graining is required.

A key concept in coarse-graining an atomistic model to a simplified model with minimal chemical composition information is the definition of the Khun segment length or the persistence length, ℓ_p :

$$\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle \sim \exp(-|j-i|\ell/\ell_p) \quad (2.1)$$

where $\mathbf{u}_i$ is the orientation of the i -th segment of the polymer chain. ℓ is the bond length of a segment, ℓ_p is a measure of the rigidity of the polymer molecule. A pictorial illustration of this concept is shown in Figure 2.2. The angle formed between two bonds are becoming less correlated as the distance between the two bonds increases. Sampling the bond angle formed between two bonds that are far apart from each other yields a totally uncorrelated bond angle and at that point, the evolution of two bond vectors are said to be uncorrelated.

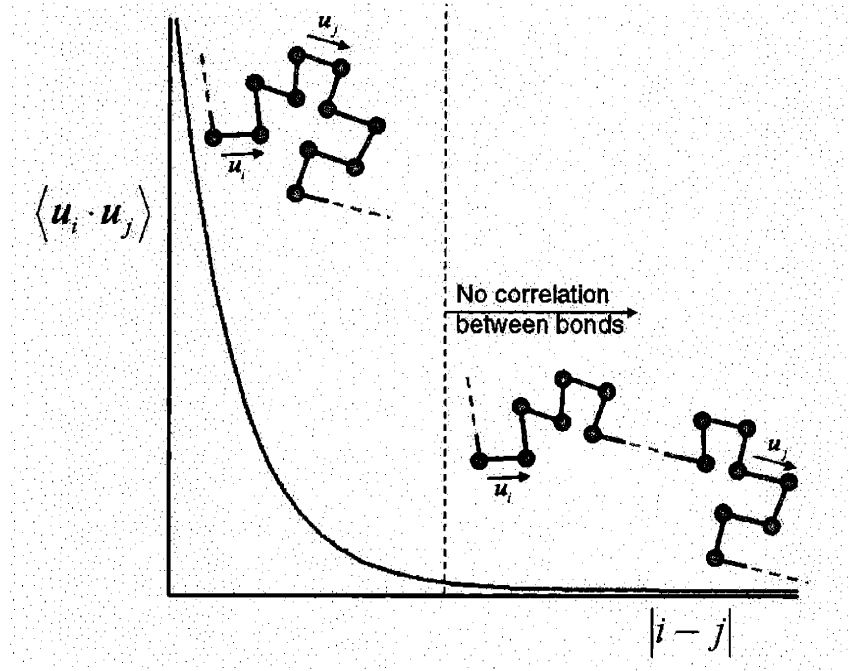


Figure 2.2: Concept of persistence length, ℓ_p

For ℓ_p much smaller than the contour length of a polymer molecule, the polymer molecule is considered to be flexible for lengths larger than ℓ_p . If one defines a segment with length scale of order ℓ_p , then the orientations of the segments are independent of one another. The resulting model is normally known as the freely-joint-bead-rod (or the Kramers) chain (the middle figure in Figure 2.1). Most synthetic polymers such as polystyrene, polyethylene, and polypropylene are flexible and therefore the Kramers chain model can be used as the micromechanical model for describing the universal behavior of this class

of polymers. As ℓ_p approaches the maximum extension of the molecule (contour length), the macromolecule corresponds to a rigid-like macromolecule (left bottom figure in Figure 2.1). Examples of molecules that can be represented by a rigid rod model include liquid crystalline polymers, tobacco mosaic virus, and protein molecules. The rigid dumbbell, multibead rod (shish kabob), and an elongated object (such as an ellipsoid) are commonly used to represent these molecules.

Although the Kramers chain is a very coarse-grained model relative to an atomistic description, the large number of degrees of freedom of the Kramers chain limits its usefulness in complex flow calculations. Hence, further coarse-graining is required. The most commonly used models in fluid mechanical calculations are elastic dumbbell models, in which polymer molecules are represented by two beads joined by an elastic spring (right middle figure in Figure 2.1). The elastic dumbbell model is normally considered as the end-to-end vector of a Kramers' chain or more detailed model (such as the worm-like chain). For the Kramers' chain, the spring force law between the two beads is derived based on the equilibrium, force-extension relationship and is given by the *inverse Langevin force law*.

$$F^c = \frac{HQ_0}{3} \mathcal{L}^{-1}\left(\frac{Q}{Q_0}\right) \quad (2.2)$$

In this equation, F^c is the scalar connector force required to maintain the end-to-end distance of the Kramers chain at Q . H is an elastic modulus, and Q_0 is the maximum extensibility of the spring. $\mathcal{L}^{-1}$ is the inverse Langevin function given by $\mathcal{L}(x) = \coth(x) - x^{-1}$. The complicated functional form of $\mathcal{L}$ makes computation expensive. Furthermore, the force law is not directly proportional to the extension Q . This makes generalization to a vector form difficult. Therefore, various empirical spring force laws are proposed to further simplify the spring force. The two most commonly used empirical spring force laws are the Hookean (linearly elastic) force law and the FENE (Finitely Extensible Nonlinearly

Elastic) spring force law. The Hookean force law is $F^c = HQ$, and the FENE force law is given by $F^c = HQ/(1 - (Q/Q_0)^2)$. A comparison between the inverse Langevin force law, FENE force law and the Hookean force law is given in Figure 2.3.

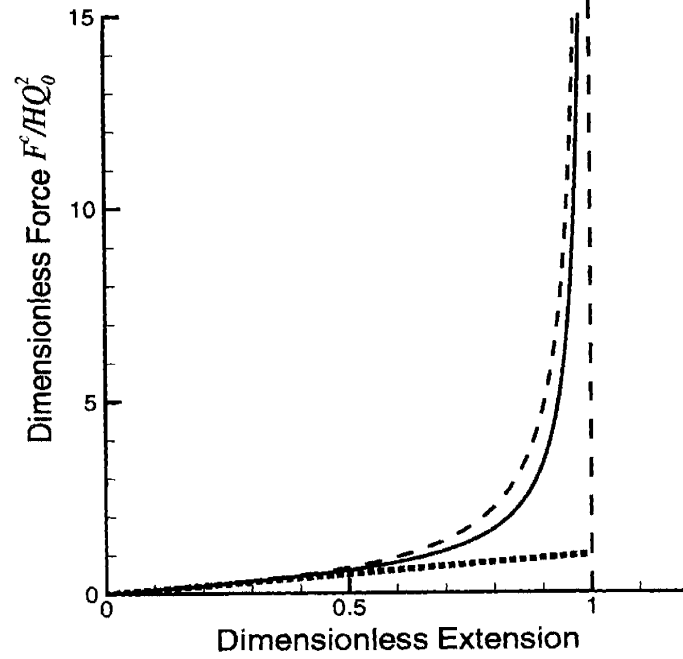


Figure 2.3: Comparison of different force-extension relationships for three spring laws: Inverse Langevin force law (solid line), FENE force law (dash line), and Hookean force law (dotted line). The dashed line at $Q/Q_0 = 1$ corresponds to the maximum possible extension for inverse Langevin and FENE force law at which both of these force laws will diverge.

As shown in Figure 2.3, these three force law are identical to each other for small extensions ($Q/Q_0 \leq 0.5$). The Hookean force law is considered as the linear approximation to the inverse Langevin force law, and therefore, it underpredicts the spring force at large extensions. More importantly, the Hookean dumbbell is extensible to an extension that is greater than the contour length. This is aphysical and may lead to singularity in the resulting constitutive equations. FENE force law, on the other hand, is closely replicate the behavior of the inverse Langevin force law throughout the domain of Q/Q_0 . Furthermore, FENE force law is directly proportional to Q and hence generalization to a vector form is as simple as replacing the scalar Q by a vector $\mathbf{Q}$, which corresponds to the orientation and the length of the spring in the three-dimensional space. Therefore, FENE force law is the

most commonly used in derivation of kinetic theory models for both viscoelastic flow calculations.

A micromechanical model with more detail in its microstructure is needed to describe experiments with rapidly changing kinematics that induce fast stretching of the macromolecules (such as inception of elongational flow with a large elongation rate) or experiments that are capable of capturing the conformation of the macromolecules (such as video microscopy). Most Brownian dynamics simulations for these experiments are based on the multi-bead-rod/spring chain model.

In addition to the Kramers' chain model, a class of detailed molecular models consists of the bead-spring-chain models (Right bottom figure in Figure 2.1). These models are generated by joining beads with springs derived for the elastic dumbbell models. While most researchers consider each spring in a bead-spring-chain model to sample a certain segment of the Kramers' chain, Laso et.al. [121] show that such coarse-graining will result in non-uniform bond and torsional angle distributions, and hence the resulting bead-spring model is not freely jointed. Therefore, while both the Kramers chain and the multi-bead-spring chain provide more detailed descriptions of the microstructure than a dumbbell model, there is no direct relationship between these two model. When Hookean springs are used in a multi-bead-spring model, the resulting model is known as the *Rouse* model. Explicit molecular architecture such as found in branched or star polymers can be incorporated into the multi-bead-rod/spring chain model. There has been limited work done using multi-bead-rod/spring models for polymers with complex molecular architecture, and much research is needed in this area.

An alternative, single mode description for a chain molecule is through the use of field theory, where a space curve, $\mathbf{R}_s$, is used to describe the orientation along the backbone (bottom middle figure in Figure 2.1). In the case of the Kramers' chain, the field model

reduces to the random walk model. In the case of a long Rouse chain, the following transformation is used to pass from the discrete to the continuum limit

$$(\mathbf{R}_n - \mathbf{R}_{n-1})^2 = \left(\frac{\partial \mathbf{R}_n}{\partial n} \right)^2 dn \quad (2.3)$$

and the corresponding canonical configuration distribution function at equilibrium Ψ is

$$\Psi(\{\mathbf{R}_n\}) = \left(\frac{3}{2\pi b^2} \right)^{\frac{3N}{2}} \exp \left(-\frac{3}{2b^2} \int_0^N \left(\frac{\partial \mathbf{R}_n}{\partial n} \right)^2 dn \right) \quad (2.4)$$

This is called the Wiener distribution. The Hamiltonian of the continuous Rouse chain provides the basic connectivity and topology of a linear polymer chain for studying effects such as excluded volume and systems such as polymer solutions and melts, polymer blends, and block copolymers.

While most of studies to date for the continuous model are based on analytical calculations, computer simulation strategies for the field theory are starting to emerge [84]. Application of the field theory models to study rheological properties have been limited to linear polymer melts through the use of the reptation model [59]. Extension of the field-theoretic treatments of other polymer systems for nonequilibrium properties is crucial. Much work has to be done in this area.

2.3 The Geometry and Coordinate Systems used for Chain-like Molecules

In the discussion of micromechanical models such as bead-spring or bead-rod models, it is useful and important to devise coordinate system to describe the chain conformation or configuration. In general, defining the best set of coordinates is more of an art than science. Some traditional coordinate systems such as the Cartesian coordinate system are particularly easy to use but are not well-suited for deriving general equations to describe the motion of systems with constraints or interaction potentials that depend on the com-

plex geometrical interaction between the molecules. Other choices of coordinate systems may introduce undesirable singularities into the evolution equation which make simulations difficult. In this section, a number of the standard notation systems for describing chain configuration will be discussed. The first set of coordinates discussed is the generalized coordinate system, which consist of the minimum number of degrees of freedom that are sufficient for describing the chain conformation. Another set of coordinate systems that will be discussed is based on constraint coordinates, which are defined to eliminate singularity in the equation of motion for the molecular systems. Before starting the discussion, the labelling system used in this section is shown in Table 2.1:

$\alpha, \beta, \gamma, \dots$	Label for chemical species	1, 2, 3, ...
$i, j, k, \dots$	Label for internal configuration vector number	1, 2, 3, ...
$s, t, u, \dots$	Label for generalized coordinate	1, 2, 3, ..., $d \leq 3N - 3$
$\mu, \nu, \eta, \dots$	Label for bead number	1, 2, 3, ..., N

Table 2.1: Notation and symbols used in describing generalized coordinates

2.3.1 Generalized coordinates

To define generalized coordinates, we consider a macromolecular model that consists of N beads connected by either springs or rigid rods, with the location of each bead ν in the model denoted by position vector $\mathbf{r}_\nu$ and the mass of each bead as m_ν ($\nu = 1, 2, \dots, N$). Defining a reference vector, $\mathbf{r}_a$, by some weighted mean of the bead position vectors, one may then create another set of position vectors, $\mathbf{R}_\nu^a$, which correspond to the location of each bead relative to the reference vector. This set of relative position vectors, $\{\mathbf{R}_\nu^a\}$, is sufficient to describe fully the internal configuration of the molecular model. The reference vector, $\mathbf{r}_a$, is normally defined such that it moves with the solvent molecules unless an external force is present. Some typical choices of the reference vectors used in kinetic theory include the location of the center of mass ($\mathbf{r}_c = \sum m_\nu \mathbf{r}_\nu / \sum m_\nu$) and hydrodynamic

center of resistance ($\mathbf{r}_h = \sum l_\nu \mathbf{r}_\nu$ with l_ν chosen such that $\sum l_\nu H_{\mu\nu} \bar{B}_{k\mu} = 0$ where $H_{\mu\nu}$ is the hydrodynamic interaction matrix and $\bar{B}_{k\mu}$ is a connectivity matrix that will be defined in Equation 2.10).

Given the set of relative vectors $\{\mathbf{R}_\nu^a, \nu=1,2,\dots,N\}$, generalized coordinates are the smallest set of coordinates that can fully describe the internal coordinate of the molecule. A set of generalized coordinates is denoted as $\{Q_s, s=1,2,\dots,d\}$, with d as the total number of degrees of freedom for the internal coordinates. By definition, $\sum_{\nu=1}^N w_\nu \mathbf{R}_\nu = 0$, where w_ν are the weighting factors used to define the reference vector, and therefore, there are at most $3N-3$ degrees of freedom or internal coordinates to be specified. In models with no constraints, these internal coordinates can be defined in any convenient manner. In addition to the typical choice of Cartesian coordinates, some typically used generalized coordinates are defined for the fast computation of the intramolecular potential. For a molecular model with stretching, bending, and torsional potentials, a set of generalized coordinates could include the length of each bond ($N-1$), and the included angles ($2N-2$). The included angles consist of three contributions: the angle between two consecutive bonds ($N-2$), the torsional angles formed by three consecutive bonds ($N-3$), and a set of Euler angles (3) that define the overall orientation of the model.

For constrained systems, the total number of degrees of freedom is reduced by one for each constraint. For a molecular model with 5 rigid rod connectors and $N-5$ springs (c.f. a micromechanical model representing a copolymer molecule), the total numbers of degrees of freedom will be $3N-8$. For a Kramers chain model, the total numbers of degrees of freedom will be $2N-2$. Two typical choices of generalized coordinates for describing the internal configuration of a Kramers chain are the polar angle for the orientation of each rod in the model, or the included angle.

After choosing a set of generalized coordinates, it is important to transform the set of relative vectors into generalized coordinates. Many of the details are discussed in Chapter 12 of Bird et.al. [20], and here we focus on couple of the important concepts. The major idea for the transformation is analogous to the transformation from a Cartesian coordinate system to cylindrical or spherical system. To start with, one introduces the base vectors $\mathbf{b}_{vs}$ as:

$$\mathbf{b}_{vs}^a = \sqrt{w_v} \frac{\partial \mathbf{R}_v^a}{\partial Q_s} \quad (2.5)$$

For the convenience in representing the kinetic energy of a system, the center of mass is normally used to define the relative vector; and hence the kinetic energy of the system, $\mathcal{H}$, is represented as:

$$\mathcal{H} = \frac{1}{2} \sum_v m_v (\dot{\mathbf{r}}_v \cdot \dot{\mathbf{r}}_v) = \frac{1}{2} m_p (\dot{\mathbf{r}}_c \cdot \dot{\mathbf{r}}_c) + \frac{1}{2} \sum_s \sum_t \left[\sum_v (\mathbf{b}_{vs}^m \cdot \mathbf{b}_{vt}^m) \right] \dot{Q}_s \dot{Q}_t \quad (2.6)$$

the quality in $[\cdot]$ is the component of the metric matrix, g_{st} , and the square root of the determinant of the metric matrix is directly related to the momentum space contribution to the equilibrium, canonical distribution function. If G_{st} denotes the inverse of the metric matrix, then the generalized momenta, P_s are related to $\dot{Q}_s$ as $P_s = \sum_t G_{st} \dot{Q}_t$. The generalized force associated with a degree of freedom s , $\mathcal{F}_s$ is written as $\mathcal{F}_s = \sum_v (\mathbf{b}_{vs} \cdot \mathbf{F}_v) / \sqrt{m_v}$, and the generalized force acting on bead v is $\mathcal{F}_v = \sum_{s,t,\mu} (\mathbf{b}_{\mu s} \cdot \mathbf{F}_\mu) G_{st} \mathbf{b}_{vt}$.

In addition to the generalized coordinates, it is also useful to define a set of vectors $\{\mathbf{Q}_j\}$ to denote the link or the internal conformation of the molecules. The general expressions for converting between $\{\mathbf{Q}\}$ and $\{\mathbf{r}\}$ are:

$$\mathbf{Q}_k = \sum_v \bar{B}_{kv} \mathbf{r}_v \quad (2.7)$$

$$\mathbf{r}_v - \mathbf{r}_c = \sum_k B_{vk} \mathbf{Q}_k \quad (2.8)$$

For linear molecules with beads numbered from one end to the other, and with $\mathbf{Q}$ defined as the bond vector between two successive beads, $\bar{B}_{kv}$ is defined as

$$\bar{B}_{kv} = \delta_{k+1,v} - \delta_{k,v}, \quad (2.9)$$

and the associated matrix B_{vk} is defined as

$$B_{vk} = \begin{cases} k/N & \text{for } k < v \\ k/N - 1 & \text{for } k \geq v \end{cases} \quad (2.10)$$

Arbitrary topologies like branched, star, ring, and other shapes for the molecule can be described by appropriately defining $\bar{B}_{kv}$. In kinetic theory development, one often uses the dot product of $\bar{B}_{kv}$ and hence it is convenient to define the dot product as A_{ij} , such that $A_{ij} \equiv \sum_v \bar{B}_{iv} \bar{B}_{jv}$. The inverse of this matrix is denoted as C_{ij} , which can in turn defined by $C_{ij} = \sum_v B_{vi} B_{vj}$. The matrix A is known as the Rouse matrix for linear molecules. The Rouse matrix is the same as the stiffness matrix for a finite difference discretization of the diffusive operator; and this justifies the transformation from the discrete to continuous Rouse chain (Eqn. 2.3). The inverse of the Rouse matrix is the Kramers matrix. Other properties of the Rouse and the Kramers matrices can be found in Chapter 11 of [20].

2.3.2 Constrained coordinates

Although generalized coordinates provide the minimum set of variables to describe completely the degree of freedom in the model, they are not necessarily the best choice for computation because of the introduction of singularities. For example, consider the stochastic differential equation for a dilute suspension of rigid dumbbells¹,

$$d\mathbf{u} = -\text{De}(\boldsymbol{\kappa} \cdot \mathbf{u} - \boldsymbol{\kappa} : \mathbf{u}\mathbf{u}\mathbf{u})dt + \sqrt{2}d\mathbf{W}_t \quad (2.11)$$

1. For more information on of stochastic differential equations, see Chapter 3.

where $\mathbf{u}$ is the unit vector parallel to the orientation of a rigid dumbbell, $\boldsymbol{\kappa}$ is the transpose of the velocity gradient expressed in Cartesian coordinates, and W_t is the stochastic noise. If generalized coordinates are used with $(Q_1 = z = \cos\theta, Q_2 = \phi)$, then the component form of Equation 2.11 is:

$$\begin{bmatrix} dz \\ d\phi \end{bmatrix} = -D\epsilon\boldsymbol{\kappa} \cdot \begin{bmatrix} \sqrt{(1-z^2)}C \\ \sqrt{(1-z^2)}S \\ z \end{bmatrix} dt + \begin{bmatrix} \sqrt{2(1-z^2)}dW_z \\ 1/(1-z^2)dW_\phi \end{bmatrix} \quad (2.12)$$

where $S \equiv \sin\phi$ and $C \equiv \cos\phi$. W_z and W_ϕ are independent Wiener processes with zero mean and unit variance. The presence of $1/(1-z^2)$ in Equation 2.12 means that the stochastic force for the ϕ component will amplify the statistical noise significantly when z approaches -1 or 1. With z equal to -1 or 1, the stochastic differential equation becomes undefined.

A possible solution is the use of constraint coordinates, i.e. an extra (often redundant) unknown or variable is used to eliminate any singularity in the stochastic differential equation. One of the most popular strategies is to use Cartesian coordinates to specify the orientation of the molecules, and the resulting stochastic differential equation becomes:

$$\begin{bmatrix} du_1 \\ du_2 \\ du_3 \end{bmatrix} = -D\epsilon\boldsymbol{\kappa} \cdot \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} dt + \begin{bmatrix} dW_1 \\ dW_2 \\ dW_3 \end{bmatrix} \quad (2.13)$$

with the constraint that $u_1^2 + u_2^2 + u_3^2 = 1$. The constraint can be implemented through the use of a Lagrangian multiplier or a simple rescaling after each time step. The implementation details will be described in Chapter 4.

Another example of constraint coordinates involves the equation of motion for an arbitrary object, whose orientation is described by the Euler angles. The presence of divergence problems in the equations of motion for the orientation of the object is eliminated

by the use of a quaternion, $\mathbf{Q}$. The quaternion is a set of four scalar quantities (q_0, q_1, q_2, q_3) , with constraint $q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1$, for describing the orientation of an arbitrary, hard object. In molecular dynamics, this constraint is implemented through a rotational matrix acting on the equation of motion for the angular momentum. As a result, no nonlinear solution strategy or rescaling is necessary to preserve the constraint. This treatment is common in molecular dynamics and the book by Allen and Tildesley [1] is an excellent source for more detail regarding the implementation of quaternion.

2.4 Kinetic Theory

A formal treatment of phase-space kinetic theory for polymeric liquids is presented in Bird, et.al. [20] and is reviewed by Curtiss and Bird [44] for bead-spring models. In this section we highlight the principal results in kinetic theory that are important in rheology and fluid mechanics. Much of the material presented in this section is based on the series of papers presented by Curtiss and Bird in the late 1990s [44,45,46,47] and DPL2 [20].

The goal of the phase space kinetic theory is to develop constitutive equations at both the macroscopic and microscopic levels. Given a micromechanical model with specific intermolecular and intramolecular force expressions, the focus of statistical mechanics is on the equations of change. The fundamental equation of change in statistical mechanics is the Liouville equation:

$$\frac{\partial f}{\partial t} = -\mathcal{L}f \quad (2.14)$$

in which the Liouville operator, $\mathcal{L}$, for models without constraints is

$$\begin{aligned}
\mathcal{L} &\equiv \sum_{\alpha} \sum_i \sum_{\nu} \left(\frac{\partial}{\partial \mathbf{r}_{\nu}^{\alpha i}} \cdot \mathbf{r}_{\nu}^{\alpha i} + \frac{\partial}{\partial \mathbf{p}_{\nu}^{\alpha i}} \cdot \mathbf{p}_{\nu}^{\alpha i} \right) \\
&= \sum_{\alpha} \sum_i \sum_{\nu} \left(\frac{\mathbf{p}_{\nu}^{\alpha i}}{m_{\nu}^{\alpha i}} \cdot \frac{\partial}{\partial \mathbf{r}_{\nu}^{\alpha i}} + \mathbf{F}_{\nu}^{\alpha i} \cdot \frac{\partial}{\partial \mathbf{p}_{\nu}^{\alpha i}} \right)
\end{aligned} \tag{2.15}$$

The second line is obtained through the use of Newton's second law of motion ($\mathbf{F} = \dot{\mathbf{p}}$). For general descriptions of an arbitrary model, the Liouville operator can also be rewritten in generalized coordinates as in Equation 2.16 with $\mathbf{r}^{\alpha i}$ as the reference vector (normally taken as the center of mass).

$$\begin{aligned}
\mathcal{L} = \sum_{\alpha} \sum_i \left(\frac{1}{m^{\alpha}} \left(\mathbf{p}^{\alpha i} \cdot \frac{\partial}{\partial \mathbf{r}^{\alpha i}} \right) + \sum_s \sum_t G_{st} \mathbf{p}_t^{\alpha i} \frac{\partial}{\partial Q_s^{\alpha i}} + \right. \\
\left. [\mathbf{F}^e + \mathbf{F}^{\alpha i}] \cdot \frac{\partial}{\partial \mathbf{p}^{\alpha i}} + \sum_s \mathcal{F}_s^{\alpha i} \frac{\partial}{\partial P_s^{\alpha i}} \right)
\end{aligned} \tag{2.16}$$

For a classical N -body Hamiltonian system whose dynamics is governed by Hamilton's equations of motion, The Liouville operator (operating on an arbitrary dynamic variable B) is equivalent to the Poisson bracket, which is given by Eqn. 2.17.

$$\{\mathcal{H}, B\} = \sum_{\alpha} \sum_i \sum_{\nu} \left(\frac{\partial}{\partial \mathbf{p}_{\nu}^{\alpha i}} \mathcal{H} \cdot \frac{\partial B}{\partial \mathbf{r}_{\nu}^{\alpha i}} - \frac{\partial}{\partial \mathbf{r}_{\nu}^{\alpha i}} \mathcal{H} \cdot \frac{\partial B}{\partial \mathbf{p}_{\nu}^{\alpha i}} \right) \tag{2.17}$$

where $\mathcal{H}$ is the Hamiltonian of the system. If $\mathcal{H}$ does not depend explicitly on time, then it corresponds to the total energy of the system.

Given an initial distribution at t_0 , the formal solution to the Liouville equation is

$$f(x^N, t_1) = e^{(t_1 - t_0)\mathcal{L}} f(x^N, t_0) \tag{2.18}$$

Here, x^N correspond to all the independent variables in the momentum and configuration space. Furthermore, the *Liouville theorem* also suggests that the density of system points in the phase space does not change with time along a trajectory executed by a system point in the phase space, i.e. $f(x', t') = f(x, t)$ if and only if $x = \exp((t - t')\mathcal{L})x'$, where x' is

the location in phase space of a system point a time t' , and x is the location of the same system point at time t along the trajectory in the phase space. One may imagine time t as the present time and t' as the past time. The relationship between x and x' can also be written as a Liouville-like equation of motion, $\dot{x} = \mathcal{L}x$.

Although a general solution to the Liouville equation is available, its formality and extremely large dimension makes it impractical for any engineering calculation. Furthermore, most measurable experimental quantities can be expressed in terms of a contracted distribution or even just moments of the distribution function. One may derive a general equation of change for an arbitrary dynamical variable $B(\mathbf{r}^{\alpha i}, \mathbf{p}^{\alpha i}, Q_s^{\alpha i}, P_s^{\alpha i})$ by multiplying Equation 2.14 by B and integrating over the phase space. After an integration by parts, the general equation of change becomes:

$$\frac{\partial}{\partial t} \langle B \rangle = \langle \mathcal{L}B \rangle \quad (2.19)$$

in which the angular brackets indicate an average over the whole phase space that is defined by the arguments of the distribution function.

This general equation of change plays a central role in kinetic theory. By making suitable choices of the dynamic variable B , we can obtain the macroscopic equations of change, Fokker-Planck equation that governs the time evolution of the distribution function of the molecular orientation and the position of the center of mass, and other important evolution equations. A summary of the some particular choices of B and the corresponding evolution equations are show in Fig. 2.4. In the following subsections, the derivation of the Fokker-Planck equation, as well as various constitutive equations for the equation of continuity and the equation of motion through the use of kinetic theory will be reviewed. Without losing generality, we focus on the elastic dumbbell model. This models has no internal constraints, and Cartesian coordinates can be used as the generalized coor-

ordinates. As a result, presentation of the basic ideas and procedures of the kinetic theory is rather simple with minimal mathematics complications due to the non-constant metric matrix or base vectors.

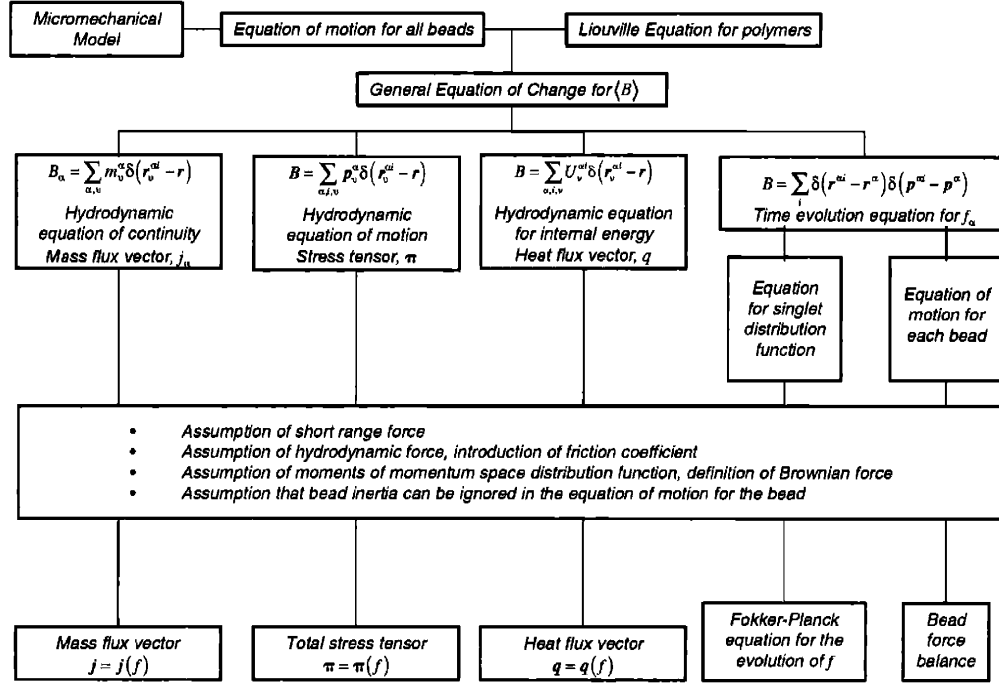


Figure 2.4: Equations of change and the flux expressions obtained from the general equation of change (Eqn. 2.19) and how the five main assumptions are used to get expressions for the fluxes for a specific molecular model. Here, $\delta(x)$ is the Dirac delta function.

2.4.1 Polymer Singlet Distribution Function

Assuming all the molecules of the same species in the system behave in a statistically similar manner, a singlet distribution function for species α can be defined by choosing B such that it picks all the molecules of species α with specific phase space coordinates.

$$B = \sum_i \prod_v \delta(\mathbf{r}_v^{\alpha i} - \mathbf{r}_v^\alpha) \delta(\mathbf{p}_v^{\alpha i} - \mathbf{p}_v^\alpha) \quad (2.20)$$

and the resulting singlet distribution function is given by $f_\alpha = \langle B \rangle$. The quantity $f_\alpha d\mathbf{r}^{\alpha,N} d\mathbf{p}^{\alpha,N}$ is interpreted as the number of molecules of species α for which bead v is located in the range $d\mathbf{r}_v^\alpha$ about $\mathbf{r}_v^\alpha$ with momentum in the range $d\mathbf{p}_v^\alpha$ about $\mathbf{p}_v^\alpha$, for

$\nu = 1, 2, \dots, N$. The symbols $d\mathbf{r}^{\alpha, N}$ and $d\mathbf{p}^{\alpha, N}$ are the shorthand for $d\mathbf{r}_1^\alpha d\mathbf{r}_2^\alpha \dots d\mathbf{r}_N^\alpha$ and $d\mathbf{p}_1^\alpha d\mathbf{p}_2^\alpha \dots d\mathbf{p}_N^\alpha$ respectively. Furthermore, we denote the collection of bead position vectors $\{\mathbf{r}_\nu^\alpha, \nu = 1, 2, \dots, N_\alpha\}$ as $\mathbf{r}^{N_\alpha}$ and bead momentum vectors $\{\mathbf{p}_\nu^\alpha, \nu = 1, 2, \dots, N_\alpha\}$ as $\mathbf{p}^{N_\alpha}$. Making use of the general equation of change and Eqn. 2.20 and assuming pair-wise intermolecular force for non-bonded interaction, the time evolution equation for the singlet distribution function for species α is

$$\frac{\partial f_\alpha}{\partial t} + \sum_\nu \left(\frac{\mathbf{p}_\nu^\alpha}{m_\nu} \cdot \frac{\partial f_\alpha}{\partial \mathbf{r}_\nu^\alpha} + \mathbf{F}_\nu^{(s)\alpha} \cdot \frac{\partial f_\alpha}{\partial \mathbf{p}_\nu^\alpha} \right) = K_\alpha \quad (2.21)$$

where $\mathbf{F}_\nu^{(s)\alpha}$ is the sum of all forces acting on bead ν that do not depend on the configuration of molecules other than the test molecule itself. The quantity K_α is known as the collision integral that accounts for the intermolecular interaction

$$\begin{aligned} K_\alpha(\mathbf{r}^\alpha, \mathbf{p}^\alpha, t) &= -\sum_\nu \left(\frac{\partial}{\partial \mathbf{p}_\nu^\alpha} \cdot \left\langle \sum_i \mathbf{F}_\nu^{(d)\alpha i} \delta(\mathbf{r}_\nu^\alpha - \mathbf{r}_i^\alpha) \delta(\mathbf{p}_\nu^\alpha - \mathbf{p}_i^\alpha) \right\rangle \right) \\ &= -\sum_{\nu\beta\mu} \left(\frac{\partial}{\partial \mathbf{p}_\nu^\alpha} \cdot \iint \mathbf{F}_{\nu\mu}^{(d)\alpha\beta} f_{\alpha\beta}(\mathbf{r}_\nu^\alpha, \mathbf{p}_\nu^\alpha, \mathbf{r}_\mu^\beta, \mathbf{p}_\mu^\beta) d\mathbf{r}_\mu^\beta d\mathbf{p}_\mu^\beta \right) \end{aligned} \quad (2.22)$$

Here $\mathbf{F}_\nu^{(d)\alpha}$ is the total force acting on bead ν by all the other molecules in the system, and $\mathbf{F}_{\nu\mu}^{(d)\alpha\beta}$ is the intermolecular force on species α , bead μ exerted by bead ν of species β .

$f_{\alpha\beta}(\mathbf{r}^{\alpha, N}, \mathbf{p}_\nu^{\alpha, N}, \mathbf{r}^{\beta, N}, \mathbf{p}_\mu^{\beta, N})$ is the distribution function for any pair of molecules in the system and is defined by choosing B such that it picks the position and momentum of two molecules, i.e. $B = \sum_i \sum_j \prod_\nu \prod_\mu \delta(\mathbf{r}_\nu^{\alpha i} - \mathbf{r}_\nu^\alpha) \delta(\mathbf{p}_\nu^{\alpha i} - \mathbf{p}_\nu^\alpha) \delta(\mathbf{r}_\mu^{\beta j} - \mathbf{r}_\mu^\beta) \delta(\mathbf{p}_\mu^{\beta j} - \mathbf{p}_\mu^\beta)$. The appearance of this pair distribution function $f_{\alpha\beta}$ on the right hand side of Equation 2.21 couples this equation with the evolution equation for the evolution of $f_{\alpha\beta}$, which in turn couples with the next higher order equation in a hierarchy of equations that is equivalent to the original Liouville equation. This hierarchy is a generalization of the BBGKY (Bogolyubov-Born-Green-Kirkwood-Yvon) hierarchy. Assumptions are therefore unavoidable if a closed equation for the singlet distribution function f_α is desired. Most of these assump-

tions are based on the time-smoothing argument, where three distinct time scales exist: the time interval for molecular collision (λ_c), the characteristic time for time averaging operation (τ), and the characteristic time scale for the hydrodynamic motion or macroscopic process (λ_h). Assuming these three time scales are widely separated ($\lambda_c \ll \tau \ll \lambda_h$), a closure approximation for the pair distribution function can be derived or postulated based on the time smoothed, singlet distribution function, $\bar{f}_\alpha$, where $\bar{f}_\alpha \equiv \frac{1}{\tau} \int_{t-\tau}^t f_\alpha dt'$. For example, by choosing $\bar{f}_{\alpha\beta}(x, y) \approx \bar{f}_\alpha(x) \cdot \bar{f}_\beta(y)$, Equation 2.21 reduces to the classical Boltzmann kinetic equation. A detailed derivation is summarized by [97] and is not repeated here. The classical Boltzmann equation is the key for a wide range of transport predictions for simple gases and liquids. Furthermore, this classical Boltzmann equation has been extended and simulated directly for calculating the hydrodynamics and transport phenomena of simple and complex fluid systems. This simulation method is known as the Lattice Boltzmann method.

The most important development in the polymer kinetic theory involves one that eventually leads to a Fokker-Planck, or diffusion, equation for the singlet distribution function evolution. An example of the derivation is provided by Curtiss and Bird [45], and several of the important steps are highlighted as below. The central idea of their derivation is the postulate regarding the doublet distribution function. In the derivation of Curtiss and Bird, the doublet distribution function is:

$$\begin{aligned} \overline{f^{\alpha i, \beta j}} = e^{(t-t')\mathcal{L}} & \left[\delta(x^{\alpha i} - x^\alpha) \delta(x^{\beta j} - x^\beta) \right. \\ & \left. \cdot f_{h0}^{\alpha\beta}(x, t) \frac{\bar{f}_\alpha(x^\alpha, t)}{f_{\alpha 0}(x^\alpha, t)} \frac{\bar{f}_\beta(x^\beta, t)}{\bar{f}_{\beta 0}(x^\beta, t)} \right] \end{aligned} \quad (2.23)$$

in which $f_{h0}^{\alpha\beta}(x, t)$ is the zeroth order expansion of the hydrodynamic solution ($f_h^{\alpha\beta}(x, t)$) with a small parameter as the ratio of collision time to the relaxation time. The hydrody-

dynamic solution, $f_h^{\alpha\beta}(x, t)$, in turn is associated with the steady-state solution of the Liouville equation, $\mathcal{L}f_h^{\alpha\beta}(x, t) = 0$. $\bar{f}_{\alpha 0}(x^\alpha, t)$ is the momentum-equilibrated singlet distribution function for species α where the dependence on the momentum space variables is expressed by the Boltzmann distribution.

$$\bar{f}_{\alpha 0} = J^{-1} \Psi_\alpha(\mathbf{r}_v^\alpha, t) \exp \left[- \sum_v \frac{(\mathbf{p}_v^\alpha - [\mathbf{p}_v^\alpha])^2}{2m^\alpha kT(\mathbf{r}_v^\alpha, t)} \right] \quad (2.24)$$

In this equation, J is the normalization constant; and $\Psi_\alpha(\mathbf{r}_v^\alpha, t)$ is the nonequilibrium singlet distribution function in the configuration space, which can ultimately be obtained from the solution of an appropriate Fokker-Planck or diffusion equation. The physical interpretation for Equation 2.23 is as follows: In the limit of $t' \rightarrow t$ and $\epsilon = \lambda_c/\lambda_h \rightarrow 0$, the doublet distribution function $\bar{f}^{\alpha i, \beta j}$ approaches to the local equilibrium solution $f_{h0}^{\alpha\beta}(x, t)$. For finite ϵ and duration, $\bar{f}^{\alpha i, \beta j}$ at time t is given by the local equilibrium solution corrected by the ratio of $\bar{f}_\alpha \bar{f}_\beta / \bar{f}_{\alpha 0} \bar{f}_{\beta 0}$. Then the projection from time t to t' is performed by the operator $e^{(t-t')\mathcal{L}}$.

By substituting Equation 2.24 into the collision integral (Eqn. 2.22), a simplified equation for the singlet distribution function is obtained:

$$\frac{\partial \bar{f}_\alpha}{\partial t} + \sum_v \left(\frac{\mathbf{p}_v^\alpha}{m^\alpha} \cdot \frac{\partial \bar{f}_\alpha}{\partial \mathbf{r}_v^\alpha} + \mathbf{F}_v^\alpha \cdot \frac{\partial \bar{f}_\alpha}{\partial \mathbf{p}_v^\alpha} \right) = 0 \quad (2.25)$$

with

$$\begin{aligned} \mathbf{F}_v^\alpha = & \mathcal{F}_v^{(e)\alpha} + \mathcal{F}_v^{(\phi)\alpha} + \mathcal{F}_v^{(h)\alpha} + \mathcal{F}_v^{(b)\alpha} \\ & + \sum_{\beta\mu} \int g_{\alpha\beta,0}(x^\alpha, x^\beta, t) \bar{f}_\beta \mathbf{F}_{v\mu}^{(d)\alpha\beta} dx^\beta \end{aligned} \quad (2.26)$$

in which $g_{\alpha\beta,0}(x^\alpha, x^\beta, t)$ is the equilibrium radial distribution function between two molecules. $\mathcal{F}_v^{(e)\alpha}$ and $\mathcal{F}_v^{(\phi)\alpha}$ are the generalized contributions due to the external force and intramolecular forces acting on bead v respectively. Two new contributions, the hydrody-

dynamic force ($\mathcal{F}_\nu^{(h)\alpha}$) and Brownian force ($\mathcal{F}_\nu^{(b)\alpha}$) are introduced to represent the short range, intermolecular interactions. These contributions are represented in the form of a generalized force on a bead as follows:

$$\mathcal{F}_\nu^{(h)\alpha} = \sum_{\beta\eta\mu} \bar{f}_\beta \left[E_{\nu\mu,\eta}^{\alpha\beta} \cdot \frac{\partial}{\partial \mathbf{p}_\eta^\alpha} \ln \bar{f}_{\alpha 0} + \Delta_{\nu\mu,\eta}^{\alpha\beta} \cdot \frac{\partial}{\partial \mathbf{r}_\eta^\alpha} \ln \bar{f}_{\alpha 0} \right] dx^\beta \quad (2.27)$$

$$- \sum_{\beta\lambda\mu} \bar{f}_\beta \left[E_{\nu\mu,\lambda}^{\beta\alpha} \cdot \frac{\partial}{\partial \mathbf{p}_\lambda^\beta} \ln \bar{f}_{\beta 0} + \Delta_{\nu\mu,\lambda}^{\beta\alpha} \cdot \frac{\partial}{\partial \mathbf{r}_\lambda^\beta} \ln \bar{f}_{\beta 0} \right] dx^\beta$$

$$\mathcal{F}_\nu^{(b)\alpha} = \sum_{\beta\eta\mu} \bar{f}_\beta \left[E_{\nu\mu,\eta}^{\alpha\beta} \cdot \frac{\partial}{\partial \mathbf{p}_\eta^\alpha} \ln \bar{f}_\alpha + \Delta_{\nu\mu,\eta}^{\alpha\beta} \cdot \frac{\partial}{\partial \mathbf{r}_\eta^\alpha} \ln \bar{f}_\alpha \right] dx^\beta \quad (2.28)$$

$$- \sum_{\beta\lambda\mu} \bar{f}_\beta \left[E_{\nu\mu,\lambda}^{\beta\alpha} \cdot \frac{\partial}{\partial \mathbf{p}_\lambda^\beta} \ln \bar{f}_\beta + \Delta_{\nu\mu,\lambda}^{\beta\alpha} \cdot \frac{\partial}{\partial \mathbf{r}_\lambda^\beta} \ln \bar{f}_\beta \right] dx^\beta$$

where $E_{\nu\mu,\eta}^{\alpha\beta}$ and $\Delta_{\nu\mu,\eta}^{\alpha\beta}$ are averaged correlation functions¹ that are derived from the integrals of time correlation functions ($E_{\nu\mu,\eta}^{\alpha i, \beta j}$ and $\Delta_{\nu\mu,\eta}^{\alpha i, \beta j}$):

$$E_{\nu\mu,\eta}^{\alpha i, \beta j} \equiv \int_0^\tau \left(1 - \frac{s}{\tau} \right) F_\eta^{\alpha i} e^{-s\mathcal{L}} F_{\nu\mu}^{(d)\alpha i, \beta j} ds \quad (2.29)$$

$$\Delta_{\nu\mu,\eta}^{\alpha i, \beta j} \equiv \int_0^\tau \left(1 - \frac{s}{\tau} \right) \frac{\mathbf{p}_\eta^{\alpha i}}{m^\alpha} e^{-s\mathcal{L}} F_{\nu\mu}^{(d)\alpha i, \beta j} ds$$

The physical interpretations of these functions are that $E_{\nu\mu,\eta}^{\alpha i, \beta j}$ correlates the total force acting on bead η of molecule i from species α ($F_\eta^{\alpha i}$) with the intermolecular force ($e^{-s\mathcal{L}} F_{\nu\mu}^{(d)\alpha i, \beta j}$) and $\Delta_{\nu\mu,\eta}^{\alpha i, \beta j}$ correlates the velocity of bead η ($\mathbf{p}_\eta^{\alpha i}/m^\alpha$) with $e^{-s\mathcal{L}} F_{\nu\mu}^{(d)\alpha i, \beta j}$. For models with no internal constraints, the generalized forces ($\mathcal{F}_\nu^{(\cdot)\alpha}$) are the same as the forces on the bead. Although Eqn 2.25 can be, in principle, solved for the time-smoothed, singlet distribution function, a more elegant and useful form for Eqn. 2.25 is in the form of a Fokker-Planck equation. To simplify Eqn 2.25 into a Fokker-Planck equation, three major assumptions are required:

1. Neglect the last term in Equation 2.26

1. The averaged correlation for $B^{\alpha i, \beta j}$ is defined as $B^{\alpha\beta} \bar{f}_\alpha \bar{f}_\beta \equiv \sum_{ij} \int B^{\alpha i, \beta j} \delta(x^{\alpha i} - x^\alpha) \delta(x^{\beta j} - x^\beta) f_{h0}^{\alpha\beta} dx$

2. Neglect all the correlation functions in the hydrodynamic force and Brownian force except for the self-correlation tensors, i.e. $E_{\nu\mu, \eta}^{\alpha i, \beta j} = \delta_{\eta\nu} E_{\nu\mu}^{\alpha i, \beta j}$ and $\Delta_{\nu\mu, \eta}^{\alpha i, \beta j} = 0$. This assumption is identical to the short range bead-bead force assumption.

3. Assume all the self-correlation tensors are independent of the momentum space variables. This assumption leads to the definition of the friction tensor as follows:

$$\zeta_{\nu}^{\alpha} = \frac{1}{kT(r_{\nu}^{\alpha}, t)} \sum_{\beta\mu} \int E_{\nu\mu}^{\alpha\beta} \bar{f}_{\beta} dx^{\beta} \quad (2.30)$$

and the definition for $W_{\nu}^{\alpha}(r_{\nu}^{\alpha}, t)$ that accounts the deviation from the Stokes law for the hydrodynamics force because of the interdiffusion between various species

$$\zeta_{\nu}^{\alpha} \cdot W_{\nu}^{\alpha} = \sum_{\beta\mu} \int \bar{f}_{\beta} E_{\nu\mu}^{\alpha\beta} \cdot \frac{\partial}{\partial p_{\mu}^{\beta}} \ln \bar{f}_{\beta 0} dx^{\beta} \quad (2.31)$$

With these three assumptions, Equation 2.26 becomes

$$\begin{aligned} \mathbf{F}_{\nu}^{\alpha} &= \mathcal{F}_{\nu}^{(e)\alpha} + \mathcal{F}_{\nu}^{(\phi)\alpha} + \mathcal{F}_{\nu}^{(h)\alpha} + \mathcal{F}_{\nu}^{(b)\alpha} \\ &= \mathcal{F}_{\nu}^{(e)\alpha} + \mathcal{F}_{\nu}^{(\phi)\alpha} - \zeta_{\nu}^{\alpha} \cdot \left[\frac{\mathbf{p}_{\nu}^{\alpha}}{m^{\alpha}} - \mathbf{v}(r_{\nu}^{\alpha}, t) - W_{\nu}^{\alpha}(r_{\nu}^{\alpha}, t) \right] \\ &\quad - \zeta_{\nu}^{\alpha} kT(r_{\nu}^{\alpha}, t) \cdot \frac{\partial}{\partial \mathbf{p}_{\nu}^{\alpha}} \ln \bar{f}_{\alpha} \end{aligned} \quad (2.32)$$

The various contributions in this equation of motion for a bead in the phase space can be identified as the external, intramolecular, hydrodynamic (dissipative), and Brownian (fluctuating) forces. Effects of polymer entanglement, hydrodynamic interaction, and other physics for describing the motion of polymer molecules can be incorporated by appropriate choosing the functional form of ζ_{ν}^{α} and $W_{\nu}^{\alpha}(r_{\nu}^{\alpha}, t)$. Combining 2.25 and 2.32, the Fokker-Planck equation for the time-smoothed phase-space distribution function becomes:

$$\begin{aligned}
\frac{\partial \bar{f}_\alpha}{\partial t} + \sum_\nu \left(\frac{\mathbf{p}_\nu^\alpha}{m_\nu^\alpha} \cdot \frac{\partial \bar{f}_\alpha}{\partial \mathbf{r}_\nu^\alpha} + (\mathbf{F}_\nu^{(e),\alpha} + \mathbf{F}_\nu^{(\phi),\alpha}) \cdot \frac{\partial \bar{f}_\alpha}{\partial \mathbf{p}_\nu^\alpha} \right) \\
= \sum_\nu \frac{\partial}{\partial \mathbf{p}_\nu^\alpha} \left(\boldsymbol{\zeta} \cdot kT_\nu^\alpha \frac{\partial \bar{f}_\alpha}{\partial \mathbf{p}_\nu^\alpha} + \boldsymbol{\zeta}_\nu^\alpha \cdot \left(\frac{\mathbf{p}_\nu^\alpha}{m_\nu^\alpha} - \mathbf{v}(\mathbf{r}_\nu^\alpha, t) - \mathbf{W}(\mathbf{r}^\alpha, t) \right) \bar{f}_\alpha \right)
\end{aligned} \tag{2.33}$$

This Fokker-Planck equation can be further reduced to the Fokker-Planck equation for the configuration space singlet distribution by integrating Equation 2.33 over the momentum space. The resulting Fokker-Planck equation is

$$\frac{d\Psi_\alpha}{dt} = - \sum_\nu \left(\frac{\partial}{\partial \mathbf{r}_\nu^\alpha} \cdot \frac{1}{m_\nu^\alpha} [\mathbf{p}_\nu^\alpha] \Psi_\alpha \right) \tag{2.34}$$

where $[\mathbf{p}_\nu^\alpha] \Psi_\alpha = \int \mathbf{p}_\nu^\alpha \bar{f}_\alpha(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{p}^N$. The expression for $[\mathbf{p}_\nu^\alpha]$ can in turn be derived by the same contraction procedure by multiplying Eqn. 2.33 by $\mathbf{p}_\nu^\alpha$ and integrating over the momentum space. The resulting equation for $[\mathbf{p}_\nu^\alpha]$ is:

$$\begin{aligned}
\frac{\partial [\mathbf{p}_\nu^\alpha]}{\partial t} + \sum_\mu \frac{[\mathbf{p}_\mu^\alpha]}{m_\mu^\alpha} \cdot \frac{\partial [\mathbf{p}_\mu^\alpha]}{\partial \mathbf{r}_\mu^\alpha} &= \mathbf{F}_\nu^{(e)\alpha} + \mathbf{F}_\nu^{(\phi)\alpha} + \mathbf{F}_\nu^{(h)\alpha} + \mathbf{F}_\nu^{(b)\alpha} \\
&= \mathbf{F}_\nu^{(e)\alpha} + \mathbf{F}_\nu^{(\phi)\alpha} \\
&\quad - \frac{1}{\Psi_\alpha} \sum_\mu \frac{1}{m_\mu^\alpha} \left(\frac{\partial}{\partial \mathbf{r}_\mu^\alpha} \cdot [(\mathbf{p}_\mu^\alpha - [\mathbf{p}_\nu^\alpha])(\mathbf{p}_\mu^\alpha - [\mathbf{p}_\nu^\alpha])] \Psi_\alpha \right) \\
&\quad - \boldsymbol{\zeta}_\nu^\alpha \cdot \left(\frac{[\mathbf{p}_\nu^\alpha]}{m_\nu^\alpha} - \mathbf{v}(\mathbf{r}_\nu^\alpha, t) - \mathbf{W}(\mathbf{r}^\alpha, t) \right)
\end{aligned} \tag{2.35}$$

The presence of the second moment $[(\mathbf{p}_\mu^\alpha - [\mathbf{p}_\nu^\alpha])(\mathbf{p}_\mu^\alpha - [\mathbf{p}_\nu^\alpha])]$ in the Brownian force contribution requires a closure approximation in order to obtain a closed equation of motion for $[\mathbf{p}_\nu^\alpha]$ for the Fokker-Planck equation. Whereas most kinetic theory development assumes that the momentum space distribution function for each bead in the molecule is Gaussian or Maxwellian, Öttinger and Petrillo [169] showed that such assumption is insufficient for evaluating higher moments of the momentum space distribution function. Therefore, a systematic method for evaluating various moments of the singlet distribution function and their deviations from the Maxwellian distribution function is essential.

This is done by solving the Fokker-Planck equation directly as a perturbation problem. For molecular models with no internal constraints, identical mass beads $m_v^\alpha = m_0^\alpha$, and isotropic $E_{v\mu}^{\alpha\beta}$ and drag coefficient ($\zeta_v^\alpha = \zeta\delta$), Curtiss and Bird [45] first defined the momentum equilibrated singlet distribution function through $\bar{f}_\alpha = \Xi \cdot \bar{f}_{\alpha 0}$. They then expanded the deviation of the momentum equilibrated distribution function (Ξ_{eq}) from the exact momentum distribution function (Ξ) with normalized tensor Hermite polynomials $\{\mathbf{h}^{[n]}\}$ with a dimensionless momentum variable defined as $\mathbf{P}_v^\alpha \equiv (\mathbf{p}_v^\alpha - [\mathbf{p}_v^\alpha]) / \sqrt{2m_0^\alpha kT}$. In this expansion $(\Xi(\mathbf{r}^\alpha, \mathbf{P}^\alpha, t) = 1 + \sum_n \varepsilon^n \mathbf{g}_\alpha^{[n]} \cdot \mathbf{h}^{[n]}(\mathbf{P}^\alpha))$, ε is the square root of the ratio of the collision time scale to the hydrodynamic time scale, $\varepsilon = \sqrt{\lambda_c/\lambda_h}$, and the coefficients of $\mathbf{g}_\alpha^{[n]}$ are the projection of Ξ onto $\mathbf{h}^{[n]}$, i.e. $\mathbf{g}_\alpha^{[n]} = \int \mathbf{h}^{[n]}(\mathbf{P}^\alpha) \Xi(\mathbf{r}^\alpha, \mathbf{P}^\alpha, t) d\mathbf{P}^\alpha$. By including the first order contribution, the first three moments of the singlet distribution function are:

$$\begin{aligned} [\mathbf{p}_v^\alpha/m_0^\alpha - \mathbf{v}_v^\alpha] &= -\frac{1}{\zeta_0 \Psi_\alpha} \frac{\partial}{\partial \mathbf{r}_v^\alpha} (kT_v^\alpha \Psi_\alpha) + \frac{1}{\zeta_0} (\mathbf{F}_v^{(e),\alpha} + \mathbf{F}_v^{(\phi),\alpha}) \\ &\quad + \varepsilon \left(\mathbf{W}_{v1}^\alpha + \lambda_h \frac{D^\alpha \mathbf{v}_v^\alpha}{Dt} \right) \end{aligned} \quad (2.36)$$

$$\begin{aligned} \frac{[(\mathbf{p}_v^\alpha/m_0^\alpha - \mathbf{v}_v^\alpha)(\mathbf{p}_v^\alpha/m_0^\alpha - \mathbf{v}_v^\alpha)]}{kT_v^\alpha} &= \delta \\ -\varepsilon \frac{\lambda_h}{8} \left[\left(\frac{D^\alpha}{Dt} \ln T_v^\alpha \right) \delta + \left(\frac{\partial \mathbf{v}_v^\alpha}{\partial \mathbf{r}_v^\alpha} \right) + \left(\frac{\partial \mathbf{v}_v^\alpha}{\partial \mathbf{r}_v^\alpha} \right)^\top \right] \end{aligned} \quad (2.37)$$

$$\begin{aligned} \frac{[(\mathbf{p}_v^\alpha/m_0^\alpha - \mathbf{v}_v^\alpha)(\mathbf{p}_v^\alpha/m_0^\alpha - \mathbf{v}_v^\alpha)(\mathbf{p}_v^\alpha/m_0^\alpha - \mathbf{v}_v^\alpha)]}{kT_v^\alpha} &= \\ \frac{T_v^\alpha}{T_0} ([\mathbf{p}_v^\alpha/m_0^\alpha - \mathbf{v}_v^\alpha] \delta) + \varepsilon \left(\frac{kT_v^\alpha}{m_0} \right)^2 \end{aligned} \quad (2.38)$$

Substituting Eqn. 2.36 into Eqn. 2.34 and ignoring hydrodynamic interaction, the Fokker-Planck equation for the configuration space single distribution function becomes:

$$\begin{aligned} \frac{\partial \Psi_\alpha}{\partial t} = & - \sum_v \left(\frac{\partial}{\partial \mathbf{r}_v} \cdot \left[\mathbf{v}_v^\alpha + \frac{1}{\zeta_0} (\mathbf{F}_v^{(e), \alpha} + \mathbf{F}_v^{(\phi), \alpha}) \right. \right. \\ & \left. \left. + \epsilon \left(\mathcal{W}_{v1}^\alpha + \lambda_h \frac{D^\alpha \mathbf{v}_v^\alpha}{Dt} \right) \right] \Psi_\alpha \right) + \sum_v \frac{\partial}{\partial \mathbf{r}_v} \cdot \frac{1}{\zeta_0} \frac{\partial}{\partial \mathbf{r}_v} (k T_v^\alpha \Psi_\alpha) \end{aligned} \quad (2.39)$$

Equation 2.39 can be rewritten into contributions due to center of mass and internal configuration through the use of $\{\mathbf{Q}_j\}$ defined in the previous section. Truncating the first order terms in ϵ and ignoring the effect of external forces, the resulting Fokker-Planck equation for the configuration space distribution function is:

$$\begin{aligned} \frac{\partial \Psi}{\partial t} + \mathbf{v}_c \cdot \frac{\partial \Psi}{\partial \mathbf{r}_c} - \frac{\partial}{\partial \mathbf{r}_c} \cdot \frac{k T_c}{N \zeta_0} \frac{\partial \Psi}{\partial \mathbf{r}_c} = \\ - \sum_j \frac{\partial}{\partial \mathbf{Q}_j} \cdot \left\{ \left[\sum_v \bar{B}_{kv} \mathbf{v}_v^\alpha \right] - \frac{1}{\zeta_0} \sum_k A_{jk} \left(\left[k \sum_v \bar{B}_{kv} T_v^\alpha \right] \frac{\partial \Psi_\alpha}{\partial \mathbf{Q}_k} + \mathbf{F}_k^{(e)} \Psi \right) \right\} \end{aligned} \quad (2.40)$$

The two quantities due to local velocity ($\sum_v \bar{B}_{kv} \mathbf{v}_v^\alpha$) and temperature ($\sum_v \bar{B}_{kv} T_v^\alpha$) fluctuations can be further simplified by a Taylor series expansion with the small parameter, ϵ , as the ratio of molecular length to macroscopic length, ℓ/L . As will be demonstrated later in this section, the expansions have to be truncated consistently such that the resulting Fokker-Planck equation and the macroscopic constitutive flux expressions are of the same order of ℓ/L . In the limit of the zeroth-order expansion, the Fokker-Planck equation for an isothermal, homogeneous suspension of elastic dumbbells is:

$$\frac{\partial \Psi}{\partial t} + \mathbf{v}_c \cdot \frac{\partial \Psi}{\partial \mathbf{r}_c} = - \frac{\partial}{\partial \mathbf{Q}} \cdot \left\{ \nabla \mathbf{v}^T \cdot \mathbf{Q} \Psi - \frac{1}{2 \zeta_0} \left(k T \frac{\partial \Psi}{\partial \mathbf{Q}} + \mathbf{F}^{(c)} \Psi \right) \right\} \quad (2.41)$$

In Equation 2.41, the vector $\mathbf{Q}$ connecting the two beads describes the orientation and the end-to-end distance of the macromolecule. The distribution function, $\psi(\mathbf{Q})$, is the configuration space distribution function normalized by the number density of the macromolecules in the system, i.e. $\psi = \Psi/n$. $\psi(\mathbf{Q})$ is defined such that $\psi(\mathbf{Q})d\mathbf{Q}$ is the probability

that a molecule has configuration within a region $d\mathbf{Q}$ about $\mathbf{Q}$ with normalization $\int \psi(\mathbf{Q})d\mathbf{Q} = 1$.

The Fokker-Planck equation (Eqn. 2.41) can be made dimensionless by scaling time by a characteristic flow time scale T , and length by the equilibrium length of the macro-molecule. The resulting Fokker-Planck equation is

$$\text{De} \left(\frac{\partial \psi}{\partial t^*} + \mathbf{v}_c^* \cdot \frac{\partial \psi}{\partial \mathbf{r}_c^*} \right) = \frac{\partial}{\partial \mathbf{Q}^*} \cdot \left\{ \text{De} \nabla^* \mathbf{v}^{*\text{T}} \cdot \mathbf{Q}^* \psi - \frac{\partial \psi}{\partial \mathbf{Q}^*} + \mathbf{F}^{(c)*} \psi \right\} \quad (2.42)$$

where De is the Deborah defined in Chapter 1. For simplicity, the asterisk will be dropped for the rest of this chapter and all quantities are assumed to be dimensionless.

The Fokker-Planck equation can be used to calculate directly the dynamics of the distribution function and, hence, the evolution of molecular conformations. Alternatively, one can obtain a general evolution equation for any function of the internal conformation, $B(\mathbf{Q})$, by multiplying Eq. 2.42 by $B(\mathbf{Q})$ and integrating over $\mathbf{Q}$; this is called a contraction operation. The evolution equation for $\langle \mathbf{Q}\mathbf{Q} \rangle$, obtained by choosing $B = \mathbf{Q}\mathbf{Q}$, is

$$\text{De} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = - \langle \mathbf{Q}\mathbf{F}^{(c)} \rangle + \delta \quad (2.43)$$

where $\Lambda_{(1)} = \frac{\partial \Lambda}{\partial t} + \mathbf{v} \cdot \nabla \Lambda - \nabla \mathbf{v} \cdot \Lambda - \{ \nabla \mathbf{v} \cdot \Lambda \}^{\text{T}}$ is the (upper) convected derivative of a second rank tensor Λ . For the FENE dumbbell model, the evolution equation for $\langle \mathbf{Q}\mathbf{Q} \rangle$ can be derived by substituting $\mathbf{F}^{(c)}$ by the FENE force law ($\mathbf{F}^{(c)} = \mathbf{Q}/(1 - Q^2/b)$):

$$\text{De} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = - \left\langle \frac{\mathbf{Q}\mathbf{Q}}{(1 - Q^2/b)} \right\rangle + \delta \quad (2.44)$$

Here, b is the ratio of the square of the maximum contour length to the mean square equilibrium distance. In order to calculate the dynamics of $\langle \mathbf{Q}\mathbf{Q} \rangle$ from Eq. 2.44, we need to introduce a closure approximation so that $\langle \mathbf{Q}\mathbf{Q}/(1 - Q^2/b) \rangle$ can be written in terms of $\langle \mathbf{Q}\mathbf{Q} \rangle$. Although we can derive an equation for $\langle \mathbf{Q}\mathbf{Q}/(1 - Q^2/b) \rangle$ by using the method just described, the resulting equation requires a closure approximation for higher moments

of the configuration distribution function. One of the simplest closure approximation is due to Peterlin, where $\langle \mathbf{Q}\mathbf{Q}/(1 - Q^2/b) \rangle \approx \langle \mathbf{Q}\mathbf{Q} \rangle / \langle (1 - Q^2/b) \rangle$. This is equivalent to assuming the configuration distribution function to be a Dirac delta function around a fixed vector $\mathbf{Q}^*$, $\psi(\mathbf{Q}) = \delta(\mathbf{Q} - \mathbf{Q}^*)$ [218]. The resulting moment equation for $\langle \mathbf{Q}\mathbf{Q} \rangle$ becomes:

$$\text{De} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = - \frac{\langle \mathbf{Q}\mathbf{Q} \rangle}{(1 - \text{tr} \langle \mathbf{Q}\mathbf{Q} \rangle / b)} + \delta \quad (2.45)$$

This moment equation is important for deriving a closed constitutive equation for mapping molecular motion to macroscopic contributions to the stress tensor.

2.4.2 Equation of Continuity

The general equation of change for the equation of continuity for a species α in a multicomponent mixture with no chemical reactions is:

$$\frac{\partial \rho_\alpha}{\partial t} = -(\nabla \cdot \mathbf{v} \rho_\alpha) - (\nabla \cdot \mathbf{j}_\alpha) \quad (2.46)$$

where ρ_α is the mass density of species α , $\mathbf{v}$ is the mass-average velocity of the liquid mixture, and $\mathbf{j}_\alpha$ is the mass flux of α with respect to the mass average velocity. A scalar function B_α in the phase space, such that $\langle B_\alpha \rangle$ is the mass concentration ρ_α , can be defined by choosing B_α as $B_\alpha = \sum_{i, \nu} m_v^{\alpha, i} \delta(\mathbf{r}_v^{\alpha, i} - \mathbf{r})$. The mass density expressed in the molecular variables is

$$\rho_\alpha = \langle \sum_{i, \nu} m^\alpha \delta(\mathbf{r}_v^{\alpha, i} - \mathbf{r}) \rangle \quad (2.47)$$

This expression accounts explicitly for the extension of the polymer molecules in space, and the mass of the polymer molecule is distributed throughout the polymer molecule at each bead of the chain. This is different from the kinetic theory of polyatomic

gases, in which the entire mass is presumed to be located at the center of mass of the molecule. Hence the number density of a polymer species is different from the mass density.

To derive the mass flux vector, one substitutes the expression, $\sum_{i,v} m_v^{\alpha,i} \delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r})$, into the general equation of change (Eqn. 2.19):

$$\begin{aligned}
\frac{\partial \rho_\alpha}{\partial t} &= \left\langle \sum_{\beta,j,\mu} \frac{\mathbf{p}_\mu^{\beta j}}{m^\beta} \cdot \frac{\partial}{\partial \mathbf{r}_\mu^{\beta j}} \left(\sum_i \sum_v m^\alpha (\delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r})) \right) \right\rangle \\
&= \left\langle \sum_{\beta,j,\mu} \frac{\mathbf{p}_\mu^{\beta j}}{m^\beta} \cdot \frac{\partial}{\partial \mathbf{r}_\mu^{\beta j}} \left(\sum_i \sum_v m^\alpha (\delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r})) \right) \right\rangle \\
&= - \left\langle \sum_{i,v} \left(\mathbf{p}_v^{\alpha i} \cdot \frac{\partial}{\partial \mathbf{r}} (\delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r})) \right) \right\rangle \\
&= -\nabla \cdot \left\langle \sum_{i,v} \mathbf{p}_v^{\alpha i} \delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r}) \right\rangle
\end{aligned} \tag{2.48}$$

The identity, $\frac{\partial}{\partial x} \delta(x-y) = -\frac{\partial}{\partial y} \delta(x-y)$ is going from line 2 to line 3. The quantity, $\left\langle \sum_{i,v} \mathbf{p}_v^{\alpha i} \delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r}) \right\rangle$, is identified as $\rho_\alpha \mathbf{v}_\alpha$ and can be related to the configuration space distribution function with the following operations:

$$\begin{aligned}
\left\langle \sum_{i,v} \mathbf{p}_v^{\alpha i} \delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r}) \right\rangle &= \int \left(\sum_{i,v} \mathbf{p}_v^{\alpha i} \delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r}) f(\mathbf{x}, t) \right) d\mathbf{x} \\
&= \int \sum_{i,v} \int \mathbf{p}_v^{\alpha i} \delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r}_v^\alpha) \delta(\mathbf{r}_v^\alpha - \mathbf{r}) f(\mathbf{x}, t) d\mathbf{p}^\alpha d\mathbf{r}^\alpha d\mathbf{x} \\
&= \sum_v \int \mathbf{p}_v^\alpha \delta(\mathbf{r}_v^\alpha - \mathbf{r}) \left(\int \delta(\mathbf{r}_v^{\alpha,i} - \mathbf{r}_v^\alpha) f(\mathbf{x}, t) d\mathbf{x} \right) d\mathbf{p}^\alpha d\mathbf{r}^\alpha \\
&= \sum_v \int \mathbf{p}_v^\alpha \bar{f}_\alpha(\mathbf{r}^\alpha, \mathbf{p}^\alpha, t) d\mathbf{p}^\alpha d\mathbf{r}^\alpha \\
&= \sum_v \int [\mathbf{p}_v^\alpha] \Psi_\alpha(\mathbf{r}^\alpha, t) \delta(\mathbf{r}_v^\alpha - \mathbf{r}) d\mathbf{r}^\alpha \\
&= \sum_v \int [\mathbf{p}_v^\alpha] \Psi_\alpha(\mathbf{r} - \mathbf{R}_v^\alpha, \mathbf{Q}^\alpha, t) d\mathbf{Q}^\alpha
\end{aligned} \tag{2.49}$$

The mass flux vector, $\mathbf{j}_\alpha$, is then found by subtracting $\rho_\alpha \mathbf{v}_\alpha$ from Equation 2.49. By incorporating the definition for ρ_α (Eqn. 2.47), the resulting mass flux vector expression is found to be:

$$j_\alpha(\mathbf{r}, t) = \sum_v (\int (\mathbf{p}_v^\alpha] - m^\alpha \mathbf{v}(\mathbf{r}, t)) \Psi_\alpha(\mathbf{r} - \mathbf{R}_v^\alpha, \mathbf{Q}^\alpha, t) d\mathbf{Q}^\alpha) \quad (2.50)$$

For a dilute solution of a bead-spring-chain model, one may substitute Equation 2.36 into Equation 2.50. Comparing the resulting expression with the stress tensor expression, the mass flux vector becomes:

$$\begin{aligned} j_p &= -\frac{mkT}{\zeta_0} [\nabla \rho - \nabla \cdot \langle \mathbf{Q} \mathbf{F}^{(c)} \rangle] \\ &= -\frac{mkT}{\zeta_0} (\nabla \cdot \boldsymbol{\pi}_p) \end{aligned} \quad (2.51)$$

where $\boldsymbol{\pi}_p$ is the total stress tensor expression derived by projecting the Liouville equation to the equation of motion. The details of the derivation of $\boldsymbol{\pi}_p$ are presented in the next section.

2.4.3 Equation of Motion

The equation of motion for a fluid mixture is:

$$\frac{\partial}{\partial t} \rho \mathbf{v} = -[\nabla \cdot \rho \mathbf{v} \mathbf{v}] - [\nabla \cdot \boldsymbol{\pi}] + \mathbf{G} \quad (2.52)$$

where $\boldsymbol{\pi}$ is the total stress tensor defined such that $\mathbf{n} \cdot \boldsymbol{\pi} dS$ is the force transmitted across a fluid element surface dS from the *negative* side to the *positive* side. The positive is defined as the direction towards which $\mathbf{n}$ points. $\mathbf{G}$ is the external force per unit volume acting on the fluid. Some typical external forces include gravitational and electromagnetic forces. In parallel to the development for the equation of continuity, one first defines a quantity $\mathbf{B}$ such that $\langle \mathbf{B} \rangle = \rho \mathbf{v}$. One of the most typical choice is:

$$\mathbf{B} = \sum_{i, v} \mathbf{p}_v^{\alpha, i} \delta(\mathbf{r}_v^{\alpha, i} - \mathbf{r}) \quad (2.53)$$

Substituting this expression into the general equation of change (Eqn. 2.19) and following the developments in Eqn. 2.48 gives the equation of motion in terms of the configuration space distribution function:

$$\frac{\partial}{\partial t} \rho \mathbf{v} = -\nabla \cdot \left\langle \sum_{\alpha v} \frac{1}{m^\alpha} [\mathbf{p}_v^\alpha \mathbf{p}_v^\alpha] \delta(\mathbf{r}_v^\alpha - \mathbf{r}) \right\rangle - \left\langle \sum_{\alpha v} \mathbf{F}_v^\alpha \delta(\mathbf{r}_v^\alpha - \mathbf{r}) \right\rangle \quad (2.54)$$

The first term in Equation 2.54 can be split into two contribution by writing $\mathbf{p}_v^\alpha$ as $[\mathbf{p}_v^\alpha - m^\alpha \mathbf{v}] + m^\alpha \mathbf{v}$ and expanding this term as follows:

$$\begin{aligned} \left\langle \sum_{\alpha v} \frac{1}{m^\alpha} [\mathbf{p}_v^\alpha \mathbf{p}_v^\alpha] \delta(\mathbf{r}_v^\alpha - \mathbf{r}) \right\rangle &= \left\langle \sum_{\alpha v} \frac{1}{m^\alpha} [(\mathbf{p}_v^\alpha - m^\alpha \mathbf{v})(\mathbf{p}_v^\alpha - m^\alpha \mathbf{v})] \delta(\mathbf{r}_v^\alpha - \mathbf{r}) \right\rangle \\ &+ \left\langle \sum_{\alpha v} [\mathbf{p}_v^\alpha \mathbf{v} + \mathbf{v} \mathbf{p}_v^\alpha - m^\alpha \mathbf{v} \mathbf{v}] \delta(\mathbf{r}_v^\alpha - \mathbf{r}) \right\rangle \\ &= \boldsymbol{\pi}^{(k)} + \rho \mathbf{v} \mathbf{v} \end{aligned} \quad (2.55)$$

where $\boldsymbol{\pi}^{(k)}$ is the kinetic contribution to the stress tensor, which is the momentum flux resulting from the motion of the beads across a surface moving with velocity $\mathbf{v}$. Similar to the derivation of the mass flux vector, this contribution can be written as a Taylor expansion for a configuration distribution function that varies slowly over the molecular length scale. It is important to notice that the macroscopic velocity, $\mathbf{v}$, has to be taken *outside* the integral so that it will *not* be operated on by the spatial derivative.

The momentum source, the last term in Equation 2.54, can be rewritten as a total stress tensor by employing a generalized Taylor series. The resulting expression is:

$$\begin{aligned}
\langle \sum_{\alpha\nu} F_{\nu}^{\alpha} \delta(\mathbf{r}_{\nu}^{\alpha} - \mathbf{r}) \rangle &= \sum_{\alpha\nu} \int F_{\nu}^{\alpha} \Psi_{\alpha}(\mathbf{r}^{\alpha}, t) \delta(\mathbf{r}_{\nu}^{\alpha} - \mathbf{r}) d\mathbf{r}^{\alpha} \\
&= \sum_{\alpha\nu} \int F_{\nu}^{\alpha} \Psi_{\alpha}(\mathbf{r} - \mathbf{R}_{\nu}^{\alpha}, \mathbf{Q}^{\alpha}, t) d\mathbf{Q}^{\alpha} \\
&= \sum_{\alpha\nu} \int F_{\nu}^{\alpha} \Psi_{\alpha}(\mathbf{r}, \mathbf{Q}^{\alpha}, t) d\mathbf{Q}^{\alpha} \\
&\quad + \nabla \cdot \sum_{\alpha\nu} \int \int_0^1 \mathbf{R}_{\nu}^{\alpha} F_{\nu}^{\alpha} \Psi_{\alpha}(\mathbf{r} - \epsilon \mathbf{R}_{\nu}^{\alpha}, \mathbf{Q}^{\alpha}, t) d\epsilon d\mathbf{Q}^{\alpha} \\
&= \mathbf{G} + \nabla \cdot \boldsymbol{\pi}^{(S)}
\end{aligned} \tag{2.56}$$

The stress tensor, $\boldsymbol{\pi}^{(S)}$, can further be split into contributions from intramolecular force, intermolecular force, and external force fields. For spatially slowly varying configuration space distribution functions, $\boldsymbol{\pi}^{(S)}$ can be expanded in a series in terms of a small parameter defined as the ratio of molecular length scale to the macroscopic length scale (ℓ/L).

For micromechanical models that have constraints (such as rigid connectors or fixed bond angles), the force term in Equation 2.56 has to be replaced by the generalized force ($\mathcal{F}_{\nu}^{\alpha}$). The derivation has been described in Section 2.3. For inhomogeneous kinetic theory for liquid crystalline polymers, the mean-field intermolecular potential is normally written as an expansion in (ℓ/L) . Therefore, the derivation of $\boldsymbol{\pi}^{(S)}$ should be truncated accordingly such that the same order of ℓ/L is retained in both the Fokker-Planck equation and the stress tensor expression.

For a homogeneous, isothermal suspension of elastic FENE dumbbells, the stress tensor expression is:

$$\frac{\boldsymbol{\tau}_p}{nkT} = -\left\langle \frac{\mathbf{Q}\mathbf{Q}}{(1 - \mathbf{Q}^2/b)} \right\rangle + \boldsymbol{\delta} \tag{2.57}$$

A closed form constitutive equation can be derived with the aid of a closed form of the moment equation (e.g. Eqn. 2.45). The derivation begins by taking the trace of the stress tensor expression and expressing $\langle \mathbf{Q}\mathbf{Q} \rangle$ in terms of $\boldsymbol{\tau}_p/nkT$. This is done by first writing $\text{tr}\langle \mathbf{Q}\mathbf{Q} \rangle$ in terms of $\text{tr}(\boldsymbol{\tau}_p/nkT)$ and substituting the resulting expression into Eqn 2.57:

$$\langle \mathbf{Q}\mathbf{Q} \rangle = -\left(1 - \left(1 - \frac{b}{\text{tr}(\boldsymbol{\tau}_p/nkT) - 3}\right)^{-1}\right)\left(\frac{\boldsymbol{\tau}_p}{nkT} - \boldsymbol{\delta}\right) \quad (2.58)$$

Substituting this expression into Equation 2.45 gives

$$\text{De}\left\{\left(1 - \left(1 - \frac{b}{\text{tr}(\boldsymbol{\tau}_p/nkT) - 3}\right)^{-1}\right)\left(\frac{\boldsymbol{\tau}_p}{nkT} - \boldsymbol{\delta}\right)\right\}_{(1)} = -\frac{\boldsymbol{\tau}_p}{nkT} \quad (2.59)$$

Denoting $Z = 1 + 3/(b + 2) - \text{tr}\boldsymbol{\tau}_p/b$, the closed form constitutive equation becomes:

$$Z\boldsymbol{\tau}_p + \text{De}\boldsymbol{\tau}_{p(1)} - \text{De}(\boldsymbol{\tau}_p - \boldsymbol{\delta})\frac{D\ln Z}{Dt} = -\text{De}\boldsymbol{\gamma} \quad (2.60)$$

This highly nonlinear constitutive equation makes numerical simulation extremely difficult, and the use of a coupled moment equation (Eqn. 2.45) and stress tensor expression (Eqn. 2.57) is easier and more efficient for numerical calculation and physical understanding of the numerical or analytical results.

2.5 Nonequilibrium thermodynamics

Another active research area for developing new models at different levels of molecular detail is nonequilibrium thermodynamics. The premise of this method is the postulation of the evolution equation in terms of thermodynamics quantities such as energy and entropy and derivation of the coefficients to satisfy certain specific properties. One of the most popular approach today is the GENERIC (General Equation for the Non-Equilibrium: Reversible-Irreversible Coupling) by Grmela and Öttinger [91,170]. The key innovation in this new structure is the application of two separate generators for the reversible and irreversible dynamics, together with the symmetric degeneracy requirements:

$$\frac{d\mathbf{x}}{dt} = \mathbf{L}(\mathbf{x}) \cdot \frac{\partial E}{\partial \mathbf{x}} + \mathbf{M}(\mathbf{x}) \cdot \frac{\partial S}{\partial \mathbf{x}} \quad (2.61)$$

$$\mathbf{L}(\mathbf{x}) \cdot \frac{\partial S}{\partial \mathbf{x}} = 0 \quad (2.62)$$

$$\mathbf{M}(\mathbf{x}) \cdot \frac{\partial E}{\partial \mathbf{x}} = 0 \quad (2.63)$$

Here $\mathbf{x}$ is a set of independent state variables, $E(\mathbf{x})$ and $S(\mathbf{x})$ are the total energy and entropy expressed in terms of $\mathbf{x}$, and $\mathbf{L}(\mathbf{x})$ and $\mathbf{M}(\mathbf{x})$ are linear operators acting on the energy and entropy gradients respectively. The degeneracy requirement that the gradient $\partial S / \partial \mathbf{x}$ is in the null space of $\mathbf{L}(\mathbf{x})$ corresponds the reversible dynamics represented by operator $\mathbf{L}(\mathbf{x})$. The degeneracy requirement that the gradient $\partial E / \partial \mathbf{x}$ is in the null space of $\mathbf{M}(\mathbf{x})$ is necessary to ensure the conservation of total energy: the total energy contribution is not affected by the operator generated by the irreversible operator and hence would not be dissipated (first law of thermodynamics).

Various brackets or inner products can be defined with the operators $\mathbf{L}(\mathbf{x})$ and $\mathbf{M}(\mathbf{x})$. The two most common brackets are:

$$\{A, B\} \equiv \left\langle \frac{\partial A}{\partial \mathbf{x}}, \mathbf{L} \cdot \frac{\partial B}{\partial \mathbf{x}} \right\rangle \quad (2.64)$$

$$[A, B] \equiv \left\langle \frac{\partial A}{\partial \mathbf{x}}, \mathbf{M} \cdot \frac{\partial B}{\partial \mathbf{x}} \right\rangle \quad (2.65)$$

where $\langle \cdot, \cdot \rangle$ is the $L^2(\Omega)$ inner product. The bracket associated with $\mathbf{L}(\mathbf{x})$ (Equation 2.64) is the Poisson bracket c.f. Equation 2.17, and that associated with $\mathbf{M}(\mathbf{x})$ (Equation 2.65) is called the dissipative bracket. In addition to the degeneracy requirements, $\mathbf{L}(\mathbf{x})$ is required to be antisymmetric (Eqn. 2.66) and $\mathbf{M}(\mathbf{x})$ is required to be symmetric (Eqn. 2.67) and positive-semidefinite (Eqn. 2.68). Furthermore, $\mathbf{L}(\mathbf{x})$ has to satisfy the Jacobi identity (Eqn. 2.69), which ensures that the operator $\mathbf{L}(\mathbf{x})$ is consistent with the structure of the equivalent Poisson bracket.

$$\{A, B\} = -\{B, A\} \quad (2.66)$$

$$[A, B] = [B, A] \quad (2.67)$$

$$[A, A] \geq 0 \quad (2.68)$$

$$0 = \{\{A, B\}, C\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} \quad (2.69)$$

Equations 2.62 and 2.68 guarantee a non-negative production rate of entropy within the system (second law of thermodynamics) and enforce the Onsager reciprocal relations.

Both the first and second laws of thermodynamics can be easily recovered by considering an arbitrary function A in terms of the bracket formulation, which is derived by multiplying $\partial A / \partial x$ to Equation 2.61:

$$\frac{dA}{dt} = \{A, E\} + [A, S] \quad (2.70)$$

The GENERIC equation (Eqn. 2.61) is recovered by choosing $A = x$. For the first law of thermodynamics, one considers $A = E$: The antisymmetric requirement (Eqn. 2.66) suggests $\{E, E\} = 0$ and the degeneracy requirement (Eqn. 2.63) suggests $[E, S] = 0$ and therefore the resulting equation for the total energy is $dE/dt = 0$ (first law of thermodynamics). For the second law of thermodynamics, consider $A = S$: The degeneracy requirement suggests $\{S, E\} = 0$, and the positive-definite requirement (Eqn. 2.68) suggests $[S, S] \geq 0$ and hence the second law of thermodynamics.

A large class of nonequilibrium thermodynamics formulations and molecular models have been proven to be representable by the GENERIC structure [65,170]. These include classic hydrodynamics, polymer kinetic theory, chemical reaction, the bracket formalism, the extended irreversible thermodynamics, the matrix model, and the Boltzmann kinetic equation. To illustrate the application of GENERIC, the structure that corresponds to the homogeneous, isothermal elastic dumbbell model is summarized. The dynamic variables are then given by $x = \{\rho(\mathbf{r}), \rho \mathbf{v}(\mathbf{r}), \psi(\mathbf{r}, \mathbf{Q})\}$. Then, the molecular potential V that leads

to the spring force law is split into an energetic component V_E and an entropic component V_S . Now, the total energy E and the entropy S can be expressed in Equation 2.71:

$$E = \int \left[\frac{1}{2} \rho v^2 + \epsilon + \int V_E \psi d\mathbf{Q} \right] d\mathbf{r} \quad (2.71)$$

$$S = \int \left[s - \int \psi \left[\frac{V_S}{T} + k \ln \psi \right] d\mathbf{Q} \right] d\mathbf{r}$$

where ϵ is the internal energy density and s is the entropy density of the solvent. The derivative of E and S over $\mathbf{x}$ is expressed as:

$$\frac{\partial E}{\partial \mathbf{x}} = \begin{bmatrix} -\frac{1}{2} v^2 \\ v \\ V_E \end{bmatrix} \quad (2.72)$$

$$\frac{\partial S}{\partial \mathbf{x}} = \begin{bmatrix} \frac{\partial s}{\partial \rho} \\ 0 \\ -\frac{V_S}{T} - k \ln \psi - k \end{bmatrix} \quad (2.73)$$

The Poisson operator $\mathbf{L}$ and the operator for the irreversible dynamics $\mathbf{M}$ can be derived by substituting the proper expressions (through continuum mechanics, kinetic theory or other physical knowledge) for the upper triangle of the matrix and then deriving the lower triangle components through the use of the anti-symmetric or symmetric properties of $\mathbf{L}$ and $\mathbf{M}$ respectively. The resulting matrix representations for $\mathbf{L}$ and $\mathbf{M}$ for a homogeneous, isothermal elastic dumbbell model are:

$$\mathbf{L} = - \begin{bmatrix} 0 & \nabla \rho & 0 \\ \rho \nabla & (\nabla \rho v + \rho v \nabla)^T & \psi \nabla - \nabla \cdot \psi \mathbf{Q} \frac{\partial}{\partial \mathbf{Q}} \\ 0 & \nabla \left(\psi + \frac{\partial}{\partial \mathbf{Q}} \psi \mathbf{Q} \cdot \nabla \right) & 0 \end{bmatrix} \quad (2.74)$$

$$\mathbf{M} = \begin{bmatrix} 0 & 0 & 0 \\ 0 - [\nabla \eta_s T \nabla]^T + \delta(\nabla \cdot \eta_s T \nabla) & 0 & \\ 0 & 0 & -\frac{\partial}{\partial \mathbf{Q}} \cdot \frac{2T}{\zeta} \Psi \frac{\partial}{\partial \mathbf{Q}} \delta(\mathbf{Q} - \mathbf{Q}') \end{bmatrix} \quad (2.75)$$

The corresponding degeneracy properties (Equations 2.62 and 2.63) can be easily verified. To extract or derive the time-evolution equation from the matrix form, one multiplies Equations 2.72, 2.73, 2.74, and 2.75 according to the GENERIC structure (Eqn. 2.61) and integrates over $\mathbf{Q}'$. The resulting equations are exactly the same as those derived from kinetic theory.

Similar to the use of continuum mechanics, nonequilibrium thermodynamics provides guidelines and admissibility conditions for a model to be consistent with thermodynamics. However, it provides no criteria or help in deriving equations that describe the topological evolution of a polymer molecule, nor the physics necessary to describe the dynamics of the polymer molecule. For example, the extension of the elastic dumbbell model to inhomogeneous solutions requires additional physics that is not included or provided by the GENERIC structure. Furthermore, in a general thermodynamics framework, the postulated equation structure may not be sufficiently general and could lead to a misleading interpretation. For example, a formulation by Jongschaap [113] suggested the stress tensor for a double reptation model developed by Curtiss and Bird [20] is not thermodynamics admissible. However, by choosing an appropriate expression for the osmotic pressure, the stress tensor expression is self-consistent with the GENERIC formulation and hence is thermodynamically admissible. Thus, nonequilibrium thermodynamics should be used with a great deal of caution: Whereas a model derived with the use of nonequilibrium thermodynamics is guaranteed to be thermodynamically admissible, it may not describe the molecular dynamics correctly; on the other hand, inconsistency of a model with a postulated equation structure is a necessary, but not sufficient, condition to conclude that a

model is thermodynamically inconsistent. In this thesis, a recent reptation model derived by using the GENERIC formulation [74] is simulated by using the wavelet-Galerkin/finite element method. The simulation result for a complex flow calculation will be presented in Chapter 9.

2.6 Issue of coarse-graining and mapping evolution equations of different micromechanical models for representing the same polymer species.

The issue of mapping two or more micromechanical models that represent the same polymer species at different levels of detail has been a challenge over decades in polymer physics. Ideally, any pair of such micromechanical models should predict identical macroscopic properties in certain regions of a parameter space. The deviations between the models is then attributed to the lack of fine scale physics in the coarser model. However, molecular micromechanics and kinetic theory are always built with a specific micromechanical model to begin with. Therefore, there are occasions when two micromechanical models will predict totally different rheological response even in the regions close to equilibrium. The mapping between different micromechanical model then becomes an art, more than a science, in deciding what and how different parameters can be matched between different models. In this section, three of these strategies will be considered. The first one involves parameter mapping, where the coarse and the fine grained models are defined a priori and the parameters in the models are chosen to match certain macroscopic properties. The second one is purely fundamental, where the fine-grained model is coarse-grained or projected onto a simpler model by a systematic projection operator. The last strategy is a hybrid between the first two methods, where the coarse model is loosely defined with certain additional parameter chosen to allow a better mapping of macroscopic properties between the two models.

2.6.1 Model development through parameter mapping

The most straight-forward approach to mapping two different models is to match a number of prediction by both models through fine-tuning or fitting the available parameters in the coarse model. In a series of papers, Binder and coworkers have mapped a realistic model onto a bond-fluctuation model by matching a set of moments and kinetic rates of bond fluctuation between both models. In their most recent publication on this mapping procedure, they required that the jump probability for each Mont Carlo step in the simulation match the average jump rate of the torsional degree of freedom. Schweizer et al. have used the PRISM (Polymer Reference Interaction Site Model) integral equation theory as the base to study a spectrum of molecular models with various levels of detail. Their mapping scheme requires the equality of the zero angle scattering between different molecular models used to describe polyethylene and polypropylene. The predicted radial distribution function and solubility parameter for various coarse-grain models agree quantitatively (within a small uncertainty) with each other. Mattice and his students have developed a second nearest neighbor diamond (2nd) lattice model to map the rotational isomeric state (RIS) model and 2nd lattice model. They have also proposed a fine-graining procedure for the 2nd lattice model by minimizing the energy for snapshots of the 2nd model. Their fine-graining procedure is similar to the reverse Monte Carlo algorithm, which is commonly used to regenerate the configuration space based on experimental data for the structural factor or the radial distribution function.

The parameter mapping strategy described above is designed for equilibrium systems. For nonequilibrium or flowing systems, one maps parameters in the Fokker-Planck equation of different models for matching specific physical properties or material functions. For example, Doyle et al. attempt to match a FENE dumbbell model and a Kramers' chain with the following criteria: the hydrodynamic drag coefficient ζ is chosen such that the

zero shear-rate viscosity of the FENE dumbbell matches with that of the Kramer's chain; the spring constant is chosen such that the equilibrium mean square end-to-end distance of the Kramer's chain matches with the equilibrium mean square extension of the FENE dumbbell model; and the maximum extension Q_0 of the FENE dumbbell model is chosen to be the contour length of the Kramer's chain. This mapping procedure provides a close match for the viscosity but fails to describe the first normal stress coefficient or elongational viscosity at low deformation rates. In the case of a Rouse chain, we denote the traditional mapping as one that matches nkT and the viscosity based on the physical significance of n and T .

An alternative parameter mapping based on the mapping of viscosity and first normal stress difference is considered below. The two models considered are a 6-bead Rouse chain model and a Hookean dumbbell model. Material functions and distribution functions for both models can be derived analytically, owing to the linearity of the underlying diffusion equation. For an N -bead Rouse chain, the steady state shear flow material properties are given by Equations 2.76, 2.77, and 2.78:

$$\eta - \eta_s = nkT\lambda_H \frac{(N^2 - 1)}{3} \quad (2.76)$$

$$\Psi_1 = 2nkT\lambda_H^2 \left[\frac{(N^2 - 1)(2N^2 + 7)}{45} \right] \quad (2.77)$$

$$\Psi_2 = 0 \quad (2.78)$$

where n is the number density of the polymer molecules, k is Boltzmann's constant, and T is the absolute temperature. $\lambda_H = \zeta/4H$ is the relaxation time scale of the Hookean dumbbell model. The mapping strategy for the 6-bead Rouse chain model and the Hookean dumbbell model is chosen to match the polymer contribution of the viscosity and the first normal stress coefficient. For this mapping strategy, we have

$$nkT\lambda_H|_{\text{dumbbell}} = \frac{35}{3}nkT\lambda_H|_{6 \text{ bead}} \quad (2.79)$$

$$\lambda_H|_{\text{dumbbell}} = \frac{79}{15}\lambda_H|_{6 \text{ bead}}$$

By construction, this mapping strategy exactly matches the viscosity and first normal stress coefficient. The results of using this mapping strategy for the linear viscoelastic properties are shown in Figure 2.5. The exact mapping for the viscosity and first normal stress coefficient guarantee the exact mapping for η' and η'' for small frequency for a small amplitude oscillatory shear flow. The deviation at higher frequency for the 6 bead Rouse chain and the Hookean dumbbell based on the new mapping strategy can be attributed to the relaxation of the fast relaxation time scales.

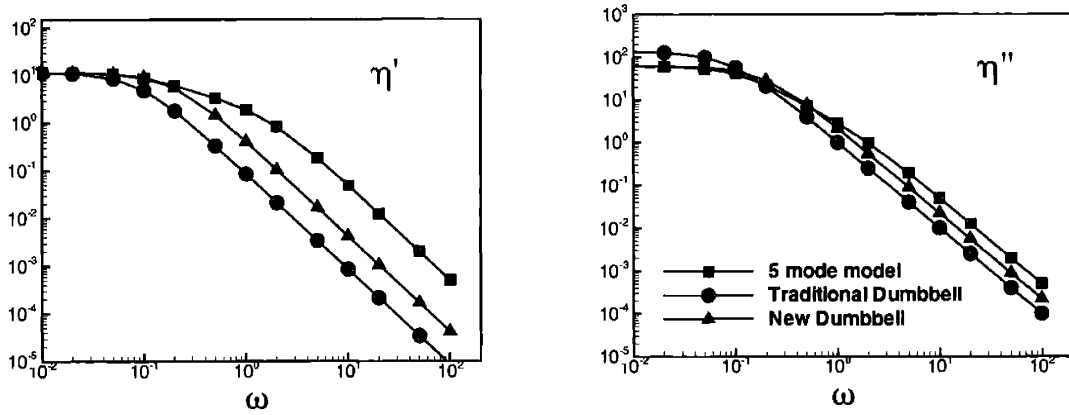


Figure 2.5: Linear viscoelastic properties for the 6-bead Rouse chain, the mapping between a 6-bead Rouse chain and a Hookean dumbbell model based on nkT and λ , and the new mapping (Eqn. 2.79) strategy based on the viscosity and first normal stress coefficient.

An additional advantage of the new mapping strategy is the close replication of the transient dynamics of simple elongational flow. Figure 2.6 shows the responses in the start-up of steady elongational flow for a 6 bead Rouse chain and the Hookean dumbbell model based on the traditional mapping strategy and the new mapping strategy. Nearly exact agreement in the start-up response is observed between the 6 bead Rouse chain and the Hookean dumbbell model with the alternative mapping strategy.

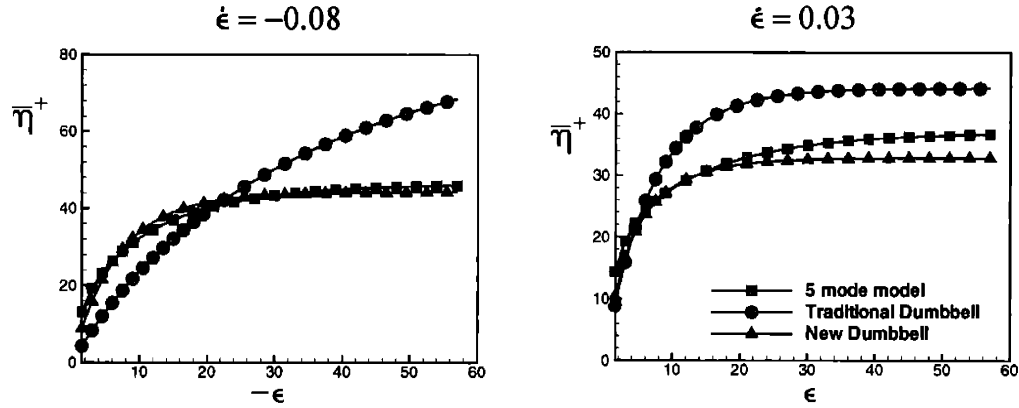


Figure 2.6: Start-up of steady elongational flow behavior for the 6-bead Rouse chain, the traditional mapping between a 6-bead Rouse chain and a Hookean dumbbell model, and the new mapping (Eqn. 2.79) strategy

Comparison between various parameter mapping strategies suggests a quantitative agreement of a wide range of rheological properties can be achieved by carefully choosing the properties for mapping parameters. For rheological calculations, these properties normally associate directly with the material functions. This choice, however, leads to an interpretation of the parameters different from their own physical meanings. For example, by mapping the viscosity and the first normal stress coefficient of Rouse chain models, one has to allow the factor of nkT to be different for Rouse chain with different number of beads. This leads to an interpretation of n and T different from the conventional meanings of number density and absolute temperature, respectively. Further research and extension is required in this area.

2.6.2 Formal projection operator method for developing dynamic equations

Instead of assuming an underlying evolution equation for two different levels of models, one may project the evolution equation of a detailed model onto that of a coarse grained model by assuming the coarse model has a fixed description of the fine-grain model. For example, it is generally assumed that the elastic dumbbell model represents the

end-to-end vector of a fine-grain model such as a multi-bead-rod/spring chain. Oono and Freed [165, 166] were the first to employ renormalization group theory to coarse grain a detailed model to a simpler model. Öttinger has proposed a coarse-graining procedure for models described by a reversible time evolution equation and models described by a Fokker-Planck equation. The time evolution equations are formulated within the framework of GENERIC. His results for mapping models will be described briefly below:

Let x and y be the spaces of the detailed model and the coarse-grained model, respectively. Furthermore, let $\Pi: x \rightarrow y$ be the mapping function from x to y , i.e. $y = \Pi(x)$. Then the mappings of each building block from x to y are:

$$E_y(y) = E_x(\Pi(x)) \quad (2.80)$$

$$\exp\left\{\frac{S_y(y)}{k}\right\} = \int \exp\left\{\frac{S_x(x)}{k}\right\} \psi(x) \delta(y - \Pi(x)) dx \quad (2.81)$$

$$L_y(y) = \int \exp\left\{\frac{S_x(x) - S_y(y)}{k}\right\} \left(\frac{\partial \Pi}{\partial x} \cdot L_x(x) \cdot \frac{\partial \Pi}{\partial x}\right) \psi(x) dx \quad (2.82)$$

$$M_y(y) = \int \exp\left\{\frac{S_x(x) - S_y(y)}{k}\right\} \left(\frac{\partial \Pi}{\partial x} \cdot M_x(x) \cdot \frac{\partial \Pi}{\partial x}\right) \psi(x) dx + M_y^2(y) \quad (2.83)$$

where $M_y^2(y)$ is given by

$$\begin{aligned} M_y^2(y) = & \iint \exp\left\{\frac{S_x - S_y}{k}\right\} \psi(x) \\ & \times \left[\langle D \cdot \Pi(x_0) D \Pi(x_t) \rangle_x - L_y \frac{\partial E_y}{\partial y} L_y \frac{\partial E_y}{\partial y} \right] dx dt \end{aligned} \quad (2.84)$$

and $D \cdot \Pi(x_0)$ and $D \Pi(x_t)$ are the mean backward time derivative and the mean forward time derivative of the stochastic process $\Pi(x)$ respectively¹. The presence of the forward

1. For Markovian stochastic processes described by $dx = A dt + B dW$, the difference between $D \cdot x$ and Dx is the time smoothed Brownian force, $-2(B \cdot B^T) \nabla \ln \psi$; $Dx = A$ and $D \cdot x = A - 2(B \cdot B^T) \nabla \ln \psi$

and backward time derivatives in the detailed model implies that the coarse-graining procedure requires the solution of the time evolution equation of the detailed model; and, hence, the procedure in fact is not useful for improving computational efficiency by studying coarse-grained models in the place of a detailed model. However, one may apply closure approximations to recover the simple model in a closed form by comparing the predictions of the simple model with various experimental data.

On the reverse mapping or fine-graining of a coarse-grained model to the fine-grained model, the mapping procedure is separated into two parts, the relevant and the irrelevant ensemble computations (based on the terminology of projection operator formulation). Reverse mapping provides sample configurations of the fine-grained model based on the simulated configuration for the simple model, which can in turn be used as the initial ensemble for various simulations such as solidification and computation of mechanical properties of solid polymers. Both relevant and irrelevant ensembles are required because in the subsequent computations, one may calculate expectations where the irrelevant ensemble may contribute significantly.

The relevant ensemble is the maximum entropy solution of the optimization problem subject to constraints of correct average value for a set of measures which corresponds to the simple model. In statistical physics, the maximum entropy principle is the most commonly used method in deriving the functional for the equilibrium distribution function in various statistical ensembles. In the past decade, there has been an increasing interest in theoretical physics in using the maximum entropy principle for nonequilibrium phenomena. The maximum entropy principle is used to assign unknown probabilities (rebuilding the details) of the fine grain model based on the simple model. In light of the projection operator technique, the maximized entropy ensemble of the fine grained model obtained by using Gibbs entropy functional is

$$\tilde{f}(x, t) = f_0(x) \int \frac{\Psi(y, t)}{\Omega(y)} \delta(y - \Pi(x)) \quad (2.85)$$

where $f_0(x)$ is the steady state solution of the Liouville equation for the fine grained model. Because Equation 2.85 is a very large dimensional integral, Monte Carlo integration is the most efficient way to compute this integral. Also, one may simulate configurations of the simple model and then fill in the details of the fine grained model based on an importance sampling scheme.

The irrelevant ensemble can be expressed formally in terms of the relevant ensemble. Traditionally, this expression was used to facilitate the derivation of the time evolution equation of the probability distribution function at the coarse grain level.

The use of projection operator methods to derive or refine a coarse-grain model is elegant and in some cases exact. However, the extremely difficult concepts and expressions behind the projection operator theory limits the popularity of this approach. Judging from the merits and limitation of the projection operator approach and the parameter mapping approach, one may naturally suggest a hybrid approach for the coarse-graining/fine-graining method. One such approach is presented below.

2.6.3 Hybrid method between parameter mapping and projection operator methods: the adaptive description method

Although models developed by pure parameter-mapping can qualitatively map two different models, the method lacks physical justification; models developed by projection operator are rigorous but lack quantitative or even qualitative description of the mapping between the coarse and the fine grain model. One approach may be to combine both approaches by allowing a floating or adaptive description of connection between the connection between the coarse model and the fine grained model. For the description of linear polymer molecules in rapidly varying, strong flows this kind of adaptive description

approach has been introduced by Ghosh, et al. [88, 89]. They first demonstrate the deficiency of the FENE dumbbell model in describing polymer configuration and stress in a rapid stretching flow by comparing the simulation results of a FENE dumbbell and a Kramers chain [88]. In particular, they demonstrate that the growth of both stress and birefringence of a FENE dumbbell model is much slower than that of a Kramers chain model in an experiment that consists of a start-up of steady, uniaxial elongation flow for large De followed by relaxation. They subsequently developed a general model based on "experiments" on the configuration changes of the Kramers chain in the start-up and relaxation of an elongational flow.

The main idea of this model is that of an adaptive length scale, which defines a segment of a Kramers chain that is short enough that the FENE force law is applicable over the segment. This is implemented by postulating Q_0 in the FENE force law as a dynamic variable whose dynamics is given by a force balance. The increase or decrease in value of Q_0 is compensated by (1) an increase of the number identical FENE dumbbell segments N through fixing the product $Q_0 \cdot N$ to be the same as the contour length of a Kramers' chain and (2) a corresponding rescaling of both H and ζ . The new model developed in this way is known as the adaptive length scale (ALS) model. A conceptual representation of a polymer molecule in terms of a FENE chain model and the ALS model is presented in Figure 2.7.

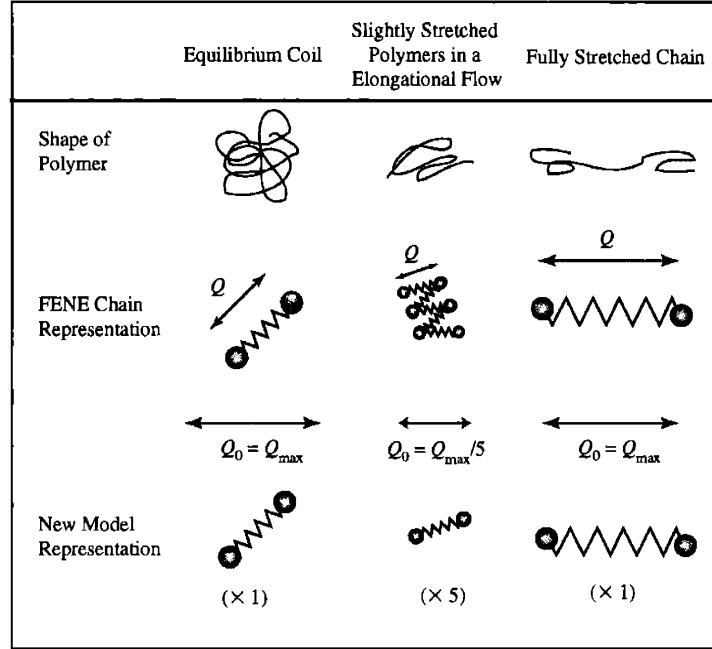


Figure 2.7: Comparison of the ALS model and a FENE chain model representation of an equilibrium coil, a polymer stretched to small strains in a rapid extensional flow, and a fully stretched polymer. $Q_{\max}$ is the maximum (contour) length of the molecule, and Q_0 is the maximum length of a segment.

Similar to the issue of parameter mapping, the ALS model does not contain a detailed representation of the molecular conformation. The lack of connectivity between segments of the molecules makes the ALS model appear to be a multi-mode FENE model, rather than a FENE chain model for a given number of segments N^1 . Furthermore, N is defined as the ratio between the contour length of the molecule and the segmental length; and, hence, N is a real number, not an integer. Therefore, at some point in the simulation, N may have 0.6 or 2.4235 segments, which makes the definition of a segment vague. More importantly, the assumption that Q_0 is a dynamic variable leads to a fluctuating configura-

1. Currently, many researchers are confused by the difference between a multimode model and a chain model. For example, Bell, et al. [8] simulated a multimode, FENE model and misstate it as a FENE-chain model. The main difference between a multimode model and chain model is the connectivity. A multimode model uses a number of similar dumbbell evolution equations, except that each has a different relaxation time; a chain-like model may also have a number of evolution equation, but each one has specific connectivity built into it. In the case of the Rouse chain, the multimode model is the same as the chain model when Q is defined as the eigenvectors of the Rouse matrix.

tion space in Q because $Q \in [0, Q_0]$. Therefore, the ALS model is normally written only in a stochastic differential equation form. Writing down a corresponding Fokker-Planck equation is possible, but extremely difficult. One possibility is to use a mapping equation to map the configuration space based on the evolution of Q_0 . Much research is still needed in this area.

Despite this restriction and the semi-empirical derivation for the governing equation for Q_0 and other disadvantages suffered by the ALS model, the ALS model provides a much better description viscometric properties as well as the transient response to start-up of steady shear or elongational flow than the traditional dumbbell models. Similar to the FENE or other elastic dumbbell models, the ALS model requires a closure approximation to obtain a closed constitutive equation for stress or a pair of equations for the evolution of $\langle QQ \rangle$, Q_0 , and τ . The corresponding model is known as ALS-C model. Despite the closure approximation, the ALS-C model still retains the accurate predictions of steady state and transient rheological dynamics of the ALS model. Furthermore, it can predict conformational hysteresis in stress-molecular extension during a uniaxial start-up elongation/relaxation flow. In complex flow calculations, the ALS-C model is able to describe complex flow phenomena such as drag enhancement (Figure 2.8); and it is the first, and so far the only, constitutive equation that is capable of predicting the asymmetric structure of the disturbance seen in the viscoelastic instability for a flow around a cylinder confined in a channel (Figure 2.9).

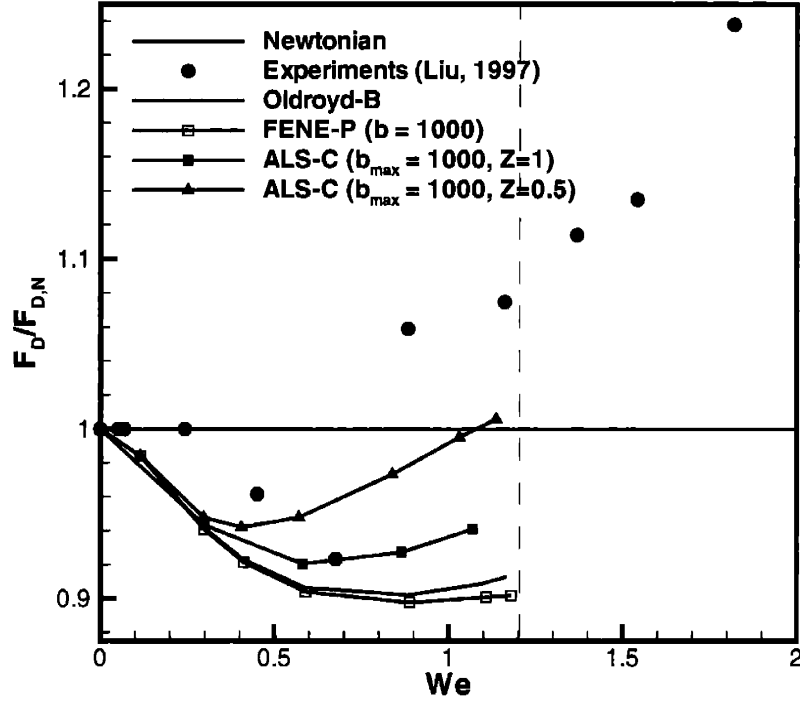


Figure 2.8: Total drag on a cylinder in flow past a linear array of cylinders confined in a channel. Predictions of the Oldroyd-B, FENE-P, ALS-C (closed version of the adaptive length scale model) models as a function of We are shown. Experimental data for the drag on the cylinder are also presented. Cylinder spacing $L = 6R$, where R is the radius of the cylinders. Figure reproduced from Joo et al. [89]

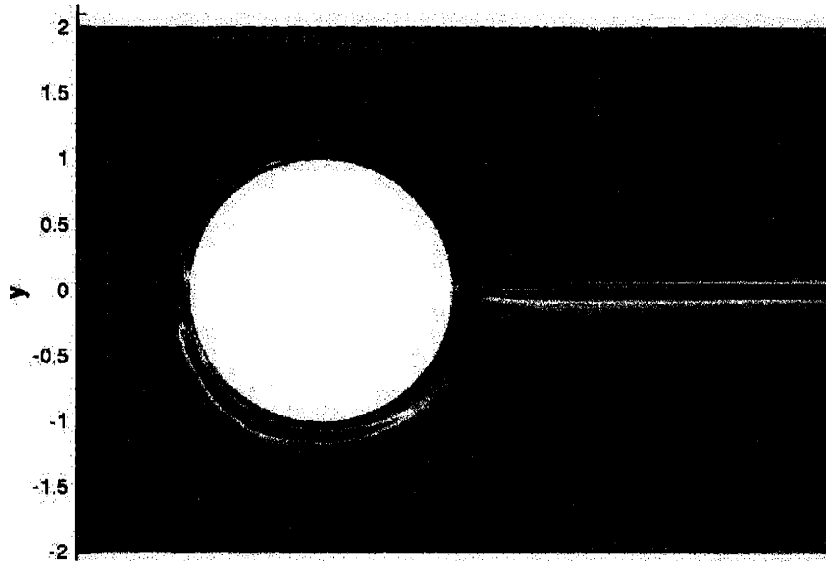


Figure 2.9: Asymmetric structure of the perturbation of $\langle \hat{Q}_x \hat{Q}_x \rangle$ in a stability analysis of a flow around a cylinder confined in a planar channel with the ALS-C model.

Chapter 3

Numerical Analysis of Molecular Orientation in Rheological Experiments

3.1 Introduction

Given a constitutive equation, such as one derived in Chapter 2, the first task is to simulate the response of the model in the rheometric flow systems such as simple shear or elongational flows. This allows evaluation of the basic rheological predictions of the model. Three approaches for using kinetic theory models to describe molecular orientations and various material functions in flows with fixed kinematics are (a) direct simulation of the Fokker-Planck equation, (b) stochastic simulation of the associated stochastic differential equation, and (c) solution of a closed model from the moment equation with a closure approximation. In this chapter, the direct numerical analysis and stochastic simulation approaches are reviewed and discussed.

3.2 Direct Simulation of the Fokker-Planck Equation

Most direct simulations of Fokker-Planck equations are based on weighted residual methods. The success of this approach relies on the accurate representation of the residual of the Fokker-Planck equation, and hence the distribution function, by a set of basis functions. A useful choice of basis functions is obtained from the eigenfunctions of the Fokker-Planck equation for some convenient limits. This idea was first utilized for simulating a Fokker Planck equation for rod-like polymers by Stewart and Sørensen [204]. Spherical harmonics were used as basis functions to compute the material functions in steady simple shear flow for a multi-bead rod model with hydrodynamic interaction. This particular choice of basis functions was used because spherical harmonics are the eigenfunctions of the operator in the Fokker-Planck equation at $De = 0$. Therefore, numerical solutions

based on this approach are most accurate for small De . The response to the start up of steady simple shear flow for this model was also simulated by Strand and Kim [207] with the same basis functions.

A limitation of using spherical harmonics is that they are the eigenfunctions of the Fokker-Planck equation only in the limit of vanishing De . Therefore, as De increases, the number of basis functions required increases and the efficiency of the algorithm decreases. If the diffusion coefficient depends on the configuration of the molecules, then spherical harmonics are no longer eigenfunctions of any operators in the Fokker-Planck equation, and they are not necessarily efficient in any limits of this problem. Observing that for large De , the distribution function is a highly localized function, Nayak [2][161] proposed using wavelets as alternative basis functions to spherical harmonics. In particular, she used the Daubechies orthonormal scaling functions as basis functions and demonstrated both accuracy and convergence in predicting the material functions in simple shear flow for a wide range of De .

A sample calculation and comparison between the wavelet-Galerkin method, Brownian dynamics simulation, and a spherical harmonics expansion is shown in Table 3.1 and Figure 3.1. Figure 3.1 shows the contour plot for the shape of the distribution function calculated by the wavelet-Galerkin method and that by a spherical harmonics expansion.

The expected sharp peak due to flow-induced alignment is demonstrated. For a more quantitative comparison, calculations for the viscosity and the first normal stress coefficient are shown in Table 3.1; 2000 trajectories are used for the Brownian dynamics calculation; a 32×64 Daubechies 6 scaling function expansion is used to calculate the orientational distribution function in the wavelet-Galerkin approach.

De	Brownian Dynamics	Wavelet-Galerkin method	Spherical Harmonics
0.1	1.036/1.640	0.9948/1.1866	0.9949/1.1872
1	0.7407/0.6674	0.7676/0.6465	0.7676/0.6467
10	0.3341/0.0521	0.3343/0.0515	0.3344/0.0517
100	0.1480/0.0025	0.1461/0.0025	0.1470/0.0026
1000	0.0682/0.000106	0.0672/0.000108	N/A

Table 3.1: Comparison of numerical accuracy of various methods for solving the Fokker-Planck equation for a dilute suspension of rigid dumbbells in a steady, simple shear flow. In each cell, the first entry is the viscosity and the second entry is the first normal stress coefficient. The numerical results for the spherical harmonics approach are from the work by Stewart and Sørensen [204]

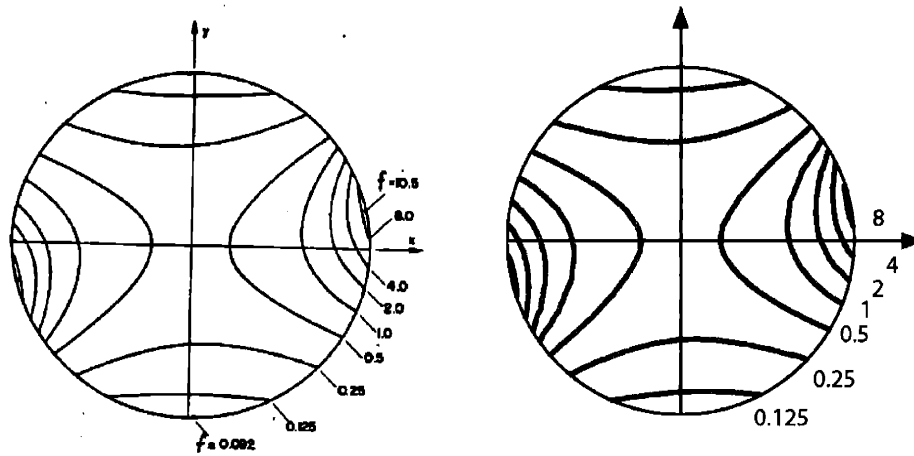


Figure 3.1: Contour plots for the rigid rod distribution function in shear flow at $De = 10$. The figure on the left is reproduced from Stewart and Sørensen [204]; the figure on the right is the calculation by the wavelet-Galerkin method with a 32×64 Daubechies 6 scaling function expansion. The peak of the function lies at $\theta = 13^\circ$.

3.2.1 Theory and computation using scaling function expansions

Because scaling function expansions are the focus of this thesis, the fundamental theory of scaling functions and wavelets will be reviewed in this section. In particular, the scaling functions introduced by Daubechies [48] are used. These functions are generally considered the first generation wavelets with compact support. The Daubechies wavelets are generated by translation and dilation of a single mother function in the independent variable x as

$$\varphi_{j,m}(x) = \varphi(2^j x - m) \quad (3.1)$$

where j denotes the scale of dilation and m corresponds to the translation. The mother function φ in Eq. 3.1, in turn, is defined by a dilation equation

$$\varphi(x) = 2 \sum_k h_0(k) \varphi(2x - k) \quad (3.2)$$

In this equation, $h_0(k)$, known as the k -th filter coefficient of the dilation equation, is derived from a general spectral factorization of a perfect construction filter bank [209]. Second generation wavelets do not employ the translation and dilation properties as well as the requirement of a single mother function. This gives flexibility for generating wavelets on manifolds, M -channel wavelets, multi-dimensional wavelets, and many others. Readers are referred to the original article by Swelden [215] for more information about second generation wavelets.

First generation wavelets, the Daubechies wavelets in particular, are used in this work because many of the mathematical and computational aspects of the Daubechies wavelets have been proved and verified. The major advantage of using Daubechies wavelets over other basis functions is the localization and compact support property of the Daubechies wavelets in *both* the spatial and Fourier domains. This is due to the smoothness of the

wavelets and their vanishing polynomial moments. The smoothness of the wavelets leads to the rapid decay at high frequencies in the Fourier domain, and the vanishing polynomial moment property corresponds to the rapid decay at low frequencies in the Fourier domain.

Applying the Daubechies wavelets in simulations requires calculation of the filter coefficients $h_0(k)$, the connection coefficients (cf. Eq. 3.2), and definition and extension of the one-dimensional scaling function to higher dimensions. Most of the computations that employ wavelets make use of the recursive relationship in Eq. 3.2 and formulate the unknowns (such as filter coefficients or connection coefficients) as an eigenvalue problem. These computational approaches for wavelets have been described extensively and various software packages have been written to compute these coefficients. Therefore, we will not repeat a discussion of these methods. Instead, we show some of the most common scaling functions used for Daubechies wavelets.

It should be noted that scaling functions with different ranges of compact support and different symmetries can be derived by properly choosing the filter coefficients. As the length of the filter coefficient increases, the scaling function loses compact support but gains better approximation ability. Therefore, choosing an appropriate length for the filter coefficients is a trade off between the sparsity of the stiffness matrix and the approximation properties of the basis functions. Testing increasingly larger sets of filter coefficients is analogous to studying the convergence behavior of polynomials with increasing order, or p -convergence. The only limitation in choosing the length of the filter coefficient is that the resulting scaling function should not overlap onto itself in the mesh. This limits the length of the filter coefficient to less than or equal to the number of grid points on the mesh. In addition to using different length filter coefficients, we can also increase the scale

of the scaling functions by mapping the mother function through Eq. 3.1. This is equivalent to mesh refinement, or h -convergence.

One of the major advantages of using Daubechies scaling functions as basis functions is that the inner products between basis functions can be computed up to machine precision accuracy. The dilation equation is used recursively to formulate the inner product computation as a eigenvalue problem. This involves the scaling equation (Eq. 3.1), the moment equation (Eq. 3.6), and a normalization condition (Eq. 3.8). Details can be found in the original article [129].

Triple products of the scaling function are defined as the connection coefficients,

$$\Lambda_{m,n}^{d1,d2,d3},$$

$$\Lambda_{m,n}^{d1,d2,d3} \equiv \int \varphi^{d1}(x) \varphi^{d2}(x-m) \varphi^{d3}(x-n) dx \quad (3.3)$$

where

$$\varphi^d(x) \equiv \frac{d^d}{dx^d} \varphi(x) \quad (3.4)$$

As shown in [129], the computation of the connection coefficient $\Lambda_{m,n}^{d1,d2,d3}$ is equivalent to computing $\Lambda_{m,n}^{0,c1,c2}$ with $d1 + d2 + d3 = c1 + c2$. By recursively differentiating the dilation equation and making use of the definition of the connection coefficients, an eigenvalue problem for calculating $\Lambda_{m,n}^{d1,d2,d3}$ is found as

$$A \Lambda^{0,c1,c2} = \frac{1}{2^{c1+c2+2}} \Lambda^{0,c1,c2} \quad (3.5)$$

where $A \equiv \sum_{q,r} h_0(q-m) h_0(r-n)$. This eigensystem is rank deficient and requires $c1+c2+1$ additional equations for a unique solution. These additional equations are obtained from the moment equation and the normalization equation. The moment equa-

tion, as is the scaling equation, is derived from a recursive differentiation of the expansion of x^k and is

$$\sum_l M_l^k \Lambda^{0, d2, d3} = \begin{cases} k! \int \varphi(x) \varphi_m^{d3} dx & k = d2 \\ 0 & k < d2 \end{cases} \quad (3.6)$$

In Eq. 3.6, M_l^k is defined as $\int x^k \varphi(x) dx$. These moments can be computed exactly as

$$M_l^j = \frac{1}{2(2^j - 1)} \sum_{k=0}^j \binom{j}{k} \sum_{l=0}^{k-1} \binom{k}{l} M_0^l \sum_{i=0}^{N-1} 2h_o(i) i^{k-l} \quad (3.7)$$

with $M_i^0 = 0$ for all i . This equation was first derived by Latto, *et al.* [129] by using the dilation equation. Furthermore, starting from the normalization condition $\int \varphi(x) dx \equiv 1$, recursive differentiation gives rise to the normalization equation

$$c1!c2! = \sum_{l, m} M_l^{d2} M_m^{d3} \Lambda^{0, d2, d3} \quad (3.8)$$

Combining the eigenvalue system in Eq. 3.5 with the moment equation and the normalization equation gives a full rank linear system for determining the connection coefficients.

Although the wavelets and scaling functions that have been discussed are one dimensional, higher dimensional basis functions are required for simulating the Doi model or other kinetic theory based molecular models. The simplest way to extend the one-dimensional functions is to use tensor products. To be more specific, we define a two-dimensional basis function as $\Phi(x, y) = \varphi(x)\varphi(y)$; the space spanned by the two-dimensional basis functions is defined as

$$V_0 = \left\{ f | f(x, y) = \sum_{i, j} \alpha_{i, j} \varphi(x - i) \varphi(y - j) \right\} \quad (3.9)$$

We obtain multiresolution analysis of $L_2(\mathbb{R}^2)$ by using dyadic products. For a given resolution of (m, n) along the (x, y) directions, the basis function for the two dimensional problem becomes

$$\Phi_{m,n}(x, y) = 2^{m+n-2} \varphi(2^m x) \varphi(2^n y) \quad (3.10)$$

With the generalized coordinates mapped to (x, y) by using $(x = 2\theta/\pi, y = \phi/\pi)$, the distribution function, $f(\theta, \phi)$, is represented as

$$f(\theta, \phi) = \sum_i \sum_j \hat{f}_{ij} \Phi_m(2\theta/\pi - i, \phi/\pi - j) \quad (3.11)$$

If we use the same number of basis functions along each dimension, then the dimension of the stiffness matrix for a two-dimensional problem is the square of that of a one-dimensional problem. This may not be acceptable for higher dimensional models, such as an n bead Kramers chain. It will be necessary to explore an alternative development of multidimensional wavelets, such as spherical wavelets or their variants, before adapting wavelets to simulate the diffusion equation for kinetic theory models with larger numbers of internal degrees of freedom.

3.2.2 Applications of direct simulation of Fokker-Planck equation

The most interesting and fundamentally important application of the multi-bead rod model is the study of liquid crystalline polymer systems. Doi [58] developed the first molecular theory based on the multi-bead rod model. The governing equation of the Doi model is a Fokker-Planck equation with a mean-field interaction potential Φ accounting for the intermolecular interaction between polymer molecules. Even with the simplest functional for the mean-field intermolecular potential, the stability analysis of the Doi model at equilibrium shows an isotropic-nematic (I-N) transition with increasing strength of Φ . More importantly, it has been shown that the use of closure approximations funda-

mentally changes the stability properties of the Doi model. The ability to describe I-N transition of a large class of liquid crystalline polymers and the inaccurate stability properties of the approximated closed model promote the use of the Doi model without closure approximations in the investigation of the rich dynamics of liquid crystalline polymer in various flow systems.

Marrucci and Maffettone [148] performed the first simulation of the Doi model without a closure approximation in steady, simple shear flow. They assumed that all of the molecules lie within the flow plane and thereby reduced the model to only one dimension. Even with this simplified model, they observed tumbling dynamics in the simulation. Larson and coworkers [123,124,125] relaxed the assumption made by Marrucci and Maffettone and simulated the evolution of the Doi model in two dimensions. These authors demonstrated the rich dynamics exhibited by a structure parameter, including dynamics within the flow plane as well as additional out-of-plane dynamics such as log rolling and kayaking. In a homogeneous, steady shear flow, they have also demonstrated the sign change in the normal stress difference with increase in shear rate and suggested this sign change is related to the dynamics between the inplane and out-of-plane motions. A systematic analysis of the flow dynamics of the Doi model was performed by Nayak [161] and by Faraoni, et al. [75]. Rich and interesting dynamics and bifurcation behavior are revealed in these publications. Of particular interest is the existence of a chaotic dynamics at a moderate shear rate within the biphasic region where both the isotropic branch and nematic branch coexist.

The Galerkin method has also been extended for simulations of elastic dumbbell models, for which the governing Fokker-Planck equation is

$$\frac{\partial \psi}{\partial t} = -De \frac{\partial}{\partial \mathbf{Q}} \cdot [\boldsymbol{\kappa} \cdot \mathbf{Q}] \psi + \frac{\partial}{\partial \mathbf{Q}} \cdot \left[\frac{1}{2} \frac{\partial \psi}{\partial \mathbf{Q}} + \mathbf{F}^{(c)} \psi \right] \quad (3.12)$$

where $\mathbf{Q}$ is the dimensionless end-to-end vector scaled by kT/H and $\mathbf{F}^{(c)}$ is the connector (spring) force. In this equation $\psi(\mathbf{Q}, t)$ is the configuration-space distribution function for the molecules. For FENE dumbbells the force law, $\mathbf{F}^{(c)}$, is given by

$$\mathbf{F}^{(c)} = \frac{1}{(1 - (Q/Q_0)^2)} \mathbf{Q} \quad (3.13)$$

where Q_0 is the contour length of the polymer molecule or the maximum length of the dumbbell. Fan [67] simulated the molecular conformations and material properties for a steady, simple, shear flow with a FENE dumbbell model. He used Jacobi polynomials for the length (Q) dependence and spherical harmonics for the orientation dependence of the distribution function. Although this algorithm is capable of simulating the FENE dumbbell model in a viscometric flow system, extension for simulating models with even higher degrees of freedom or for the complex flow simulation is extremely difficult because of the highly coupled stiffness matrix as suggested by the nonlinear operators in Equation 3.12. Much research is needed for extending direct simulation techniques to higher dimensions in order to incorporate more realistic models. To the best of our knowledge, however, this is the only simulation in the literature of the full distribution function for a molecular model with a higher number of degrees of freedom than the rigid rod.

3.3 Stochastic Simulations

Stochastic simulation or Brownian dynamics is a powerful numerical method for simulating the Fokker-Planck equation for models with a large number of degrees of freedom. Instead of discretizing the distribution function by using generalized coordinates, a large ensemble of stochastic trajectories is computed. Each trajectory represents a small volume under the probability distribution function. Gardiner [85] and van Kampen [229] provide intuitive introductions to stochastic processes and simulation techniques. Detailed numerical algorithms and theories for designing such algorithms are summarized by Kloeden and

Platen [119]. For a specific emphasis on the simulation of polymer dynamics in specified kinematics, the monograph by Öttinger [168] is an important contribution and it is the standard reference in rheology in this area.

3.3.1 Fundamentals of stochastic differential equations

A Brownian dynamics simulation is essentially a time integration algorithm for a stochastic differential equation. A large ensemble of equal probability, stochastic trajectories is simulated based on a given time integration scheme; and statistical quantities, such as averages of polymer configuration and the polymer contribution to the stress tensor, are collected at a given time by averaging all the trajectories with respect to the quantity desired. A typical stochastic differential equation for a one-dimensional Brownian particle is given in Equation 3.14.

$$dx = a(x, t)dt + b(x, t)dW \quad (3.14)$$

where W is a Weiner process with $\langle W_{t_1} W_{t_2} \rangle = \min(t_1, t_2)$. The first term on the right side of Eqn. 3.14 is called the drift term and the second term is called the diffusion or the noise term. Depending on whether the coefficient b depends on x , one distinguishes between *multiplicative* and *additive* noise. A multiplicative noise corresponds to dependence of the coefficient b on the stochastic process x .

Although Eqn. 3.14 is written in differential form, it is generally interpreted in an integral form:

$$x_t = x_0 + \int_{t_0}^t a(x, s)ds + \int_{t_0}^t b(x, s)dW_s \quad (3.15)$$

Depending on the interpretation of the stochastic integrals by either Ito or Stratonovich calculus, a stochastic differential equation can be transformed into a Fokker-Planck equation that governs the probability density of the Brownian particles. For additive noise,

both Ito and Stratonovich calculus yields the same result. Assuming the application of Ito calculus, the corresponding Fokker-Planck equation for Equation 3.14 with both additive and multiplicative noise is:

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial x}a(x, t)f(x, t) + \frac{1}{2}\frac{\partial^2}{\partial x^2}b^2(x, t)f \quad (3.16)$$

This establishes the correspondence between a stochastic differential equation and the diffusion equation. One should notice that if the diffusion equation contains terms such as spontaneous reaction, the diffusion equation does not have a correspondence to a stochastic differential equation; and hence Brownian dynamics may not be used as an alternative for simulating the Fokker-Planck equation.

Before proceeding to the numerical integration scheme, an important result from the Ito calculus is the Ito formula, which is the “chain rule” for deriving a stochastic differential equation for a stochastic process $y(x, t)$:

$$dy = \left[\frac{\partial y}{\partial t} + \frac{\partial y}{\partial x}a + \frac{1}{2}\frac{\partial^2 y}{\partial x^2}b^2 \right]dt + \frac{\partial y}{\partial x}bdW \quad (3.17)$$

The derivation of Ito’s formula is based on a truncated Ito-Taylor expansion at a second order of dW and first order of dt . The different order of dW and dt is because the variance of the Wiener process scales as the length of the time interval. Loosely speaking, $\Delta W \sim \sqrt{\Delta t}$ and hence an Ito-Taylor series has to include terms of order $\sqrt{\Delta t}$, $(\Delta t)^{1.5}$, $(\Delta t)^{2.5}$, and so on. A truncated expansion of a Ito-Taylor series at the first order of dt has therefore to include the second order of dW and a truncated expansion of a Ito-Taylor series at the second order has to include terms up to the forth order of dW . Given the Ito’s formula, a truncated Ito-Taylor series expansion upto a given order of dt can then be obtained through recursive application of the Ito formula, Eqn. 3.17.

All stochastic differential equations are similar in form to Eq. 3.14; each equation is a balance between a drift or deterministic force term and a stochastic force term. Since the statistical error of a simulation arises solely from the stochastic force term, a stochastic simulation is most accurate for simulating systems in which the deterministic term dominates, e.g., when De is large (c.f. Equation 3.19). Therefore, Brownian dynamics is a perfect complement to the spherical harmonics-Galerkin method for simulating the response of the multibead rod model over a wide range of De . At the same time, this suggests that usefulness of using a Brownian dynamics simulations to study systems that are close to equilibrium is very limited, unless the intramolecular interaction is much stronger than the stochastic force term.

To understand the limitations of Brownian dynamics simulations and to explore possible ways to improve the accuracy, it is helpful to look at formal results for the statistical errors. The central limit theorem can be used to show that the statistical error of a stochastic simulation scales as $\sigma/\sqrt{N}$, where σ is the variance of the underlying distribution and N is the size of the ensemble. As a result, in order to improve the accuracy of a simulation, one may decrease σ or increase N . Increasing the ensemble size is the natural way to improve accuracy. However, the unfavorable scaling for the statistical error with N suggests that improving accuracy by an order of magnitude requires increasing the size of the ensemble by two orders of magnitude. This raises questions as to the suitability of Brownian dynamics as an effective quantitative tool for exploring polymer dynamics. An alternative approach to decrease statistical error is to decrease σ . This approach has been studied, and relatively efficient methods have been developed. Most of these methods are based on either importance sampling techniques or control variate techniques [60][159]. The idea of importance sampling is based on the biased sampling in the configuration space that contributes the most to the desired quality. Another implementation of this technique is to cal-

culate the desired moments or expectations of a stochastic variable by transforming the distribution such that the most abundant sampling space (highest probability region of the transformed distribution) contributes the most to the desired moments or expectation. The most common example is the calculation of the mean square equilibrium molecular length of a suspension of Hookean dumbbell. Calculating the the mean square equilibrium length by sampling the distribution in spherical coordinates is equivalent to sampling for the fourth moment of a Gaussian distribution function; on the other hand, sampling the same quality by using the distribution in Cartesian coordinates is equivalent to sampling for three times, the second of a Gaussian distribution. It can be shown that the variance in calculating the second moment ($\text{Var}(Q_x^2 + Q_y^2 + Q_z^2) = 6$) is always smaller than that of the fourth moment ($\text{Var}(Q^4) = 96$) [168], and therefore variance reduction is achieved. This technique requires a priori knowledge of the underlying distribution function and hence is not useful for nonequilibrium Brownian dynamics simulation. The idea behind the control variate technique is the estimate of the difference of an underlying distribution function from a known distribution function. That is, for a stochastic variable X , one estimates the expectation, $E(X)$ by defining a new variable $Y = X - c(Z - E(Z))$, where $c = \text{Corr}(X \cdot Z) / \text{Var}(Z)$ for the minimum variance for Y . Given that $E(Y) = E(X)$, one can show that the variance of Y is less than that of X . As an example, for the estimation of $\langle \mathbf{Q}\mathbf{Q} \rangle$ in a nonequilibrium Brownian dynamics simulation, we first rewrite the definition of $\langle \mathbf{Q}\mathbf{Q} \rangle$ as two contributions, one from equilibrium (with distribution $\psi_{\text{eq}}(\mathbf{Q})$) and the other from nonequilibrium (with distribution $\psi(\mathbf{Q})$):

$$\begin{aligned} \langle \mathbf{Q}\mathbf{Q} \rangle &= \int \mathbf{Q}\mathbf{Q} \psi(\mathbf{Q}) d\mathbf{Q} \\ &= \int \mathbf{Q}\mathbf{Q} (\psi(\mathbf{Q}) - \psi_{\text{eq}}(\mathbf{Q})) d\mathbf{Q} + \int \mathbf{Q}\mathbf{Q} \psi_{\text{eq}}(\mathbf{Q}) d\mathbf{Q} \end{aligned} \tag{3.18}$$

On top of the issue of statistical error, other issues that contribute to the challenges of simulating molecular conformation by using Brownian dynamics simulation include finite range of the generalized coordinates, constraints such as rigid bond length or bond angle, and nonlinear effects (such as a nonlinear connector force law, excluded volume effects, and hydrodynamic interaction effects).

3.3.2 Application of Brownian dynamics for rheological calculations

The stochastic differential equation for a freely draining (no hydrodynamic interaction between the beads), elastic dumbbell with a given connector force, $\mathbf{F}^{(c)}(\mathbf{Q})$, is

$$d\mathbf{Q} = [-\text{De}[\boldsymbol{\kappa} \cdot \mathbf{Q}] + \mathbf{F}^{(c)}(\mathbf{Q})]dt + d\mathbf{W} \quad (3.19)$$

This equation is directly converted from the corresponding Fokker-Planck equation (Eqn. 3.12). If a FENE force law (Eqn. 3.13) is used for the simulation, then the length of the molecule (Q) has to be less than the maximum extensibility, i.e. $Q \in [0, \sqrt{b}]$. In an explicit time stepping algorithm such as the forward Euler method, there is no guarantee that Q would be remain within its domain even after a single time step and the numerical results calculated with out-of-bound Q would be both erratic and aphysical. There are two ways to circumulate this problem. First, one can design a rejection criteria where a single step would be repeated if a set of random number in $\mathbf{W}$ would lead to an aphysical Q . Alternatively, one may use an operator splitting method and treat the nonlinear contribution, the connect force term, implicitly.

3.3.3 Brownian dynamics simulations of wall effects on molecular conformations

An important application of Brownian-dynamics methods is for studying the effect on flow problems of boundary conditions and of the interactions between bounding surfaces and polymer molecules. Because the evolutions of molecules are simulated individually,

the wall-molecule interaction can be explicitly and easily implemented. This is not the case in the direct simulation of the Fokker-Planck equation, where the contraction of the configuration space due to wall-molecule interaction is difficult to implement. One of the most interesting characteristics in this application is the effect of flow on the thickness and the scaling of a depletion layer. A depletion layer may be defined as the distance within which the configuration of a polymer molecule would be affected by the presence of the wall. In 1992, a nonhomogeneous kinetic theory was developed by Bhawe et al [8] and was used to study molecular migration near a wall for dilute polymer solutions undergoing wall-driven shear flow in which the polymer is modeled as a Hookean dumbbell. By solving the equation of motion and a constitutive equation self-consistently, they observed a depletion layer whose thickness increased as $De^{1/2}$. A similar study employing Brownian dynamics was performed by de Pablo et al [52]. They assumed a linear velocity profile and employed a multibead-rod model as the micromechanical model. Instead of finding a monotonic scaling law for the depletion-layer thickness, they found that the depletion-layer thickness first decreased from low to moderate shear rates and then increased from moderate to high shear rates. The scaling of the thickness of the depletion-layer is roughly linear in De for moderate to high shear rates. The difference between this scaling result and that of Bhawe et al. [8] is perhaps due to the fixed linear velocity profile imposed by de Pablo et al. [52] or due to the difference in the micromechanical model. de Pablo et al. [52] further studied the effect of wall-polymer interaction and demonstrated that there was no significant difference in the depletion layer between a hard wall and a soft wall.

Since the appearance of these papers, a number of other authors have studied this problem. The most recent contribution is due to Hijazi & Khater [96] who used a much simpler, one-dimensional Brownian-dynamics simulation to represent the dynamics of the

molecules. They simulated a Boeder differential equation, which is essentially a one-dimensional Fokker-Planck equation for the rigid-rod model at steady state. They predicted similar behavior of the depletion-layer thickness to that observed by de Pablo et al. That is, the depletion-layer thickness first decreased with increasing shear rate; then above a critical shear rate, the depletion-layer thickness increased monotonically with shear rate.

3.3.4 Brownian dynamics simulation of more realistic molecular models

There are a number of ways to simulate molecular models with a large number of degrees of freedom with constraints such as fixed bond-length or bond-angles. The most intuitive way is to simulate the stochastic differential equations based on the generalized coordinates, Q_i . An alternative method is based on the SHAKE algorithm derived by Ryckaert, et al. [184]. This algorithm is a predictor-corrector method where the predictor step is an unconstrained update for the bead position and the corrector step involves the update of the bead position and the calculation of a set of Lagrange multipliers that force the constraints to be satisfied. A direct implementation of the SHAKE algorithm in Brownian-dynamics simulations of polymers rheology has been done by Liu [140]. He established the first detailed numerical method for simulating the Kramers chain model in a steady state, homogeneous flow. He was also the first to demonstrate the distinct dynamics of a Kramers chain in both steady shear and elongational flow. In steady elongational flow, the chains are oriented along the axis of elongation and are nearly fully extended at high elongational rates. In steady shear flow, the Kramer chains are in continuous tumbling-stretching motion. This prediction is shown in Figure 3.2 and has been experimentally verified by using video fluorescence microscopy [198]. Note that although the Kramers chains are in continuous tumbling-stretching motion, the predicted

material functions and average configuration do not change with time. In other words, the configuration-space distribution function is at steady state.

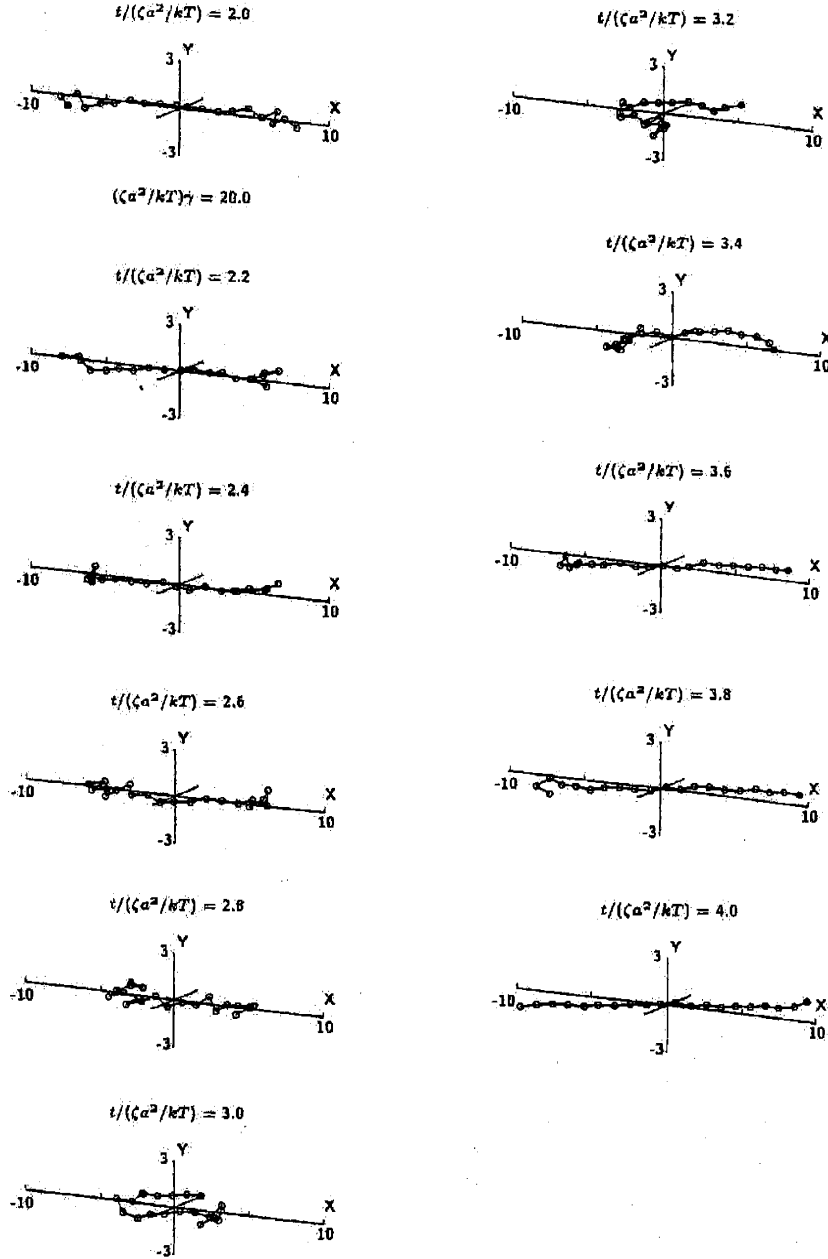


Figure 3.2: Snapshots from a sample trajectory of a 20-bead Kramers chain in steady shear flow with $(\zeta a^2/kT)\dot{\gamma} = 20.0$. One end of the chain has been tagged by a filled bead. The dimensionless time shown is $t/(\zeta a^2/kT)$. Here, ζ is the drag coefficient for a bead and a is the length of the rod connecting the beads. Reproduced from Liu [140].

The recent use of Brownian-dynamics and video-microscopy techniques for studying DNA molecules has provided much interesting and valuable information about the stretching and orientation dynamics of individual molecules. It is important to keep in mind the difference between these individual molecule dynamics and the dynamics of the distribution function, which determines the macroscopic properties. This issue has been addressed recently by Babcock et al [4]. Instead of looking at individual chain configurations, they examined both experimentally and with Brownian-dynamics simulations the ensemble-averaged chain extension and the distribution function for chain extension. They used these observations to describe and explain the overshoot in viscous stress growth coefficient observed in the inception of steady shear flow.

Many of the interesting single-molecule dynamics that have been observed in simulations and experiments since the application of video microscopy to these problems are summarized in a large collection of papers by Larson and coworkers and by Shaqfeh and coworkers. A nice overview of the current state of analysis was presented by Larson et al at the XIIIth International Congress of Rheology [128]. Recently, the focus for these systems has turned towards examining single-chain dynamics in mixed flows and comparing these dynamics with the observations that have previously been reported in the limiting cases of shear-free [173, 197, 127] and shear flows [198, 104, 135]. The mixed flow is expressed as a superposition of shearing and elongational flow. For these flow kinematics, recent stochastic simulations reveal that the shearing flow reduces the critical extension rate required to produce a coil-stretch transition as proposed by de Gennes [50]. When the ratio of strain rate to vorticity exceeds unity, the time-averaged molecular extension is found to reach the maximum contour length at high flow strength, as observed in pure extensional flow [173]. If the flow strength is scaled with the largest eigenvalue of the rate-of-strain tensor, then an overlap of steady molecular extension in these flows with

that in pure extensional flow is found. At sufficiently large Deborah numbers, single-DNA experiments show that the flow completely stretches some of the molecules. The stretched state is stable, in contrast to simple shear flow in which the molecules fluctuate between coiled and stretched conformations even at large Deborah numbers.

In addition to its use in studying the dynamics of DNA molecules, Liu's algorithm for simulating Kramers chains has also been applied to understanding a wide variety of other interactions between molecular conformations and rheological behavior. For example, Xu et al [230] studied the effect of anisotropic drag and excluded volume interactions among beads within the same polymer molecule. This is perhaps the closest simulation to date of the exact reptation model for polymer melts proposed by Curtiss and Bird [20]. Doyle et al. [60] provide one of most comprehensive sets of data for material functions of the Kramers-chain model in shear and elongational flows. They also include optical property predictions for the Kramers-chain and a comparison between the Kramers-chain and the FENE dumbbell model.

Recent advances in numerical algorithms for Brownian-dynamics simulations focus on developing a hybrid simulation approach that combines a continuum method with a stochastic simulation for the polymer molecules. The stochastic simulation includes mean-field interaction effects such as hydrodynamic interaction and intermolecular potentials. The issue with the incorporation of hydrodynamic interaction is the decomposition of the diffusion tensor. The operation count scales as the cube of the number of beads in a molecule, N^3 , and hence is extremely expensive for large molecules. Fixman [79] first proposed the idea of employing a spectral polynomial approximation to represent the weak interaction between the molecules, which reduces the operation count reduces to order N^2 . Implementation examples of this approach include those by Jendrejack [109] and Kröger

[120]. For incorporating an intermolecular potential, the issue is the calculation of the sum of interactions between each pair of molecules.

Chapter 4

Numerical Algorithm for Computing Rheological Dynamics of Microstructural Models

4.1 Introduction

The advent of advanced computers has facilitated simulations of flows in complex geometries with molecular models. Prototype complex geometries are designed to understand the effect of complex kinematics on the molecular shape and orientation of polymers. Direct simulation of these flows allows precise knowledge of the effect of flow geometry on the evolution of molecular configuration and alignment, which is critical for determining and optimizing the final product properties in polymer processing.

Simulation of a complex flow requires a self-consistent solution of the macroscopic and microscopic equations. For isothermal problems, the macroscopic governing equations include the equation of continuity, the equation of motion, and a stress tensor expression that maps the microstructural state onto the macroscopic stress-tensor. Here, the discussion focuses on differential models. Integral models resulting from the exact or perturbed solution of the Fokker-Planck equation will be considered briefly in Section 4.2.5. For elastic dumbbell models with an arbitrary spring-force law, the set of macroscopic equations for a creeping, incompressible flow is

$$\nabla \cdot \mathbf{v} = 0 \quad (4.1)$$

$$\beta \nabla \cdot [\nabla \mathbf{v} + \nabla \mathbf{v}^T] - \nabla \cdot [\boldsymbol{\tau}_p + p \boldsymbol{\delta}] = 0 \quad (4.2)$$

$$\boldsymbol{\tau}_p = \frac{(1-\beta)}{De} \{ - \langle \mathbf{Q} \mathbf{F}^{(c)}(\mathbf{Q}) \rangle + \boldsymbol{\delta} \} \quad (4.3)$$

where β is the ratio of the solvent to total viscosity in the limit of zero shear rate.

Calculating $\langle \mathbf{QF}^{(c)}(\mathbf{Q}) \rangle$ requires a microstructural equation, which can be a Fokker-Planck equation, the corresponding stochastic differential equation for the elastic dumbbell model, or a moment equation that is obtained from the Fokker-Planck equation through a contraction operation. For example, the second moment equation for an elastic dumbbell is:

$$\text{De} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = - \langle \mathbf{QF}^{(c)}(\mathbf{Q}) \rangle + \delta \quad (4.4)$$

If the second moment equation is used for calculating microstructure, then unless $\mathbf{F}^{(c)}(\mathbf{Q})$ is linear in $\mathbf{Q}$, a closure approximation is required to approximate the connector force as $\mathbf{F}^{(c)}(\mathbf{Q}) \approx H(\langle \mathbf{Q}\mathbf{Q} \rangle) \mathbf{Q}$ where $H(\langle \mathbf{Q}\mathbf{Q} \rangle)$ is a generalized spring modulus. One of the most common models of this kind is the FENE-P model. Deriving a moment equation for $\langle \mathbf{QF}^{(c)}(\mathbf{Q}) \rangle$ will introduce the need for additional closure approximations. As a result, a closure approximation is required unless the underlying distribution function of the model is fully described by a fixed number of moments. Although models that use a closure approximation will be qualitatively similar to those without the closure approximation, there is clear evidence that closure approximations can lead to incorrect or even aphysical behavior. For example, in the start-up of and relaxation following elongational flow, the FENE-P model fails to capture the observed hysteresis behavior because of the lack of higher moments in the FENE-P model, whereas the FENE model qualitatively predicts the hysteresis loop. A direct approach for eliminating the often-unknown errors in closure approximations is to replace the computation of the moment equation by solution of the Fokker-Planck equation or simulation of the corresponding stochastic differential equation at each physical point in the system. In this strategy, the local stress is then calculated by using the stress expression, which in turn is coupled with the equations of continuity and motion to obtain the velocity field and pressure distribution. This approach has been a

very active area of research during the past decade, and some of the advances are described later in this chapter.

Although purely continuum simulations may not accurately represent the dynamics of a molecular model, these are still the most popular methods, because of their (relatively) low computational requirements. More importantly, continuum simulations continue to provide a valuable platform for developing numerical algorithms and methods, which can subsequently be used with equations from kinetic theory. Adaptation of the numerical algorithms in this way is feasible because the moment equations have a similar mathematical characteristic as the Fokker-Planck equation; these equations are all hyperbolic in terms of the spatial operator. For this reason, we first review the advances and special characteristics of continuum simulations before discussing direct, hybrid simulation methods.

4.2 Continuum Simulation Methods

Continuum simulation methods such as finite element and spectral methods have been developed to solve Equations 10 to 13 self consistently. Baaijens [3] has presented a detailed review of recent advances in the use of finite element methods for viscoelastic flow simulations in which a microstructure equation is coupled with the stress-tensor expression to form a constitutive equation. In this section, only issues that are relevant to computation of the microstructure are discussed.

4.2.1 Mixed finite element analysis for the Stokes problem

The strong form of the generalized Stokes problem in a physical domain $\Omega \in \mathbb{R}^d$ with boundaries $\partial\Omega$ is given by

$$\nabla \cdot \eta \nabla \mathbf{u} - \nabla p = \mathbf{f} \quad (4.5)$$

together with the incompressibility constraint,

$$\nabla \cdot \mathbf{u} = 0 \quad (4.6)$$

and the homogeneous no-slip boundary condition on the surface Γ

$$\mathbf{u} = \mathbf{u}_b \quad (4.7)$$

The strong form of the generalized Stokes problem (Equations 4.5 to 4.7) is equivalent to a variational or Galerkin-weak form which can be derived through the application of the variation calculus. For example, the variational weak form of the Stokes equation is: find $(\mathbf{u}, p) \in V_E \times S$ such that for all $\mathbf{v} \in V_E$ and $q \in S$,

$$a(\mathbf{v}, \mathbf{u}) + b(\mathbf{v}, p) = (\mathbf{v}, \mathbf{f}) \quad (4.8)$$

and

$$b(\mathbf{u}, q) = 0 \quad (4.9)$$

where $(., .)$ is the L_2 norm, and operators $a(., .)$ and $b(., .)$ are defined as

$$a(\mathbf{u}, \mathbf{v}) \equiv \int_{\Omega} \eta \nabla \mathbf{u}^T \cdot \nabla \mathbf{v} dV \quad (4.10)$$

$$b(\mathbf{u}, q) \equiv \int_{\Omega} q (\nabla \cdot \mathbf{u}) dV \quad (4.11)$$

The functional space for $(\mathbf{u}, p)$ is given by

$$V_E = \{ \mathbf{v} \in (H^1(\Omega))^d \mid \mathbf{v}|_{\Gamma} = \mathbf{u}_b \} \quad (4.12)$$

$$S = \left\{ q \in (L^2(\Omega))^d \mid \int_{\Omega} q dV = 0 \right\} \quad (4.13)$$

Mixed finite element methods for the Stokes problem is constructed by discretizing the computation domain Ω into a set of small, non-overlapping elements $\{T_h \in \mathcal{T}_h\}$ such that $\Omega = \bigcup T_h$. These elements can be either quadrilateral or triangular and all of them are geometrically conforming: for any two elements $T_{h,1}$ and $T_{h,2}$, $\partial T_{h,1} \cap \partial T_{h,2}$ must either be (1) single vertex of *both*, (2) entire edge of *both*, or empty. Associated with the

mesh are a set of nodes for velocity and pressure. These nodes are in generally need not be coincident. For example, for a quadratic continuous velocity and linear continuous pressure on a triangular element, velocity nodes will exist at each vertex and at the midpoint of each edge, while pressure nodes will exist only at the vertices.

Associated with the functional space of $(\mathbf{u}, p)$ are the discretized space $V_h \times S_h$. The specific choices of V_h and S_h has to satisfy the *inf-sup* or LBB (Ladyzhenskaya-Babuska-Brezzi) condition to guarantee comptability and uniqueness of the solution within a constant. Denoting discretized variables $(\mathbf{u}_h, p_h)$ to distinguish from the continuous problem, the *inf-sup* condition can be written as: For all $(\mathbf{v}, q) \in V_h \times S_h$, there exists a positive constant γ such that

$$\inf_{q \in S_h} \sup_{\mathbf{u} \in V_h} \frac{b(\mathbf{v}, q)}{\|\mathbf{v}_h\|_{H_1(\Omega)}} = \gamma \quad (4.14)$$

One set of discretized space that satisfies the inf-sup condition is the Taylor-Hood element, which is resulted from the use of quadratic finite elements for velocity X_h and linear for stress Y_h . On quadrilateral elements, this corresponds to taking $X_h \subset \mathbb{Q}_2$ and $Y_h \subset \mathbb{Q}_1$, where $\mathbb{Q}_2$ is the space of biquadratic polynomials and $\mathbb{Q}_1$ is the space of bilinear polynomials. On triangular elements, this gives $X_h \subset \mathbb{P}_2$ and $Y_h \subset \mathbb{P}_1$, where $\mathbb{P}_2$ and $\mathbb{P}_1$ are the corresponding Lagrangian polynomial approximations for triangles. The corresponding finite element spaces for the discretized variables $(\mathbf{u}_h, p_h)$ are then given by $V_h = \{\mathbf{v}|_{T_h} \in X_h^d, \forall T_h \in \mathcal{T}_h\} \cap H^1(\Omega)$ and $S_h = \{q|_{T_h} \in Y_h, \forall T_h \in \mathcal{T}_h\} \cap C^0(\Omega)$. The convergence properties of these choices of finite element spaces have been shown to be optimal with the solution of the finite element method converges as $O(h^2)$. Defining $\{\phi\}$ as a set of basis functions that spans V_h and $\{\psi\}$ as a set of basis functions that spans S_h , the discretized weak form arises from the Galerkin procedure with $\mathbf{u}_h = \sum \mathbf{u}_{h,i} \phi_i$ and $p_h = \sum p_{h,i} \psi_i$ has the matrix structure as

$$\begin{bmatrix} A_h & B_h \\ B_h^T & 0 \end{bmatrix} \cdot \begin{bmatrix} \mathbf{u}_h \\ p_h \end{bmatrix} = \begin{bmatrix} F_h \\ 0 \end{bmatrix} \quad (4.15)$$

where the ij -components for A_h is $a(\phi_i, \phi_j)$ and that for B_h is $b(\phi_i, \psi_j)$. Essential or Dirichlet boundary conditions for $\mathbf{u}_h$ can then be implemented directly through a penalty method by introducing a large number at the ii -component that corresponding to the boundary nodes. Because the inf-sup condition admits a unique solution to within a constant for the pressure, a reference point (spurious mode) of the pressure has to be introduced to obtain a unique solution.

An alternative formulation of the equation of continuity is the use of a pressure equation. This is derived by taking the divergence of the momentum equation. The resulting strong form for the pressure equation is:

$$\nabla^2 p = \nabla \cdot \mathbf{f} \quad (4.16)$$

and the associated weak form is: for all $q \in S$, find $p \in S$ such that

$$A^1(q, p) \equiv \int_{\Omega} \nabla q \cdot \nabla p dV = -b(\mathbf{f}, q) \quad (4.17)$$

This pressure equation is then coupled with the equation of motion to form the new formulation for the Stokes problem. There are two distinct advantage of using the pressure equation. First, the pressure equation is decoupled from the equation of motion and therefore the pressure equation can be solved independent and then the velocity is calculated as an update with the new pressure field. Second, if the two set of equations are solved simultaneously, then the resulting stiffness matrix has no zero contribution along the diagonal. However, the use of the pressure equation implies a weak implementation of the equation of continuity and hence the resulting solution could have a significant “mass leak” for a specific class of problem. Moreover, the boundary conditions for p is not well defined for various types of boundary conditions for velocity.

4.2.2 Mathematical formulation of a viscoelastic flow calculation

Extension of the finite element analysis of the Stokes problem to viscoelastic flow calculations involves an operator splitting strategy that decouples the treatment of the stress tensor as a forcing function to the equation of motion and continuity pair from the calculation of the stress tensor through a microstructure equation represented by a hyperbolic problem. The implementation of this approach involves three stages of development: (1) formulation of the equation of motion, (2) treatment of the hyperbolic characteristics for the microstructure evolution, (3) construction of a robust and accurate time integration algorithm, and (4) development of a robust and efficient solver for the solution of the resulting linear algebra problem. In the first stage, a stable formulation for the equation of motion is derived that preserves the ellipticity of the momentum equation even for small β . This is particularly important because the explicit form of the viscous operator in the equation of motion can be used to justify the application of well-known mixed finite element methods for elliptic saddle-point problems. Furthermore, it ensures a finite determinant of the stiffness matrix. The most popular formulation is based on the EVSS (elastic viscous stress splitting) method developed by Rajagopalan et al [180]. Several subsequent improvements to the EVSS have been made that also simplify the formulation. One of the most useful improvements for both spatial and temporal stability is the DEVSS-G (discrete elastic-viscous stress splitting) formulation of Liu et al [139]. In this formulation, the equation of motion is rewritten by adding and subtracting a Newtonian term with unit viscosity:

$$\nabla \cdot [\nabla \mathbf{v} + \nabla \mathbf{v}^T] - \nabla \cdot [\boldsymbol{\tau}_p + (1 - \beta)[\mathbf{G} + \mathbf{G}^T] + p\boldsymbol{\delta}] = \mathbf{0} \quad (4.18)$$

where $\mathbf{G}$ is introduced as a least-squares interpolation of the velocity gradient:

$$\mathbf{G} - \nabla \mathbf{v} = \mathbf{0} \quad (4.19)$$

The advantage of “D” in DEVSS-G over EVSS is that no reformulation of the constitutive equation for the stress tensor is required, which can be troublesome when the constitutive equation is complicated (c.f. Equation 1.4 for FENE-P model) or when other constitutive descriptions (such as the Fokker-Planck equation or stochastic differential equation) are used to model the stress tensor. For continuous problems, Equation 4.18 reduces to Equation 4.2. For the discretized problem, $\mathbf{u}_h \in V_h(\Omega)$ and $\boldsymbol{\tau}_{p,h}, \mathbf{G}_h p_h \in (S_h(\Omega))^d$. Hence $\nabla \mathbf{u}_h$ and $\mathbf{G}_h$ are represented by different functional spaces. This difference provides the necessary stability and guarantee the finite determinant of the stiffness matrix in the limit when that β vanishes. In addition to providing numerical stability to the equation of motion, the $\mathbf{G}_h$ interpolate also provides smooth numerical data for the velocity gradient used in the calculation of the upper convected derivatives that appear in most constitutive equations for the stress tensor.

The second stage of development involves choosing a suitable basis-function set to enhance the stability of the algorithm. In particular, the basis functions have to be suitable for simulating the hyperbolic characteristics of the microstructure equation. The general strategy is to introduce a small amount (of order of the element size h) of diffusivity to smooth out the algorithm. Three methods that have been used successfully are the Streamwise Upwinding (SU) method (Johnson 1992 [112]), the Streamline Upwind Petrov-Galerkin (SUPG) method (Brooks & Hughes 1982 [27], Johnson & Pitkaranta 1986 [111]), and the Discontinuous Galerkin (DG) method (Lesaint & Raviart 1974 [134]). Among these three methods, DG is the most robust when it is coupled with EVSS-based formulations [72]. It can also dramatically reduce the operation count in solving a given problem through an element-by-element strategy. A concise introduction of the DG method was provided by Cockburn [36]. Here, we describe the basics of the DG method.

To define DG, consider a typical stress tensor equation:

$$\frac{\partial \boldsymbol{\tau}}{\partial t} + \mathbf{v} \cdot \nabla \boldsymbol{\tau} = f(\boldsymbol{\tau}, \mathbf{G}) \quad (4.20)$$

We seek an approximation $\boldsymbol{\tau}_h$ to $\boldsymbol{\tau}$ that belong to the finite element space V_h^{DG} that does not require continuity across inter-element boundaries. One of the suitable space is

$$V_h^{\text{DG}} \equiv \{ \mathbf{v} \in L^1(\Omega) : \mathbf{v}|_{E_j} \in Q^k(E_j), j = 1, \dots, N \} \quad (4.21)$$

where E_j is a finite element and $Q^k(E_j)$ is the space of polynomials in E_j of degree k ($Q^k \subseteq \mathbb{Q}^k$ for rectangular elements and $Q^k \subseteq \mathbb{P}^k$ for triangular elements). Given the finite element space, the weak form of this stress tensor equation can be written as: For all $\Psi \in V_h^{\text{DG}}(\Omega)$, find $\boldsymbol{\tau}_h \in V_h^{\text{DG}}(\Omega)$ such that

$$\left(\Psi, \frac{\partial \boldsymbol{\tau}_h}{\partial t} \right) + (\Psi, \mathbf{v}_h \cdot \nabla \boldsymbol{\tau}_h) - (\Psi, \mathbf{v}_h \cdot \mathbf{n}(\boldsymbol{\tau}_h^+ - \boldsymbol{\tau}_h^-))_{\partial T_e^-} = (\Psi, f(\boldsymbol{\tau}_h, \mathbf{G}_h)) \quad (4.22)$$

for all the finite element E_j . On each element, the element boundaries (∂T_e) are separated into inflow (∂T_e^-) and outflow (∂T_e^+) boundaries:

$$\partial T_e^- = \{ \mathbf{x} \in \partial T_e : (\mathbf{v} \cdot \mathbf{n}) \leq 0 \} \quad (4.23)$$

$$\partial T_e^+ = \{ \mathbf{x} \in \partial T_e : (\mathbf{v} \cdot \mathbf{n}) > 0 \} \quad (4.24)$$

Because the basis functions in DG are defined only on the element, the mass matrix for the microstructure equation over the whole computational domain is block diagonal. Furthermore, if $(\mathbf{v}, \mathbf{G})$ are known and the elements are ordered according to the streamline direction, then the approximation to $\boldsymbol{\tau}$ in an element is coupled to that for other elements only through the upstream boundary integral on (∂T_e^-) . Hence, if the elements are ordered according to the streamline direction, a rigorous, fully implicit stress update can be performed by an element-by-element condensation, thereby avoiding the solution of a large matrix problem. This property is particularly important for developing or coupling the finite element analysis with other numerical methods for solving more complicated microstructure equations, as the total number of degrees of freedom represented in $\boldsymbol{\tau}_h$ for a

direct simulation of the Fokker-Planck equation, for example, will be orders of magnitude larger than for the moment equation alone.

Time-integration algorithms for viscoelastic problems often involve operator splitting or explicit methods to reduce the dimension of the stiffness matrix at each time step by solving a number of smaller problems. The premise of the time integration algorithm is that the overall set of differential algebraic equations (DAEs) resulting from the spatial discretization is of index one and therefore can be rewritten as a set of ordinary differential equations (ODEs). The set of ODEs is then discretized by various semi-implicit methods. This idea is illustrated pictorially by Figure 4.1. Two of the most commonly used time-integration algorithms for viscoelastic flow simulations are the θ -method [192] and the Runge-Kutta method [200]. In both of these methods, the variable sets are solved or updated independently in each substep of the algorithm.

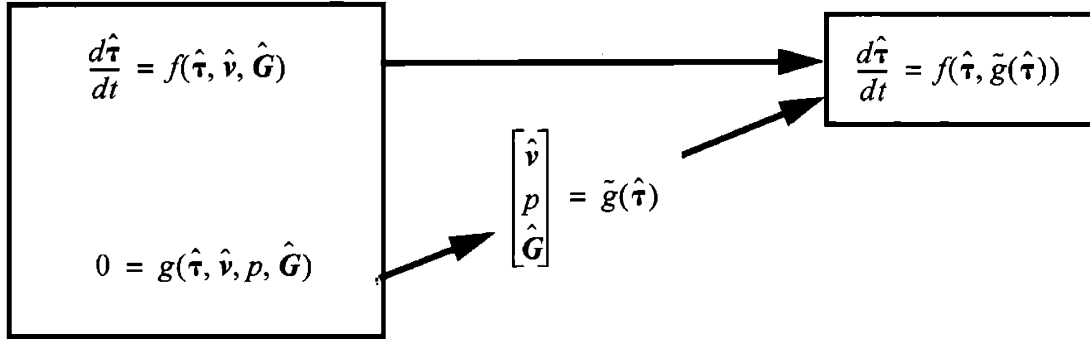


Figure 4.1: Illustration of the index one set of DAEs for a typical viscoelastic problem leading to a set of ODEs, which in turn may be solved by time integration methods such as the θ method or standard fourth order Runge-Kutta method. Developed based on Smith [199].

Both spatial and temporal discretization of the set of equations in a viscoelastic problem leads to a large set of nonlinear, algebraic equations. For steady state problems, such equations are solved by using a Newton-Raphson scheme in conjunction with continuation in We or De . For time-dependent problems, the nonlinear contributions may be updated semi-implicitly or even fully explicitly. An explicit time integration method is stable only under the Courant condition, which limits the time step size that can be taken in a time

integration. This limitation of time step size is not stiff because computation time for an explicit method in a viscoelastic flow calculation is still much faster than a fully implicit method such as implicit Euler or Crank-Nicholson method. This is because most constitutive equations are hyperbolic and hence the Courant condition scales linearly, instead of quadratically as in the case of an elliptic operator. Furthermore, in many cases, fully implicit time integration method is simply impossible to implement because of the extremely large number of degrees of freedom. In both the steady and time-dependent problems cases, the resulting linear set of equations is generally solved by using a director LU factorization or a frontal solver. Iterative methods such as BiCGSTAB or GMRES may be used, but the lack of an efficient preconditioner hinders the efficiency of these algorithm; and in many cases, their performance is even worse than the use of a frontal solver.

In the operator splitting strategy for a viscoelastic flow problem with moment equation as constitutive equation, the most time-consuming part of the time-integration is the solution of the $\{\mathbf{v}, p, \mathbf{G}\}$ problem. Therefore, effort has been focused on developing a robust and efficient iterative solver for the $\{\mathbf{v}, p, \mathbf{G}\}$ problem. A notable development is due to Caola et al [33], whose algorithm combines a parallel preconditioner with BiCGSTAB. Their preconditioner is based on the Schur block decomposition of the linear equation set applied by using a combination of additive Schwarz domain decomposition, a coarse grid preconditioner, and approximate solution of the linear systems on subdomains.

4.2.3 Development of a fully implicit, element-by-element decomposition algorithm for continuum calculations.

While the θ -method or various orders of the Runge-Kutta method provide numerical stability that allows large scale computation of viscoelastic flow with moment equations as the constitutive model, simulation at high De or We is still an extremely difficult task. Therefore, the ability to achieve an A-stable time integration method or Newton's method

for calculating the steady state solution, while retaining the operator splitting characteristics of calculating a large number of small problems rather than single enormous problem, is still very important and useful. In this section, we propose the use of the Newton iteration algorithm described by Verbeeten [222] in conjunction with a topological sort algorithm to achieve a fully implicit algorithm.

Without losing generality, consider the residual resulting from a Newton's iteration for the ν - p - G - τ problem, and let J_{xy} be the Jacobian for x -equation with respect to variable y . The block Jacobian matrix becomes:

$$\begin{bmatrix} J_{uu} & J_{uG} & J_{up} & J_{u\tau} \\ J_{Gu} & J_{GG} & 0 & 0 \\ J_{pu} & 0 & J_{pp} & 0 \\ J_{\tau u} & J_{\tau G} & 0 & J_{\tau\tau} \end{bmatrix} \cdot \begin{bmatrix} \delta u \\ \delta G \\ \delta p \\ \delta \tau \end{bmatrix} = \begin{bmatrix} f_u \\ f_G \\ f_p \\ f_\tau \end{bmatrix} \quad (4.25)$$

Algebraic manipulation of the last entries for the stress tensor equation in Equation 4.25 gives $\delta \tau = J_{\tau\tau}^{-1} \cdot f_\tau - J_{\tau\tau}^{-1} \cdot (J_{\tau u} \delta u + J_{\tau G} \delta G)$. Substituting this expression into the first entries of equation of motion gives the following decoupled block Jacobian matrix:

$$\begin{bmatrix} \tilde{J}_{uu} & \tilde{J}_{uG} & J_{up} \\ J_{Gu} & J_{GG} & 0 \\ J_{pu} & 0 & J_{pp} \end{bmatrix} \cdot \begin{bmatrix} \delta u \\ \delta G \\ \delta p \end{bmatrix} = \begin{bmatrix} f_u - J_{u\tau} \cdot J_{\tau\tau}^{-1} \cdot f_\tau \\ f_G \\ f_p \end{bmatrix} \quad (4.26)$$

where the modified Jacobians for $\tilde{J}_{uu}$ and $\tilde{J}_{uG}$ are defined respectively as $\tilde{J}_{uu} = J_{uu} - (J_{u\tau} \cdot J_{\tau\tau}^{-1} \cdot J_{\tau u})$ and $\tilde{J}_{uG} = J_{uG} - (J_{u\tau} \cdot J_{\tau\tau}^{-1} \cdot J_{\tau G})$. The stress update, $\delta \tau$, can then be calculated independent of the ν - p - G update as:

$$\delta \tau = J_{\tau\tau}^{-1} \cdot f_\tau - J_{\tau\tau}^{-1} \cdot (J_{\tau u} \delta u + J_{\tau G} \delta G) \quad (4.27)$$

Although this algorithm appears to be flexible for achieving a fully implicit algorithm, the major concern is the inverse of the stress tensor Jacobian $J_{\tau\tau}^{-1}$. If a traditional formula-

tion such as SUPG is used, then $J_{\tau\tau}^{-1}$ will be a large matrix and its storage and matrix-matrix multiplication may be difficult and expensive. If the discontinuous Galerkin method is used to discretize the stress tensor, then the Jacobian matrix for the stress tensor $J_{\tau\tau}$ can be inverted easily assuming that the exterior node value for the stress tensor is known in advance. Because of the lack of a stable and accurate solver for the linear algebra problem for ν - p - G update, Verbeeten [222] failed to implement this algorithm in a fully implicit fashion but made use of two explicit updates. One was on the G tensor update and the other was on the exterior node value for the stress tensor. For the G tensor update, the use of the frontal solver and the iterative solver strategy by Caola [33] has proven to be robust in the implicit treatment of the G update; and an fully implicit update strategy for the exterior node value for the stress tensor calculation can be devised by ordering the elements according to the streamline direction. Therefore, a fully implicit update for the whole ν - p - G - τ problem is indeed possible. Ordering the elements according to the streamline direction allows the exterior nodes of element i are always updated prior to the calculation for element i . Although this idea allows rigorous computation for the fully implicit, element-by-element update of the stress tensor, it is limited to flow calculation with no recirculation region and no periodic boundary conditions. The key to implementation is to find an update list by sorting the elements from the inflow boundary to the outflow boundary according to the streamline direction. This can be done with a topological sort algorithm.

4.2.4 Topological sort

Topological sort is one of the many graph-based algorithm that are commonly studied as an undergraduate subject in computer science [39]. The fundamental problem is to devise an order for a number of tasks which has to be performed before another, or

depends on the other. For example, it is to specify prerequisite relationships between different courses in a curriculum, but it may be harder to find an order to take the classes in sequence so that all prerequisite material for any specific course is fulfilled. In the viscoelastic flow calculation, topological sort could potentially carry an important role for devising a fully implicit time stepping algorithm while maintaining low computation demand of a semi-implicit or even fully explicit time stepping algorithm. In this section, an implementation of topological sort algorithm will be described in detail.

Consider a graph of numbers that represents the order of elements in a streamline direction:

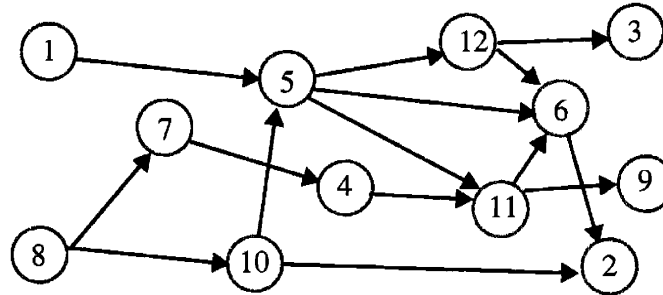


Figure 4.2: A graph of numbers that represents order of elements in a streamline direction. The flow occurs according to the blue arrows

The goal of a topological sort is to create an element list according to the flow direction. In the graph of Figure 4.2, a possible resulting update list may be [1, 8, 7, 4, 10, 5, 11, 12, 6, 9, 2, 3]. Obviously the update list is not unique, as one is not concerned about the order of two unrelated nodes (for example nodes 1 and 8). Knowing the input and output of the topological sort, the algorithm is now presented as follows:

1. Derive a list for the dependence of each node. In the graph of Figure 4.2, the dependence list is:

Node number, n	Nodes that n depends on
1	<i>none</i>

Table 4.1: Dependence list for graph in Figure 4.2

Node number, n	Nodes that n depends on
2	6,10
3	12
4	7
5	1
6	5,11,12
7	8
8	<i>none</i>
9	11
10	8
11	4,5
12	5

Table 4.1: Dependence list for graph in Figure 4.2

2. Find the inflow nodes, i.e. 1 and 8, put them at the beginning of the sorted list and also remove those nodes from the dependence list:

Node number, n	Nodes that n depends on
2	6,10
3	12
4	7
5	0
6	5,11,12
7	0
9	11
10	0
11	4,5
12	5

Table 4.2: Dependence list for graph in Figure 4.2 after step 2

3. Repeat step 2 until the dependence list is empty.

To illustrate better the idea, the resulting sorted list for graph in Figure 4.2 after each execution of step 2 is shown in Table 4.3:

Step number	Sorted list
1	1,8
2	1,8,5,7,10
3	1,8,5,7,10,4,12
4	1,8,5,7,10,4,12,3,11
5	1,8,5,7,10,4,12,3,11,6,9
6	1,8,5,7,10,4,12,3,11,6,9,2

Table 4.3: Sorted list after each execution of step 2 of the algorithm

The operation count for the topological sort is around N^2 , where N is the number of nodes in the graph. The operation count may reduce to order N for a graph with a large amount of traffic between the nodes and where a large number of nodes are eliminated at every step.

In addition to achieving a fully implicit time integration algorithm for viscoelastic flow calculations with a moment equation, the topological sort is also very useful in the multiscale calculation with direct simulation of the Fokker-Planck equation. Here, the elements are updated in the reverse of the streamline direction in order to achieve a fully explicit update for the convective operator. This allows a huge memory savings through not storing the distribution function at each node for the previous time step. Furthermore, the topological sort also provides a simple domain decomposition technique for minimizing the interfaces between each domain. This reduces the amount of communication between processors and enhances efficiency. Both these benefits will be demonstrated in Chapter 8 and Chapter 9 for the calculation of reptation models in complex flow.

4.2.5 Simulation of Integral Constitutive Models

Integral constitutive models derived from kinetic theory normally result from analytical solution of the corresponding Fokker-Planck equation. Most of the integral models can be written as the factorized *K-BKZ* equation:

$$\boldsymbol{\tau}(t) = \int_{-\infty}^t M(t-t') \left[\frac{\partial W}{\partial I_1} \boldsymbol{\gamma}_{[0]} + \frac{\partial W}{\partial I_2} \boldsymbol{\gamma}^{[0]} \right] dt' \quad (4.28)$$

where M is the linear viscoelastic memory function and $W = W(I_1, I_2)$ is known as the potential function. $\boldsymbol{\gamma}_{[0]}$ and $\boldsymbol{\gamma}^{[0]}$ are two relative finite strain tensors, related to the Finger strain tensor and Cauchy strain tensor, respectively [19]. I_1 and I_2 are the first and second invariants of the Finger strain tensor and Cauchy strain tensor, respectively. To use an integral model for a viscoelastic calculation, the stress tensor calculated from Eqn. 4.28 for a given flow field is coupled back to the equation of motion and the equation of continuity for an updated solution of the velocity and pressure field.

At first glance, it appears to be most natural to use a Lagrangian description for the flow field, and the stress is then calculated by following the flow field. However, this requires to the continuous remeshing due to the domain deformation during flow. Elliptic mapping equations may be used to reduce the amount of remeshing, but their use also introduces an extremely involved nonlinear set of equations into the system. For examples of a Lagrangian implementation of the finite element method for viscoelastic calculations with an integral model, the series of papers by Rasmussen and Hassager [182] are recommended.

The most common Eulerian strategy involves integration along particle streamlines for the evaluation of the stress tensor. A major breakthrough in this approach is due to van Heel, et al. [228], who developed the deformation field method based on the direct calcu-

lation of the displacement gradient tensors, Δ and $\mathbf{E}$ through their respective evolution equations:

$$\begin{aligned}\frac{\partial \Delta}{\partial t} + \mathbf{v} \cdot \nabla \Delta &= \nabla \mathbf{v}^T \cdot \Delta \\ \frac{\partial \mathbf{E}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{E} &= -\mathbf{E} \cdot \nabla \mathbf{v}^T\end{aligned}\quad (4.29)$$

Similar to a moment equation, these two displacement gradient tensor equations can be discretized and calculated by using various finite element formulations (such as DG) for a hyperbolic problem. The two relative strain tensors appearing in the constitutive equation are then calculated directly from their definitions:

$$\begin{aligned}\gamma^{[0]} &= \{\Delta^T \cdot \Delta\} - \delta \\ \gamma_{[0]} &= \delta - \{\mathbf{E} \cdot \mathbf{E}^T\}\end{aligned}\quad (4.30)$$

Given the relative strain tensors, the key to evaluating the stress tensor at a given time t is the calculation of the time integral, which can be evaluated by using quadrature. A number of relative strain tensors in the past times are stored and various interpolation methods can be used to approximate the relative strain tensors at the quadrature points.

A similar implementation of the deformation field method based on the “age” of the deformation, i.e. $s = t - t'$ was proposed by Huslen, et al. [103]. The constitutive equation (Equation 4.28) and the deformation equation (Equation 4.29) are modified as follows in Huslen’s approach:

$$\boldsymbol{\tau}(t) = \int_0^\infty M(s) \left[\frac{\partial W}{\partial I_1} \gamma_{[0]} + \frac{\partial W}{\partial I_2} \gamma^{[0]} \right] ds \quad (4.31)$$

$$\begin{aligned}\frac{\partial \Delta}{\partial t} + \frac{\partial \Delta}{\partial s} + \mathbf{v} \cdot \nabla \Delta &= \nabla \mathbf{v}^T \cdot \Delta \\ \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{E}}{\partial s} + \mathbf{v} \cdot \nabla \mathbf{E} &= -\mathbf{E} \cdot \nabla \mathbf{v}^T\end{aligned}\quad (4.32)$$

The introduction of a new “spatial” variable s can be easily discretized by using the discontinuous Galerkin method or even spectral methods. The obvious advantage of this formulation is that the deformation history does not need to be traced or stored. The implementation of this method into traditional finite element analysis software should be trivial and the application potential could be tremendous.

4.3 Hybrid Simulations using Brownian Dynamics

In 1998, Petruccione & Biller [175] first proposed a simulation algorithm that couples the continuum problem with Brownian dynamics. Research on this numerical method did not become active, however, until Laso & Öttinger [122] did their work on viscoelastic flow. Laso and Öttinger termed their hybrid simulation algorithm CONNFFESSIT (Calculation Of Non-Newtonian Flow: Finite Element and Stochastic Simulation Technique). Since the introduction of CONNFFESSIT, at least 30 papers have appeared in the literature either applying this approach to study a flow problem or describing a modified algorithm to improve the accuracy of the method. Whereas most of these algorithms are based on coupling finite element analysis with Brownian-dynamics simulations, Bell et al. [8] coupled Brownian-dynamics simulations with a spectral method. Because of the high convergence rate of the spectral method, the computational requirements of their method are much smaller than those of the conventional CONNFFESSIT algorithm. However, the use of the spectral method limits the range of problems to which the method can usefully be applied. Rather than reviewing this literature in depth, we highlight several critical issues and some of the recent advances.

A primary issue in using Brownian-dynamics or other trajectory-based simulation methods in a macroscopic flow calculation is the error in estimating the macroscopic stress tensor at a specific position. This is due to the fluctuation of stochastic trajectories with time even after macroscopic steady state is reached. (There does not exist a micro-

scopic steady state, as the molecular configurations are continually evolving owing to the Brownian force on the molecules.) Therefore, the macroscopic stress that is used to calculate the macroscopic flow field is erratic; and convergence is extremely difficult to achieve. A second issue in using Brownian dynamics is that most complex flow calculations are performed at relatively low De or involve significant regions of low De . As discussed in Chapter 3, Brownian dynamics is most efficient when the drift term dominates the stochastic force term. In other words, it is difficult to obtain accurate answer for low De calculations by using Brownian dynamics.

Another limitation of CONFFESSIT, as well as other hybrid simulation methods, is the number of degrees of freedom that can be allowed in the molecular model. Although Brownian dynamics is efficient for simulating a Fokker-Planck equation with a large number of degrees of freedom, the large computational overhead has limited the ensemble size of stochastic trajectories and, hence, the accuracy of the method. Therefore, although there is great potential for using CONFFESSIT to study complex flow problems with multi-bead-rod/spring models, most results have been limited to elastic dumbbell models or simplified, one-mode reptation models in CONFFESSIT calculations.

Central to using CONFFESSIT or related algorithms is the treatment of the convection term in the Fokker-Planck equation. Depending on the treatment of this term, CONFFESSIT approaches can be classified as Lagrangian or Eulerian. Qualitatively, the comparison between the Lagrangian and Eulerian method are shown in Figure 4.3. In a Lagrangian method, the location of each molecule is a continuous function, i.e. more than one molecule locating at the same node for the evaluation of the stress at that particular node is unlikely. Therefore, interpolation and tracking of the location of each molecule is necessary. This method is the more intuitive of the two approaches. In an Eulerian method, instead of treating each molecule individually, one utilizes a molecular field concept and

assumes that the stochastic force is acting on the molecular field, instead of on each molecule. Because of this field concept, the spatial variation of the molecular field can be discretized. The principal advantage of this approach is the strong correlation and hence variance reduction that results from the uniform stochastic force on each molecule field.

We next give more detailed description of both methods.

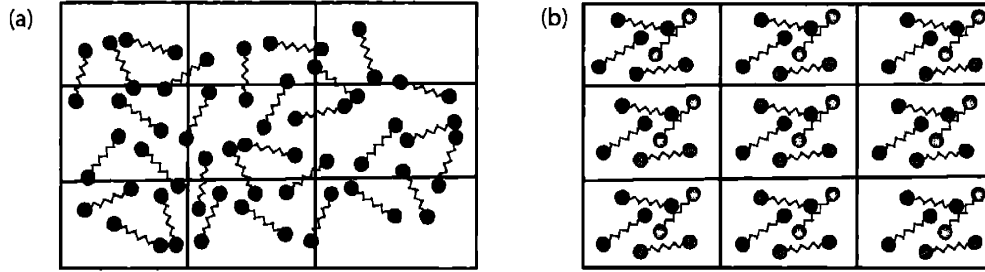


Figure 4.3: Comparison between Lagrangian and Eulerian implementation of multiscale calculation with stochastic simulation. (a) Lagrangian implementation where the location of each molecule is continuous in the computational domain; (b) Eulerian implementation where spatially, highly correlated Brownian force leads to favorable variance reduction.

4.3.1 Lagrangian CONNFESSIT Method

In the original development of CONNFESSIT, the convective term in the Fokker-Planck equation, which dictates the location of the molecule, is converted into an ordinary differential equation that describes the position of the center of mass. The conversion of the convective term results in an ordinary differential equation, because mass diffusion is not included in the Fokker-Planck equation. Hence, the difficult, or computationally intensive, part of this implementation is tracking the location of each molecule. Furthermore, molecules may be concentrated in low shear-rate regions, which leaves a limited number of trajectories in the high shear regions; this will adversely affect the accuracy of the ensemble average in those high shear-rate regions. Nevertheless, many simulations have been performed with this algorithm and various degrees of success have been attained. For example, Cormenzana et al [40] have used this algorithm coupled with a particle tracking

technique for simulating the extrudate-swell problem. Qualitative agreement between the CONNFFESSIT calculation and a continuum calculation was observed.

Keunings and coworkers have developed much-improved algorithms based on various particle-tracking techniques (for details, see Wapperom et al. [224] and references therein). The principal idea of this algorithm is to assume that the center of mass location of all the molecules in a given subensemble evolve in the same manner. As a result, rather than simulate the location of each molecule, the location of each subensemble of molecules is tracked by a single Lagrangian particle. Within each Lagrangian particle, the configuration of each molecule is updated with a standard Brownian-dynamics step. Various algorithms within this framework involve different tracking techniques for the Lagrangian particles.

An interesting, recent development based on the Lagrangian particle tracking method is that of Bell [10] and Jendrejack et al [110]. Instead of tracking the position of Lagrangian particles, they follow the convection of a fixed set of moments and then determine, in a least-squares sense, the configuration of each molecule by matching the moments computed from a convection equation with those obtained from a conventional stochastic simulation. This method is called OSMM (**O**perator-**S**plitting **M**oment **M**atching). This scheme is highly flexible in the sense that the moments, as well as some other variables, may be used for the matching criteria. This scheme is still in its infancy but appears at this point to be a major step forward in the CONNFFESSIT method.

4.3.2 Eulerian CONNFFESSIT method

One of the most successful and commonly used CONNFFESSIT implementations with an Eulerian frame of reference is the Brownian configuration fieldss method [102]. Instead of writing an independent equation for the center of mass, the configuration of the

molecule is treated as a field variable and the stochastic differential equation is rewritten as a partial, stochastic differential equation. As a result, each field equation is simulated with the same sequence of random numbers; hence, a high spatial correlation is achieved. This has proven to be a very successful strategy for variance reduction. The spatial dependence of the partial, stochastic differential equation is discretized in the same manner as a moment equation. SU, SUPG, or DG can all be used to discretize the partial stochastic differential equation. DG has the advantage, relative to the other schemes for the spatial discretization, that the total operation count for solving the DG problem is orders of magnitude less than for either SU or SUPG. As a result, for simulating large problems, a DG formulation is desirable.

A number of interesting applications have appeared based on the Brownian-configuration fields method. In a series of papers, Fan et al [71] have simulated the dynamics of fiber suspensions, including the effects of concentration fluctuations. Somasi and Khomami [202] have extended the Brownian-configuration fields technique to the study of linear stability. The drawback of this approach is that there is no steady state for a Brownian trajectory; therefore, there is no definite base state. Consequently, simulation of the base state and the perturbed state must be performed simultaneously. For a number of simple geometries, these authors demonstrate close agreement with continuum simulation results. Another drawback of this approach is that it is unable to capture the entire spectrum, which is essential in ensuring the accuracy of the simulations in complex flows. They have modified this technique by including an intermediate Arnoldi step. By using this approach, the entire eigenspectrum can be captured, and the leading eigenvalues can be obtained in significantly less CPU time [203].

4.4 Hybrid Simulations using Direct Solution of the Fokker-Planck

Equation

Although CONNFFESSIT calculations have been the dominant method for hybrid simulations, the weak convergence rate of stochastic simulations and the requirement of very large ensembles to obtain an accurate solution at low De have prompted developments in coupling direct solution of the Fokker-Planck equation with the finite element method for computing complex flows with molecular models that have a small number of degrees of freedom. Most of these simulations have focused on the dilute, multibead-rod model [69, 161] and the Doi model for monodomain liquid crystalline polymers [161]. Fan [69] studied pressure-driven channel flow for a multibead-rod model; he used the boundary-element method to discretize the physical space and the Galerkin method with spherical harmonic basis functions for the configuration space. Although the flow he considered is one dimensional, both the innovative idea and the computational difficulty at that time made this calculation both numerically challenging and fundamentally important.

Nayak [161] was the first to simulate the dynamics of the rigid dumbbell model and the Doi model in a complex flow environment. As for the CONNFFESSIT method, treatment of the convection operator is the major challenge. Nayak used DG to discretize spatially the Fokker-Planck equation and used wavelet analysis to discretize the configurational space. The coupling of DG basis functions and Daubechies scaling functions results in a different stiffness matrix for each element. Because the basis functions in a finite-element analysis are functions of the spatial coordinates, the mass or the stiffness matrix of each element is spatially dependent, and a different stiffness matrix has to be formed or stored for each element. This adversely affects the efficiency of the calculation. Finite element analysis commonly uses conforming elements to overcome this problem. As a result, the dependence on spatial coordinates is condensed into the Jacobian that

transforms the integral from the reference-element (or local) coordinates to the global spatial coordinates. If the Jacobian is independent of the local coordinates, then it may be factored from the stiffness matrix, with the result that the stiffness matrices for each element differ from one another by only a constant. Nayak employed this strategy. In particular, she used triangular elements and restricted the problems studied to planar geometries.

An alternative strategy that could maintain or even improve the computational efficiency is the use of node-by-node decomposition. This strategy is first developed in this work. The key to this strategy is exploiting the property that the basis functions in a coupled calculation are tensorial products between the basis functions in the physical space and those in the configuration space, i.e. $\{\Phi\} = \{\Psi^{\text{FE}}\} \otimes \{\varphi^{\text{Wv}}\}$.

To see this, consider an entry in the mass matrix,

$$\begin{aligned} M_{\mu\nu} &\equiv \int \Phi_\mu \Phi_\nu d\Omega \\ &= \iint (\Psi_i^{\text{FE}} \varphi_m^{\text{Wv}})_{\mu = \mu(i, m)} (\Psi_j^{\text{FE}} \varphi_n^{\text{Wv}})_{\nu = \nu(j, n)} d\Omega^{\text{FE}} d\Omega^{\text{Wv}} \end{aligned} \quad (4.33)$$

where $\mu(i, m)$ is the mapping from the i -th basis function in Ω^{FE} and m -th basis function in Ω^{Wv} to the μ -th basis function. By factoring out the integration over Ω^{FE} from that Ω^{Wv} , the stiffness matrix for a quadrilateral element can be represented as :

$$\begin{bmatrix} S_{11}^\tau & S_{12}^\tau & S_{13}^\tau & S_{14}^\tau \\ S_{21}^\tau & S_{22}^\tau & S_{23}^\tau & S_{24}^\tau \\ S_{31}^\tau & S_{32}^\tau & S_{33}^\tau & S_{34}^\tau \\ S_{41}^\tau & S_{42}^\tau & S_{43}^\tau & S_{44}^\tau \end{bmatrix} \quad (4.34)$$

where $S_{ij}^\tau \equiv (\int \Psi_i \Psi_j d\Omega^{\text{FE}})(\int \phi_m \phi_n d\Omega^{\text{Wv}})$. We first apply the inverse of the mass matrix (M^{-1}) in Ω^{FE} to Eqn 4.34 and then solve each stiffness matrix in Ω^{Wv} independently. This method can be schematically shown as,

$$\begin{bmatrix} S_{11}^\tau & S_{12}^\tau & S_{13}^\tau & S_{14}^\tau \\ S_{21}^\tau & S_{22}^\tau & S_{23}^\tau & S_{24}^\tau \\ S_{31}^\tau & S_{32}^\tau & S_{33}^\tau & S_{34}^\tau \\ S_{41}^\tau & S_{42}^\tau & S_{43}^\tau & S_{44}^\tau \end{bmatrix} \rightarrow \begin{bmatrix} M_{1j}^{-1} S_{j1}^\tau & 0 & 0 & 0 \\ 0 & M_{2j}^{-1} S_{j2}^\tau & 0 & 0 \\ 0 & 0 & M_{3j}^{-1} S_{j3}^\tau & 0 \\ 0 & 0 & 0 & M_{4j}^{-1} S_{j4}^\tau \end{bmatrix} \rightarrow \begin{bmatrix} I & 0 & 0 & 0 \\ 0 & I & 0 & 0 \\ 0 & 0 & I & 0 \\ 0 & 0 & 0 & I \end{bmatrix} \quad (4.35)$$

The mass matrix in Ω^{FE} is of dimension three (for triangular elements) and four (for quadrilateral elements) and therefore can be easily stored or even computed at each time step for each element. Hence this strategy allows us to use or study a large variety of meshes and problems where the Jacobian in the mass matrix in Ω^{2D} is different from element-to-element. Some of the applications of this method include the use of quadrilateral elements and the study of axisymmetric flow geometries.

4.5 Use of Distributed Computing Environment for Multiscale Simulation

As the number of equations (for example equation of energy and equations for the elliptic mapping in a free-surface flow) and the number of degrees-of-freedom in a multi-scale simulation increases dramatically with respect to the complexity of the problem and the realism of the molecular model used in the calculation, the utilization of parallel computing or a distributed computing environment is inevitably required and necessary. Both economic considerations and easy administration have driven the model of a parallel computer to a cluster of computers joined by a fast intercommunication network. Here, the obvious bottle-necks of a calculation are the memory available to each processor and the speed of intercommunication. Another constraint comes from the limitation of using Fortran on 32-bit processor machines. Because Fortran (g77 for example) calculates all sizes

of objects in bits, on 32-bit targets the size of a double precision array is limited to $2^{32}/64 - 1 \sim 6.7 \cdot 10^7$ elements.

A parallel computing strategy for multiscale calculation consists of two parts: the computation of the ν - p - $\mathbf{G}$ problem and the microstructure calculation. For most continuum calculations with moment equations, the time-consuming step is the solution of the ν - p - $\mathbf{G}$ problem. The development of a fast iterative solver for the ν - p - $\mathbf{G}$ problem depends on the discovery of preconditioner that captures the essential characteristics of the underlying problem. One of the most successful preconditioners was developed by Caola et al. [33]. Their preconditioner is based on the separate treatment of the pressure unknowns from the velocity and velocity gradient variables. A pressure preconditioner is constructed from a factor of the Schur complement of the pressure by using a Jacobi iteration and the viscous operator is treated by using the additive Schwarz method.

For multiscale calculation with either stochastic methods or deterministic methods, most studies show that the microstructure calculation is the most computationally intensive. A successful distributed computing strategy for a multiscale simulation requires careful consideration of domain decomposition. Whereas typical domain decomposition corresponds to dividing of the physical domain into portions, some strategies of multiscale simulation allows domain decomposition in the configuration space. In a stochastic simulation, domain decomposition in configuration space corresponds to the separation of a large ensemble into subensembles and allows each processor to simulate each subensemble separately. Because the only interesting quantity is the stress tensor for the calculation of the velocity field, only the partial sums of the stress tensor are necessary for cross network communication, and nearly ideal performance can be expected. One of the key concerns or issues is to ensure that the random number sequence used in the calculation is

different for each processor. This can be done by randomly shuffling the seed for the random number generator.

In a multiscale calculation with a deterministic method such as the wavelet-Galerkin method, domain decomposition in the configuration space does not seem to be feasible, because the whole distribution function is needed to evaluate the right hand side of the diffusion equation. In addition the mass matrix may not be the identity matrix. One exception is the simulation of reptation models with the independent alignment approximation (Chapters 8 and 9), where each discrete Fourier mode of the reptation model is independent, and domain decomposition in the configuration space is possible. Fortunately, the number of variables used to represent a distribution function is normally much less than the number of trajectories in a stochastic simulation. Therefore, domain decomposition in the physical space does not necessarily induce an excessive communication, which would significantly degrade the parallel efficiency. This domain decomposition is different from the typical domain decomposition in the solution of a linear algebra problem and only requires division into non-overlapping domains with minimum edges between each domain. While elegant theory and algorithms for the min-max boundary domain decomposition have been derived [118], a simple domain decomposition may involve grouping elements according to the order in the sorted list in a topological sort.

Chapter 5

Survey of rheological modeling of liquid crystalline polymers and polymer melts

5.1 Introduction

In this thesis, two complex fluid systems will be studied: liquid crystalline polymers and a system of entangled polymer chains in a concentrated polymer solution or melt. The reliability and accuracy of a simulation in describing the dynamics and rheology of these complex fluid systems depends on the precise and detailed modeling the stress-strain relationships for the underlying complex fluid system used to describe and predict the nonlinear viscoelastic and rheological properties. Although closed models such as the K-BKZ equation (for entangled polymer systems) and Leslie-Ericksen model (for liquid crystals) have been widely used in commercial and research software, their degree of success is limited because of the lack of physical connections to the molecular level. For example, Feng et al. [78] used the Leslie-Ericksen model in a shear flow to predict the roll cell formation in a shear flow. Although both disclination and roll cell formations are observed, the strength of the disclinations are too strong to be applicable for liquid crystalline polymers. This emphasizes the importance of using molecular-based models for realistic modeling of complex fluid systems. The goal of this chapter is to provide and extend essential background on the molecular theory used to model these two systems. Some of these molecular theories will then be studied in detail through simulation of the viscoelastic flow behavior of these models in subsequent chapters.

For liquid crystalline polymers, while the Doi model [58] describes the rheological properties of a monodomain liquid crystalline polymers, it fails to address the inhomogeneous nature of liquid crystalline polymers and hence is not capable of predicting impor-

tant structures such as disclination and defects. Various attempts have been made to extend the Doi model to include inhomogeneous effects. Most of these efforts focus only on either the mean-field intermolecular potential or the stress tensor expression. One of the goals of this chapter is to derive a self-consistent diffusion equation and the stress tensor expression for an inhomogeneous liquid crystalline polymer system by modeling the liquid crystalline polymer molecules as rigid dumbbells. The resulting kinetic theory model is derived based on the kinetic theory described in Chapter 2. Various approximations to derive approximations to the full model are described. Furthermore, a linear stability analysis is used to study the initial behavior of spinodal decomposition from an isotropic system to study the behavior of the exact model with the various approximations to the model.

For concentrated polymer solutions and melts, the reptation model has been the dominant theory used to describe the complex entanglement interactions between polymer chains. Since the emergence of the Doi and Edwards model for describing the nonlinear rheology, various non-reptative mechanisms such as constraint release, chain stretching, and alignment coupling have been explored to improve the capability of the reptation model to describe and predict the experimental data of nonlinear rheology. The vast amount of literature with inconsistent notation makes understanding and utilizing these advances difficult. It is one of the goals of this chapter to summarize and “unify” some of these advances by first presenting the ideas behind these nonreptative relaxation mechanisms and then describing the mathematical representation of the physics based on the constitutive equation or the diffusion equation.

5.2 Kinetic theory for liquid crystalline polymers

5.2.1 Model description

A solution of rod-like polymers is modelled as a suspension of rigid dumbbells in a Newtonian solvent of viscosity η_s . The polymer number density is n . This model accounts for the ability of the polymer molecules to orient in the flow and ignores the stretching and bending motions that are of minor importance in determining the rheological properties of such solutions. Each dumbbell consists of two point beads of equal mass m , connected by a massless rod of length ℓ . The configuration of the rigid dumbbell is set by the center-of-mass vector $\mathbf{r}$ and the unit vector $\mathbf{u}$ which points from bead $\nu = -1$ to bead $\nu = 1$ (Figure 5.1).

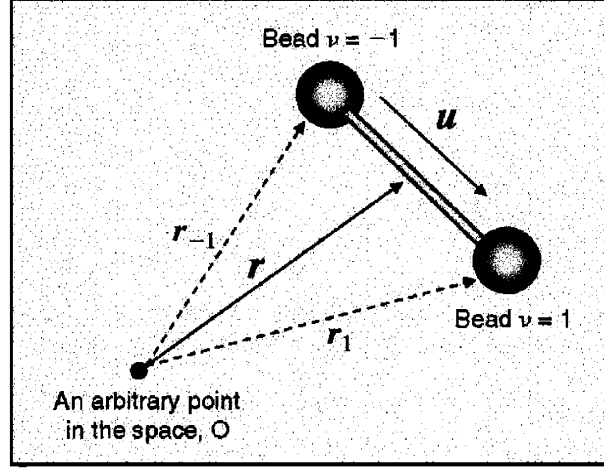


Figure 5.1: The rigid dumbbell model

Following the development in Bird *et al.*[20] and the extension to nonhomogeneous systems in Bhave *et al.*[13], the governing equations are derived starting from the full phase-space distribution function f . However, the final equations are given in terms of averages involving a contracted description of the configurational distribution function $f(\mathbf{r}, \mathbf{u}, t)$. The normalized velocity distribution is taken to be Maxwellian about the mass-average velocity $\mathbf{v}$ at the center of mass of the dumbbell. When the dumbbells are randomly distributed and all orientations are equally probable, the isotropic configurational distribution function is

$$f_{p,iso} = \frac{n}{4\pi} \quad (5.1)$$

where n_{av} is the average number density of polymer. The local number density $n(\mathbf{r}, t)$ is defined as

$$\int f_p(\mathbf{r}, \mathbf{u}, t) d\mathbf{u} = n \quad (5.2)$$

where the integral denotes integration over the surface of the unit sphere. Notice that the definition for the number density is different from the mass density. Whereas the number

density counts the number of molecules in a given region, the mass density counts the number of *beads* within that given region (c.f. Eqn. 2.47).

Average properties for the system are defined in terms of the distribution functions. A particularly useful average property for rigid rod-like polymers is the orientational order tensor or the structure tensor S , which is defined as

$$S = \frac{1}{n} \langle uu - \frac{1}{3} \delta \rangle = \frac{1}{n} \int \left(uu - \frac{1}{3} \delta \right) f(\mathbf{r}, \mathbf{u}, t) d\mathbf{u} \quad (5.3)$$

where $\langle . \rangle$ is an integral over all internal coordinates. The structure tensor S defined in Equation 5.3 is the nonhomogeneous analog of the structure tensor used in the homogeneous theories for liquid crystalline polymers [15,58].

5.2.2 The intermolecular potential

The development of orientational order with increasing concentration in liquid crystalline systems consisting of molecules with rigid backbones is a consequence of the excluded volume interaction between these molecules. A proper description of these intermolecular forces is crucial to the development of any model for the liquid crystalline material.

The earliest theory of the isotropic-nematic phase transition was developed by Onsager [164]. The theory incorporates pairwise *excluded volume* interactions between rigid rods and results in a transition from a disordered phase to an ordered phase with increasing concentration. A formal statistical mechanical development of this theory models the liquid crystalline polymer system as a “multicomponent” mixture of rigid, elongated molecules with each “component” corresponds to molecules with an specific orientation, $\mathbf{u}$. The resulting Helmholtz free energy for this multicomponent system is written as

$$\frac{\beta A}{N} = \ln c \Lambda^3 - 1 + \int f(\mathbf{u}) \ln 4\pi f(\mathbf{u}) d\mathbf{u} + \sum_{n=2}^{\infty} \frac{B_n}{n-1} c^{n-1} \quad (5.4)$$

where the first term on the right hand side is the ideal contribution to the free energy and Λ is the de Broglie thermal wavelength. The second term is the ideal entropy of mixing for different orientations. The last term is the nonideal contribution to the free energy due to the intermolecular interaction where B_n is the n -th order coefficient in the virial expansion.

For any given potential, an n -th order virial coefficient can be derived rigorously by using the Mayer-Mayer expansion. For example, the second virial coefficient, B_2 , is

$$B_2 = \int \int f(\mathbf{u}) f(\mathbf{w}) \hat{B}_2(\mathbf{u}, \mathbf{w}) d\mathbf{u} d\mathbf{w} \quad (5.5)$$

where $\mathbf{w}$ is a dummy variable and $\hat{B}_2$ is defined as

$$\hat{B}_2(\mathbf{u}, \mathbf{w}) \equiv -\frac{1}{2} \int [\exp(-\beta \Phi(\mathbf{r}_{12}, \mathbf{u}, \mathbf{w})) - 1] d\mathbf{r}_{12} \quad (5.6)$$

and $\Phi(\mathbf{r}_{12}, \mathbf{u}, \mathbf{w})$ is the orientation dependent intermolecular potential for a pair of molecules. For the hard core potential, $\Phi(\mathbf{r}_{12}, \mathbf{u}, \mathbf{w})$ is equal to infinity if the two molecules overlap and is 0 otherwise. Solving for $\hat{B}_2(\mathbf{u}, \mathbf{w})$ is identical to computing the overlapping volume between two molecules with specific orientations of $\mathbf{u}$ and $\mathbf{w}$, respectively. The overlapping volume, however, is difficult to calculate except in the limit of an *infinitely* long and thin rod or for an ellipsoid with an *infinite* aspect ratio ($\ell/d \rightarrow \infty$). In these limits, $\hat{B}_2(\mathbf{u}, \mathbf{w})$ for two adjacent molecules is

$$\hat{B}_2(\mathbf{u}, \mathbf{w}) = 2b\ell^2 \sin(\mathbf{u}, \mathbf{w}) \quad (5.7)$$

where $\sin(\mathbf{u}, \mathbf{w})$ is the sine of the positive angle between $\mathbf{u}$ and $\mathbf{w}$. Furthermore, in the limit of infinite aspect ratio and infinite dilution, it has been proven that only the second virial coefficient contributes significantly to the Helmholtz free energy [164]. As a result, the excess Helmholtz free energy of the liquid crystalline system is

$$\frac{\beta A^{\text{Ex}}}{N} = c d \ell^2 \int f(\mathbf{u}) \int f(\mathbf{w}) \sin(\mathbf{u}, \mathbf{w}) d\mathbf{w} d\mathbf{u} \quad (5.8)$$

where $\beta = 1/kT$.

The mean-field intermolecular potential between different liquid crystal polymer molecules is defined as the functional derivative of the excess Helmholtz free energy of the system as

$$\beta \Phi(\mathbf{u}) = \frac{\delta \beta A^{\text{Ex}}}{\delta f} = 2 c b \ell^2 \int f(\mathbf{w}) \sin(\mathbf{u}, \mathbf{w}) d\mathbf{w} \quad (5.9)$$

The prefactor $2 c b \ell^2$ is interpreted as the potential strength U . Equation 5.9 is the original Onsager potential. A major assumption in the development of the Onsager potential is that the solution is sufficiently dilute that only a second virial coefficient is required, and hence the theory is valid *only at infinite* dilution [97]. This contrasts with the object of the Doi model, that is, a concentrated liquid crystalline polymer solution or melt.

To extend Onsager's theory to inhomogeneous solution, we consider finite separations $\mathbf{r}_{12}$. Then, the interaction potential becomes

$$\beta \Phi(\mathbf{u}) = \frac{\delta \beta A^{\text{Ex}}}{\delta f} = 2 c b \ell^2 \int f(\mathbf{r}_2, \mathbf{w}) \sin(\mathbf{u}, \mathbf{w}) d\mathbf{w} d\mathbf{r}_2 \quad (5.10)$$

According to Straley, the distance between the two molecules $\mathbf{r}_{12} \equiv \mathbf{r}_2 - \mathbf{r}_1$ described as rigid rods can be expressed in terms of oblique coordinates along the molecule. Then, the position vector $\mathbf{r}_2$ becomes:

$$\mathbf{r}_2 = \mathbf{r}_1 + \xi \mathbf{u} + \eta \mathbf{w} + \zeta \frac{\mathbf{u} \times \mathbf{w}}{|\mathbf{u} \times \mathbf{w}|} \quad (5.11)$$

where ξ , η , and ζ are the oblique coordinate variables and the Jacobian transformation is given by $d\mathbf{r}_2 = |\mathbf{u} \times \mathbf{w}| d\xi d\eta d\zeta$; the overlapping criteria for two rods is $|\xi| < \ell/2$,

$|\eta| < \ell/2$ and $|\zeta| < b$. Combining Straley's oblique coordinates in Eq. 5.11 with Eq 5.10 shows that the only nonzero contribution to the mean field excluded volume potential is

$$\beta\Phi(\mathbf{r}, \mathbf{u}) = \int_{-\ell/2-\ell/2-b}^{\ell/2} \int_{-\ell/2}^{\ell/2} \int_b^b \int f\left(\mathbf{r} + \xi\mathbf{u} + \eta\mathbf{u}' + \zeta\frac{\mathbf{u} \times \mathbf{w}}{|\mathbf{u} \times \mathbf{w}|}, \mathbf{w}, t\right) |\mathbf{u} \times \mathbf{w}| d\zeta d\eta d\xi d\mathbf{w} \quad (5.12)$$

This intermolecular potential expression has shown to be consistent with the experimental data for Frank elasticity [206]. By implicitly assuming that the spatial variation of f is condensed onto a director field $\mathbf{n}(\mathbf{r})$, the distribution function f becomes a function of $\mathbf{u} \cdot \mathbf{n}(\mathbf{r})$. The three Frank elastic constants, K_{11} (splay mode), K_{22} (twist mode), and K_{33} (bend mode) for the rigid rod model become:

$$\beta K_{11} = -\frac{1}{6}n^2\ell^4 d \int \int f(u_x)f(w_x)u_y w_y [u_y^2 + w_y^2] |\mathbf{u} \times \mathbf{w}| d\mathbf{w} d\mathbf{u} \quad (5.13)$$

$$\beta K_{22} = -\frac{1}{6}n^2\ell^4 d \int \int f(u_x)f(w_x)u_y w_y [u_z^2 + w_z^2] |\mathbf{u} \times \mathbf{w}| d\mathbf{w} d\mathbf{u} \quad (5.14)$$

$$\beta K_{33} = -\frac{1}{6}n^2\ell^4 d \int \int f(u_x)f(w_x)u_y w_y [u_x^2 + w_x^2] |\mathbf{u} \times \mathbf{w}| d\mathbf{w} d\mathbf{u} \quad (5.15)$$

Independent of the form of the distribution, $K_{22} = K_{11}/3$. These results compare favorably with a mixture of PBLG and PBDG. This confirms the usefulness of the rigid dumbbell model for modeling liquid crystalline polymer systems.

Ideally, the intermolecular potential expression (Eqn. 5.12) should be directly used in a simulation. However, the distribution function dependence is over a finite physical spatial region and hence is difficult to evaluate. Expanding the distribution function f in Eq. 5.12 in a Taylor series about $\mathbf{r}$ allows us to account for the finite domain of interaction between the test rod $(\mathbf{r}, \mathbf{u})$ and any other rod $(\mathbf{r}', \mathbf{u}')$. If we let $\mathbf{z}$ denote $(\mathbf{u} \times \mathbf{u}')/|\mathbf{u} \times \mathbf{u}'|$, then the expansion is written as:

$$\begin{aligned}
& f_p\left(\mathbf{r} + \xi\mathbf{u} + \eta\mathbf{u}' + \zeta\frac{\mathbf{u} \times \mathbf{u}'}{|\mathbf{u} \times \mathbf{u}'|}, \mathbf{u}', t\right) \\
& = f_p(\mathbf{r}, \mathbf{w}, t) + (\xi\mathbf{u} + \eta\mathbf{w} + \zeta\mathbf{z}) \cdot \frac{\partial}{\partial \mathbf{r}} f_p(\mathbf{r}, \mathbf{u}', t) \\
& + \frac{1}{2}(\xi\mathbf{u} + \eta\mathbf{w} + \zeta\mathbf{z})(\xi\mathbf{u} + \eta\mathbf{w} + \zeta\mathbf{z}) : \frac{\partial}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{r}} f_p(\mathbf{r}, \mathbf{u}', t)
\end{aligned} \tag{5.16}$$

Note that the Taylor series inherently presupposes a gradual variation in the distribution function about the position vector $\mathbf{r}$. Substituting the Taylor series expansion 5.16 into Eq. 5.12 yields on simplification

$$\begin{aligned}
\beta\Phi_2 & = 2b\ell^2 \int |\mathbf{u} \times \mathbf{u}'| f_p(\mathbf{r}, \mathbf{u}', t) d\mathbf{u}' \\
& + \frac{1}{12} b\ell^4 kT \int (\mathbf{u}\mathbf{u} + \mathbf{w}\mathbf{w} + \mathbf{z}\mathbf{z}) : \frac{\partial}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{r}} f_p(\mathbf{r}, \mathbf{u}', t) |\mathbf{u} \times \mathbf{u}'| d\mathbf{u}'
\end{aligned} \tag{5.17}$$

where the subscript “2” in $\beta\Phi_2$ refers to truncation of the hard-rod nature of the potential at the second order. This potential is referred to as the second order potential in subsequent discussion.

Further simplifications involving substituting for the Jacobian of transformation $|\mathbf{u} \times \mathbf{u}'| = \sin(\mathbf{u}, \mathbf{u}')$ in terms of irreducible tensors and neglecting tensors of fourth-rank and higher as well as the constant first term gives the mean-field excluded volume potential as

$$\begin{aligned}
\beta\Phi^{(p)h-r} & = -\frac{3}{2}N\left(\mathbf{u}\mathbf{u} - \frac{1}{3}\delta\right) : \left(\mathbf{u}\mathbf{u} - \frac{1}{3}\delta\right) \\
& - \frac{1}{16}NL^2\nabla\nabla : (\mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u}) : \left(\mathbf{u}\mathbf{u} - \frac{1}{3}\delta\right) \\
& - \frac{1}{16}NL^2\nabla\nabla : \langle\mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u}\rangle : \left(\mathbf{u}\mathbf{u} - \frac{1}{3}\delta\right)
\end{aligned} \tag{5.18}$$

where $N = 2cb\ell^2$; c is a numerical factor of $O(1)$. The gradient terms in Eq. 5.18 account for the finite separation between two intersecting rigid rods and define a range of interaction about the test rod $(\mathbf{r}, \mathbf{u})$ that is roughly $O(\ell)$. In the absence of spatial gradients, i.e.

under conditions of spatial homogeneity, the extended hard-rod potential also reduces to the Maier-Saupe potential used in earlier homogeneous theories. The importance of the gradient terms in the nonhomogeneous theory is discussed later in this section.

Another simplification of Equation 5.12 is proposed by Marrucci and Greco [150]. These authors introduce a finite range of interaction L about a rigid rod and replace the vector $\mathbf{r}_{12}$ by $s\mathbf{u} + L\delta$. In this interpretation, all rods within this finite capsule-like domain are taken to interact equally with the test rod $(\mathbf{r}, \mathbf{u})$, while all rods outside of this region contribute nothing to the hard rod potential. The parameter L is completely arbitrary and may be chosen such that $L \sim \ell$ or $L \gg \ell$. Thus, the mean field intermolecular potential is written as

$$\beta\Phi^{\text{Mar}}(\mathbf{r}, \mathbf{u}) = -\frac{3}{2} \frac{N}{LV} \left(\mathbf{u}\mathbf{u} - \frac{1}{3}\delta \right) : \int_{-L/2}^{L/2} \int_V \left(\mathbf{u}'\mathbf{u}' - \frac{1}{3}\delta \right) f_p(\mathbf{r} + s\mathbf{u} + \mathbf{R}, \mathbf{u}', t) d\mathbf{u}' ds dV \quad (5.19)$$

The form of the potential and the range of interaction for $L \sim \ell$ is similar to Φ_2 , and in this case, no advantage is seen in adopting the form suggested by Marrucci and Greco (1992a). However, if we choose $L \gg \ell$ and neglect the variation of the distribution function over the coordinate s spanning the length of the test rod $(\mathbf{r}, \mathbf{u})$, then, expanding the distribution function f in Eq. 5.19 in a Taylor series about $\mathbf{r}$ yields on simplification

$$\beta\Phi^{\text{Mar}} = -\frac{3}{2} N \left(\mathbf{u}\mathbf{u} - \frac{1}{3}\delta \right) : \left\{ \langle \mathbf{u}\mathbf{u} - \frac{1}{3}\delta \rangle + \frac{1}{24} L^2 \nabla^2 \langle \mathbf{u}\mathbf{u} - \frac{1}{3}\delta \rangle \right\} \quad (5.20)$$

Although this yields a simpler expression as compared with the potential deduced from a second-order truncation, the assumption of $L \gg \ell$ cannot be justified. This is because in order for the Marrucci-Greco potential to predict the same order of magnitude of Frank

elastic constants as in experiments, $L \sim \ell$. Therefore, the potential in Eqn. 5.20 can only be assumed as a postulated potential for numerical convenience.

It is obvious from this section that extension of the homogeneous mean-field intermolecular potential of liquid crystalline polymers to include the effect of inhomogeneity that induces complex disclination structure and defect formation results in spatial gradient terms with the largest order to be ℓ^2 . Therefore, in the development of the diffusion equation and the various flux expressions for the equations of change, it is necessary to develop expansions to higher order in molecular length with consistent truncation in order to obtain a self-consistent set of equations. In the next section, the governing equations are developed with a general potential $\Phi^{(p)}$ and specific forms for this potential are chosen in obtaining subsequent results.

5.2.3 The kinetic theory of liquid crystalline polymers

The governing equations are now derived by using a phase space kinetic theory approach for the rigid dumbbell model described in Chapter 2. The theory accounts for the excluded volume interactions between a pair of rigid dumbbells described by a nonhomogeneous mean-field potential Φ . Specific forms for the potential were described in Section 5.2.2, and expressions for the excluded volume forces between molecules may be derived from these. The rigid dumbbells also experience Brownian forces, standard expressions for which may be obtained from Bird *et al.* (1987) or Bhawe (1992). In addition to the Brownian forces and the excluded volume interactions with the surrounding rigid dumbbells, a rigid dumbbell is also subjected to drag by the surrounding solution. The drag force experienced by each bead of the dumbbell as it moves through the solution is modelled using a Stokes'-law type expression as

$$\mathbf{F}_v^h = -\zeta \cdot (\mathbf{r}_v - \mathbf{v}_v) \quad (5.21)$$

where $\mathbf{v}_v$ is the solution velocity at the position of bead v . Defining a center of mass velocity $\mathbf{v}(\mathbf{r})$, $\mathbf{v}_v$ can be expressed as an expansion in the small parameter ℓ

$$\mathbf{v}_v = \mathbf{v}(\mathbf{r}) + \frac{\ell v}{2} \mathbf{u} \cdot \nabla \mathbf{v} + \frac{1}{2} \left(\frac{\ell v}{2} \right)^2 \mathbf{u} \mathbf{u} : \nabla \nabla \mathbf{v} \quad (5.22)$$

Hydrodynamic interaction is neglected but can be added trivially by modifying the drag coefficient ζ .

In a solution of rigid dumbbells with some degree of orientational order, the resistance to motion in the direction perpendicular to the dumbbell axis is expected to be somewhat higher than that encountered along its axis; therefore, the model for the friction tensor should give friction coefficients that are different in the directions of dumbbell rotation and axial translation. The empiricism for ζ used here is

$$\zeta^{-1} = \frac{1}{\zeta} \mathbf{Z} \equiv \frac{1}{\zeta} [\sigma \delta + (1 - \sigma) \mathbf{u} \mathbf{u}] \quad (5.23)$$

where the anisotropic drag factor σ lies in the range $0 < \sigma \leq 1$ and ζ is a scalar friction coefficient. When $\sigma = 1$, the friction tensor is isotropic with $\zeta = \zeta \delta$ and $\mathbf{Z} = \delta$. Decreasing the value of σ corresponds to increasing the ratio of resistance encountered perpendicular to the dumbbell to that encountered along the axis. The approach adopted here seeks to incorporate the effect of the surrounding medium on the drag experienced by a single rod. It is therefore reasonable to expect that the anisotropic drag factor σ is not a constant, but that it depends on the state of order in the surrounding medium. In literature, the function σ is normally embedded with ζ and kT to form a rotational diffusivity D_r , where $D_r \equiv 2\sigma\zeta/kT$. The two most commonly used expressions for the rotational diffusivity are the orientation dependent rotational diffusivity due to Doi [58], and the self consistently averaged form of Larson [125].

Doi used an angular displacement argument for the Brownian motion and determined the rotational diffusivity dependence on orientation as

$$D_r \sim [(4/\pi) \int \sin(\mathbf{u}, \mathbf{w}) f(\mathbf{w}, t) d\mathbf{w}]^{-2} \sim \sigma \quad (5.24)$$

By using the identity $D_r \equiv 2\sigma\zeta/kT$ introduced above and rewriting the right side of Equation 5.24 in terms of Φ with the help of Equation 5.9, the anisotropic drag coefficient can be written in terms of the intermolecular potential as

$$\sigma = \left(\frac{\Phi(f)}{\Phi(f_{\text{iso}})} \right)^{-2} \quad (5.25)$$

where $\Phi(f)$ corresponds to the mean field potential evaluated by using a distribution f and f_{iso} is the isotropic distribution function, $f_{\text{iso}} = 1/4\pi$. For the Onsager theory, $\Phi(f_{\text{iso}}) = 4U/\pi$.

To simplify the numerical analysis of this model, Larson approximated the orientation-dependent rotational diffusivity by a self consistently averaged rotational diffusivity. This dramatic simplification leads to an *orientation-independent*, self consistently averaged rotational diffusivity, in which the rotational diffusivity depends on the distribution function at the current time t as

$$D_{r, \text{SC}} \sim [(4/\pi) \iint \sin(\mathbf{u}, \mathbf{w}) f(\mathbf{w}, t) f(\mathbf{u}, t) d\mathbf{w} d\mathbf{u}]^{-2} \quad (5.26)$$

The power of -2 that appears in the expression for $D_{r, \text{SC}}$ has been the subject of discussion. Ilg, *et al.* [107] have suggested that the exponent should be unity rather than two based on a derivation that requires no further assumptions or adjustable parameters. For either value of the exponent, the anisotropic drag coefficient is expressed in terms of the excess Helmholtz free energy as

$$\sigma_{r, \text{SC}} = \left(\frac{A^{\text{Ex}}(f)}{A^{\text{Ex}}(f_{\text{iso}})} \right)^{-\alpha} \quad (5.27)$$

where α equals either one or two.

Following the standard procedure described in Chapters 17 and 18 of Bird *et al.* [20] and in Bhawe *et al.* [13], equations of motion can be obtained for rigid dumbbells that are subjected to Brownian, excluded volume, and hydrodynamic drag forces, as described above. Using these, expressions are derived for the governing equations are derived. Thus, the diffusion equation governing the evolution of the distribution function f is

$$\begin{aligned} \frac{\partial f}{\partial t} = & -\nabla \cdot \left(\mathbf{v}f - D_{tr}\mathbf{Z} \cdot \nabla f - \frac{D_{tr}}{kT}\mathbf{Z} \cdot \nabla \Phi f \right) \\ & - \frac{\partial}{\partial \mathbf{u}} \cdot \left[(\boldsymbol{\delta} - \mathbf{u}\mathbf{u}) \left(\sum_{\mathbf{v}} \mathbf{v}\mathbf{v} \right) f - D_r \frac{\partial f}{\partial \mathbf{u}} - D_r \frac{\partial \Phi}{\partial \mathbf{u}} f \right] \end{aligned} \quad (5.28)$$

where D_{tr} is the translational diffusivity and D_r is the rotational diffusivity. The series $\sum_{\mathbf{v}} \mathbf{v}\mathbf{v}$ has to be truncated such that it is consistent with Φ . If the full expression (Eqn. 5.12) is used for Φ , then it may be desirable to keep all the terms in $\sum_{\mathbf{v}} \mathbf{v}\mathbf{v}$. Furthermore, the truncation of Φ in the center of mass evolution should be different from that in the orientation evolution. This is because $D_{tr} \sim \ell^2$ and hence the zeroth order expansion in Φ produces a second order contribution in the translational term. Therefore, for the zeroth order truncation (homogeneous case), the resulting diffusion equation is the same as the Doi model and is given by

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f = -\frac{\partial}{\partial \mathbf{u}} \cdot [\boldsymbol{\kappa} \cdot \mathbf{u} - \boldsymbol{\kappa} : \mathbf{u}\mathbf{u}\mathbf{u}] f + \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\sigma}{6\lambda} \left[\frac{\partial f}{\partial \mathbf{u}} + \frac{\partial \Phi}{\partial \mathbf{u}} f \right] \quad (5.29)$$

The center of mass diffusion is given in terms of the stress tensor by the general kinetic theory. Therefore, knowledge of the stress tensor expression will automatically generate the mass flux expression. Based on the results from the general phase space kinetic theory,

the polymer contribution to the stress tensor can be written in terms of the hydrodynamic force acting on the polymer molecule

$$\tau_p = -\sum_v \int \int_0^1 \frac{v\ell}{2} \mathbf{u} F_v^i f\left(\mathbf{r} - \epsilon \frac{v\ell}{2} \mathbf{u}, \mathbf{u}, t\right) d\epsilon d\mathbf{u} \quad (5.30)$$

For a homogeneous suspension, the distribution function f is expanded and truncated at the zeroth order. For an inhomogeneous suspension, the truncation of the distribution function has to be done such that the resulting stress tensor expression should contain all the terms of the same order. As an example, we consider a second order contribution for the intermolecular potential, i.e. $\Phi = \Phi_0 + \ell^2 \Phi_2$, then the resulting diffusion equation for the distribution function evolution becomes:

$$\begin{aligned} \frac{\partial f}{\partial t} = & -\nabla \cdot \left(\mathbf{v} f - D_{tr} \mathbf{Z} \cdot \nabla f - \frac{D_{tr}}{kT} \mathbf{Z} \cdot \nabla \Phi_0 f \right) \\ & - \frac{\partial}{\partial \mathbf{u}} \cdot [\boldsymbol{\kappa} \cdot \mathbf{u} - \boldsymbol{\kappa} : \mathbf{u} \mathbf{u} \mathbf{u}] f + \frac{\partial}{\partial \mathbf{u}} \cdot D_r \left[\frac{\partial f}{\partial \mathbf{u}} + \frac{\partial \Phi}{\partial \mathbf{u}} f \right] \end{aligned} \quad (5.31)$$

where $\boldsymbol{\kappa}$ is the transpose of the velocity gradient tensor. The normalization condition is then given by $\int \int f(\mathbf{r}, \mathbf{u}, t) d\mathbf{u} d\mathbf{r} = N$, where N is the total number of molecule in the system. The self-consistent stress tensor expression is then given by

$$\begin{aligned} \tau_p = & -3 \langle \mathbf{u} \mathbf{u} - \frac{1}{3} \delta \rangle - 6 \boldsymbol{\kappa} : \langle \mathbf{u} \mathbf{u} \mathbf{u} \mathbf{u} \rangle + \langle \mathbf{u} \frac{\partial \Phi}{\partial \mathbf{u}} \rangle \\ & - \ell^2 \int \left(3 \mathbf{u} \mathbf{u} - \delta + 6 \boldsymbol{\kappa} : \mathbf{u} \mathbf{u} \mathbf{u} \mathbf{u} - \mathbf{u} \frac{\partial \Phi_0}{\partial \mathbf{u}} \right) \mathbf{u} \mathbf{u} : \nabla \nabla f d\mathbf{u} \end{aligned} \quad (5.32)$$

In this expression, the first line is analogous to the homogeneous stress tensor expression with an inhomogeneous molecular potential and the second line corresponds to the stress tensor gradient contribution arises from the extension of the molecule in the space. This stress tensor expression is applicable for the various intermolecular potentials developed in the previous section.

5.2.4 Linear stability analysis around the isotropic state

In this section, a linear stability analysis is used to study the initial behavior of spinodal decomposition from an isotropic system. The purpose of this study is to examine the effects of various truncation methods (Eqns 5.17 and 5.19) for deriving a computationally affordable intermolecular potential and, hence, whether such truncations are appropriate. Bhattacharya have conducted a similar study, but her results are limited by the use of a distribution function that is represented by a linear combination of the zeroth and second order surface spherical harmonics in approximating the Onsager potential. Here we employ a wavelet-Galerkin method to discretize the configuration space; and hence the Onsager potential is evaluated exactly. Translational diffusion effects are included in the simulation.

In the linear stability analysis of spinodal decomposition, the distribution function is perturbed around an isotropic steady state by a prescribed wave vector, $\mathbf{k}$,

$$f(\mathbf{r}, \mathbf{u}, t) = f_0 + \sum_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{u}) e^{-\sigma t} e^{-i(\mathbf{k} \cdot \mathbf{r})} \quad (5.33)$$

The linearized diffusion equation for the distribution function in Eq. 5.33 is

$$\sigma f_{\mathbf{k}} = \left\{ -D_{tr} \mathbf{k} \mathbf{k} : \mathbf{Z} + D_r \frac{\partial^2}{\partial \mathbf{u}^2} \right\} [f_{\mathbf{k}} + f_0 \Phi_{\mathbf{k}}] \quad (5.34)$$

Here D_{tr} and D_r are the translational and rotational diffusion coefficients, respectively. In light of the kinetic theory for rigid dumbbells, the ratio of D_{tr} to D_r is ℓ^2 , where ℓ is the length of the molecule. $\Phi_{\mathbf{k}}$ is the intermolecular potential evaluated with the $\mathbf{k}$ th mode of the distribution function. The Fourier transform of the exact Onsager potential is given by Eq. 5.35

$$\Phi_{\mathbf{k}} = U \int f_{\mathbf{k}}(\mathbf{w}) \sin(\mathbf{u}, \mathbf{w}) \frac{\sin(0.5 \ell \mathbf{k} \cdot \mathbf{u})}{0.5 \ell \mathbf{k} \cdot \mathbf{u}} \frac{\sin(0.5 \ell \mathbf{k} \cdot \mathbf{w})}{0.5 \ell \mathbf{k} \cdot \mathbf{w}} \quad (5.35)$$

in which $U = 2b\ell^2$.

A series of approximate models can be derived from Eq. 5.35 by expanding and collecting the low order coefficients in a Taylor series for the sine function. For example, the second-order expansion of Eq. 5.35 yields

$$\Phi_k = U \int_k(\mathbf{w}) \sin(\mathbf{u}, \mathbf{w}) \left(1 - \frac{\ell^2}{24} \mathbf{k} \mathbf{k} : (\mathbf{u} \mathbf{u} + \mathbf{w} \mathbf{w}) \right) \quad (5.36)$$

Other approximations that have been used include replacing the $\sin(\mathbf{u}, \mathbf{w})$ by the homogeneous, Maier-Saupe potential. If one chooses $\mathbf{k} \mathbf{k} = 0.5k^2 \delta$ and treats ℓ as an interaction parameter, Eq. 5.36 becomes the Marrucci and Greco potential. For comparison purposes, we take ℓ to be the length of molecules, which is consistent with the exact and approximated Onsager potential and guarantees the predicted Frank elastic constants to be of same order of magnitude as experimental data. Higher order approximate models can be obtained in a similar fashion.

The zeroth-order approximation of Eq. 5.36 yields the homogeneous Onsager potential as appears in the Doi model. Without translational diffusion ($D_{tr} = 0$), the dominant eigenvalue is independent of wave number. A positive eigenvalue corresponds to a homogeneous nematic solution, and a negative eigenvalue corresponds to a homogeneous isotropic solution. In a complex flow simulation, the nonuniform velocity gradient causes formation of disclinations. Since the dominant eigenvalues are independent of wave number, there is no mechanism to limit the disclination growth at any wave number. Consequently, the structure or disclinations will grow beyond the spatial resolution of the numerical method, and the simulation fails.

The dispersion relationship for the Onsager potential without approximation is shown in Fig. 5.2. The value of U is 12, and the dimensionless wavenumber is scaled by $\ell/2$. Rotational diffusion is turned off by setting $D_r = 0$. The most dominant wavenumber is

found to be one half, and the structure of the system becomes stable at a wavenumber of two. At a wavenumber of unity, the most dangerous mode changes from a low harmonic to a higher harmonic mode. At high wavenumbers, the dominant growth rate is negative and decays as k^2 .

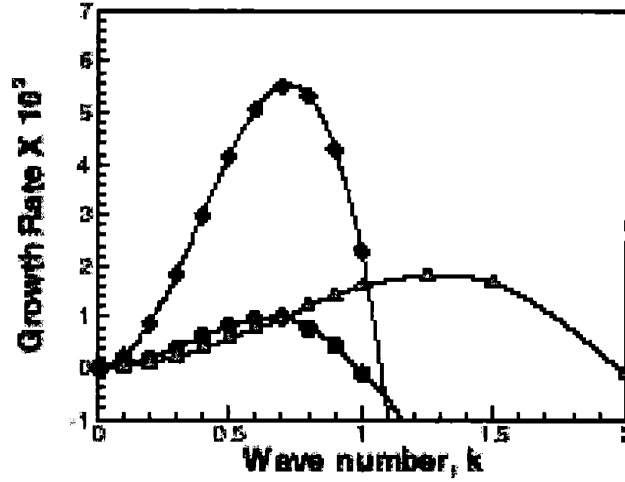


Figure 5.2: Dispersion relationship for the three most dangerous modes for the exact Onsager model with $U = 12$

Two approximate potentials considered in this work are the second-order approximate Onsager model and the Maccurri and Greco potential. The dispersion relationship for the most dangerous mode predicted by each of these models is shown in Fig. 5.3 where they are compared with the exact Onsager potential. For the approximate Onsager potential and for the Maccurri and Greco potential, the value of U is 12 and 6, respectively. At small wave numbers, the dispersion relationships predicted by these three models are qualitatively similar. At large wave numbers, whereas the dominant growth rate for both the exact Onsager potential and the Maccurri and Greco potential decays quadratically, the dominant growth rate for the approximate Onsager potential grows as k^4 . This suggests that at high wavenumbers, the dominant mode of interaction for the exact Onsager potential and the Marrucci-Greco potential is between translation diffusion and the distribution func-

tion. The dominant interaction for the approximate Onsager potential is between translation diffusion and the intermolecular potential. This result suggests that even with an intermolecular potential that would lead to distortional stresses, there is no guarantee that infinite disclination refinement in a flow simulation would not be predicted.

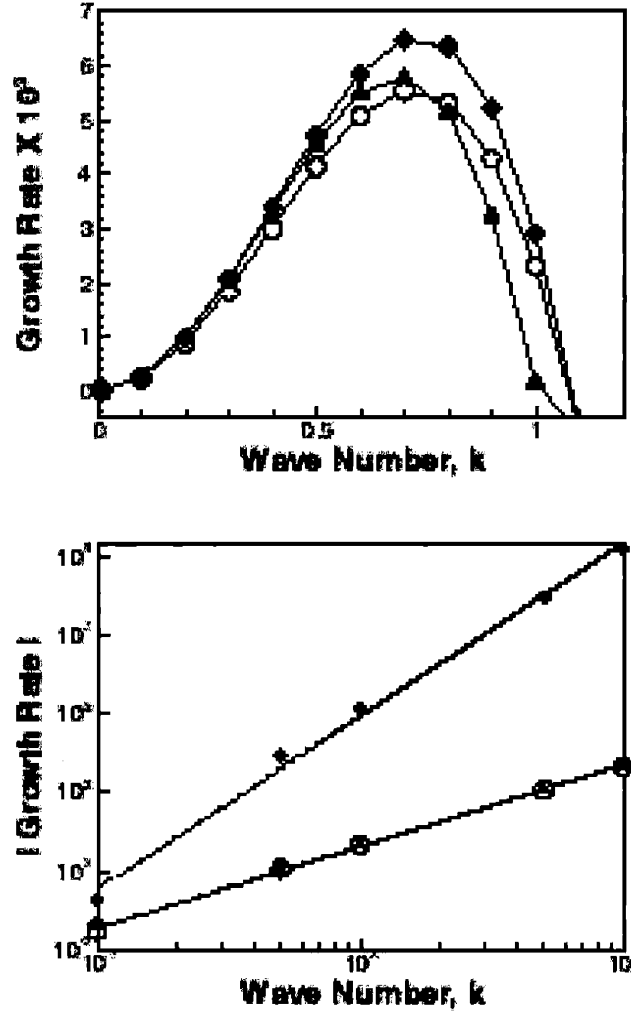


Figure 5.3: Comparison between the dispersion relationship for the second-order approximate model (diamonds), Maccurri and Greco potential (upper triangle), and the exact Onsager model (empty circles) at small (upper figure) and large wavenumbers (lower figure).

Homogeneous molecular models yield unrealistic dispersion relationships in spinodal decomposition. Hence, in viscoelastic flow simulations, polydomain structures form and are refined beyond the resolution of the finite element method. This is consistent with the

observations in Nayak's simulations. Research efforts need to be focused on developing inhomogeneous kinetic theory models and associated numerical methods.

The only inhomogeneous intermolecular potentials with physically reasonable dispersion relationships are the exact hard rod molecular potential and that of Maccurri and Greco. Approximation of the exact hard rod molecular potential by a simple expansion around the local distribution function results in aphysical dispersion relationships.

5.3 Reptation models for concentrated polymer solutions and melts

Modeling of concentrated polymer solutions and melts has long been a challenge for the constitutive modeling of polymer rheology. The main difficulty is due to the large interpenetration or entanglement between polymer chains, and hence most of the nonlinear viscoelasticity is due to the intermolecular rather than intramolecular interaction. Most molecular models nowadays are built on the reptation idea introduced by de Gennes [49]. For a linear chain trapped in a fixed network, he considered the large scale motion of the chain to be limited to the direction of the chain backbone because of the topological constraint imposed by the network that constraints the lateral chain motion over distances larger than the network mesh size. This reptation idea has been used extensively in molecular simulation, as well as in developing constitutive equations for polymer melt rheology.

In this section, we describe the basic ideas and various improvements of using reptation dynamics to describe the complex viscoelastic behavior of entangled polymer chains. Our discussion begins with a presentation of the traditional Doi-Edwards model, followed by the application of kinetic theory described in Chapter 2 to obtain a systematic, self-consistent presentation of the reptation model. Then, the various physical ideas that most researchers believe to be essential for relaxing the various assumptions used in the Doi-Edwards or Curtiss-Bird model will be discussed. Some of the models described in this

section will be subsequently used in Chapters 8 and 9 for simulating the complex flow behavior of concentrated polymer solutions.

5.3.1 Doi-Edwards model with independent alignment

The first comprehensive model for polymer melt rheology with the reptation picture is due to Doi and Edwards [54, 55, 56, 57]. The chains in the entangled melt/solution form a dynamic mesh to mutually constrain their large scale motion. For a given chain, the Doi-Edwards model (DE) assumes that the large scale motion is constrained in a tube-like region surrounding the backbone of a test or probe molecule, and this constraint survives over a time scale of the relaxation of the probe molecule. The modeling effort then focuses on the dynamics of the tube and that of a primitive (or test) chain. By assuming the tube deforms affinely with an imposed flow field and the primitive chain is an inextensible continuous Gaussian chain at equilibrium, the DE model can be represented by a pair of stochastic differential equations,

$$d\mathbf{u} = [\boldsymbol{\kappa} \cdot \mathbf{u} - \boldsymbol{\kappa} : \mathbf{u}\mathbf{u}\mathbf{u}]dt \quad (5.37)$$

$$d\sigma = \sqrt{\frac{2}{\lambda}} dW \quad (5.38)$$

where $\mathbf{u}$ is the orientation of the tube and $\sigma \in [0, 1]$ is a Wiener process that denotes the segment of the chain that is confined by tube with orientation $\mathbf{u}$. $\mathbf{u}$ and σ interact with each other through a boundary condition, where a randomized orientation of $\mathbf{u}$ is assumed at $\sigma = 0$ and $\sigma = 1$. The corresponding diffusion equation to this pair of stochastic equation is given by

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \mathbf{u}} [\boldsymbol{\kappa} \cdot \mathbf{u} - \boldsymbol{\kappa} : \mathbf{u}\mathbf{u}\mathbf{u}]f + \frac{1}{\lambda} \frac{\partial^2 f}{\partial \sigma^2} \quad (5.39)$$

with boundary conditions as

$$f(\mathbf{u}, 0, t) = f(\mathbf{u}, 0, t) = \frac{1}{4\pi} \quad (5.40)$$

Considering the Laplacian operator in σ acting on f and the boundary condition for f , one may decompose the diffusion equation (Eqn. 5.39) by a finite Fourier transform [53]. The resulting diffusion equation for each mode k is given by:

$$\frac{\partial f_k}{\partial t} = 3\boldsymbol{\kappa}:\mathbf{u}\mathbf{u}f_{\text{iso}} - \frac{\partial}{\partial \mathbf{u}}[\boldsymbol{\kappa} \cdot \mathbf{u} - \boldsymbol{\kappa}:\mathbf{u}\mathbf{u}\mathbf{u}]f_k - \frac{(k\pi)^2}{\lambda}f_k \quad (5.41)$$

This decomposition is key for the success of using a fully deterministic method for simulating the reptation model in a complex flow environment. Furthermore, each mode expressed in Equation 5.41 can be solved exactly by using a Green's function formulation and the solution is given by

$$f_k(\mathbf{u}, \sigma, t) = \int_0^t \frac{n \exp(-(n\pi)^2(t-t')/\lambda)}{\lambda(1 + \boldsymbol{\gamma}^{[0]}:\mathbf{u}\mathbf{u})^{3/2}} dt' \quad (5.42)$$

where $\boldsymbol{\gamma}^{[0]}$ is the finite strain tensor defined in Bird, et.al. [19].

The stress tensor is taken directly from “rubber elasticity” and is given by Equation 5.43 with G as a relaxation modulus.

$$\boldsymbol{\tau} = G \int \langle \mathbf{u}\mathbf{u} - \frac{1}{3}\boldsymbol{\delta} \rangle d\sigma \quad (5.43)$$

where $\langle B \rangle \equiv \int B f(\mathbf{u}, \sigma, t) d\mathbf{u}$. Substituting the exact solution for the DE model (Equation 5.42) into the stress tensor expression yields the constitutive equation for the DE model in the form of an integral model.

$$\boldsymbol{\tau} = G \int_{-\infty}^t \left(\frac{d}{dt'} P(t-t') \right) \boldsymbol{Q}(t, t') dt' \quad (5.44)$$

where P is known as the survival probability and is given by

$$P(s) = \sum_{k, \text{ odd}} \frac{8}{(k\pi)^2} \exp\left(- (k\pi)^2 \frac{s}{\lambda}\right) \quad (5.45)$$

and the tensor $\mathbf{Q}$ is given by

$$\mathbf{Q} = 5 \int \left(\frac{\mathbf{u}\mathbf{u}}{4\pi(1 + \gamma^{[0]}:\mathbf{u}\mathbf{u})^{3/2}} \right) d\mathbf{u} \quad (5.46)$$

While the DE model incorporates a number of insightful physical idea, certain aspects and implementations of the model are very vague, and sometimes even self-contradictory. For example, the primitive chain in the DE model is represented by an *inextensible*, continuous Gaussian chain, whereas the stress tensor expression is taken directly from rubber elasticity, which corresponds to an *extensible* Gaussian chain. In addition, the DE model fails to describe the following nonlinear rheological behavior when compared with experimental observations: (1) irreversible effects in a double-step strain experiment with flow reversal; (2) correct amount of shear thinning of the viscosity; (3) overlap of the viscosity for different molecular weights of a given polymer as a single curve in the high shear rate region; (4) overshoot of the shear stress in start-up of steady shear flow at low shear rates; (5) overshoot of the first normal stress difference in the start-up of steady state shear flow at moderate shear rates; (6) shear rate dependence of the stress relaxation rate following cessation of steady shear flow; (7) gradual decrease in the steady state extinction angle; (8) undershoot of the transient extinction angle in the startup of shear flow at high shear rates; (9) immediate undershoot of the transient extinction angle when the shear rate is suddenly decreased after steady state, followed by a higher than measured steady state extinction angle; (9) non-monotonic dependence of uniaxial extensional viscosity on the extension rate.

5.3.2 Application of kinetic theory in modeling reptation dynamics of polymer melts

A comprehensive and systematic approach in implementing the reptation idea into the modeling of polymer melt rheology is proposed by Curtiss, Bird, and coworkers [17, 18, 42, 43, 66, 185, 193]. Their model is generally known as the Curtiss-Bird model (CB). They make use of a phase space kinetic theory described in Chapter 2 and model the macromolecule as a Kramers chain. The notion of reptation motion is described by using an anisotropic friction tensor and postulating the second moment of the momentum space distribution function to describe the hindrance of the sideways motions of the polymers in concentrated systems. A reduced description of the Kramers chain is then obtained by projecting the distribution function of the Kramers chain onto a single link distribution function, that is,

$$f(\mathbf{u}, \sigma, t) = \int \Psi(Q, t) \delta(\mathbf{u} - \mathbf{u}_j) dQ \quad (5.47)$$

where σ is the fractional distance along the chain and $\mathbf{u}$ is the orientation of the polymer segment at σ . Q is the set of generalized coordinate for describing the configuration of the Kramers chain. By making three major assumptions: (a) the short-range-force approximation that neglects all the intermolecular interactions and assumes the polymer system to be athermal; (b) the anisotropic Stokes' law approximation and the anisotropic Brownian motion approximation that accounts for the reptation dynamics of the polymer chain; and (c) the mild curvature approximation that assumes limited change in the orientation of any two adjacent link (i.e. $\mathbf{u}_j \cdot \mathbf{u}_{j+1} \sim O(1)$). This last assumption eliminates all the Rouse matrix in the diffusion equation for the segment connectivity and hence decouples the diffusion equation for the orientation of each link. In principle, this last assumption is similar to the independent alignment assumption in the DE model.

In the pure reptation limit, the diffusion equation for the Curtiss-Bird model is the same as that in the DE model. The stress tensor expression, however, is derived consistently with the three assumptions and can be expressed as follows:

$$\boldsymbol{\tau} = NnkT \int \left(\langle \mathbf{u}\mathbf{u} - \frac{1}{3}\boldsymbol{\delta} \rangle + \epsilon_{\text{hyd}} \lambda \boldsymbol{\kappa} : \langle \sigma(1 - \sigma) \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle \right) d\sigma \quad (5.48)$$

where ϵ_{hyd} is known as the link tension coefficient. This stress tensor expression simplifies to that for the DE model in the limit of $\epsilon_{\text{hyd}} = 0$. The use of a finite link tension coefficient is of both fundamental and practical importance. From a fundamental point of view, the finite ϵ_{hyd} ensures a finite tension along the link; from a practical point of view, the finite ϵ_{hyd} corrects the aphysical shear-thinning viscosity predicted by the DE model. It also contributes to the prediction of the Weissenburg effect, which is not predicted by the DE model [142]. Although the inclusion of a finite link tension coefficient greatly improves the description of the nonlinear rheology, the Curtiss-Bird model does not agree with the stress-optical law. Therefore, numerous modifications and improvements to the reptation models focus on modifying the governing equations of the DE model to capture and extend the successes of the Curtiss-Bird model in describing the rheological dynamics of entangled polymer systems.

5.3.3 Advanced physics and non-repetative relaxation mechanisms

In order to improve the ability of the DE model to capture and predict the complex rheological phenomena of concentrated solutions and polymer melts, many attempts have been made to modify the original DE model. Eventually, it has been realized that some of the deviations between the DE model and experimental observations are due to relaxation processes other than reptation. Thus, a satisfactory theory for flow and relaxation of entangled polymers needs to account for the nonreptative processes. Some of these mechanism include the alignment coupling mechanism (commonly known as the no independent

alignment approximation), constraint release mechanism, chain stretching, and anisotropic tube cross section.

The various “advanced physical concepts” of the reptation model have to be incorporated into a constitutive equation. Most of these attempts generally fall into three categories: (1) modifying the constitutive equation by introducing new variable or by adding new functional forms into G and $P(s)$ in Equation 5.44 [158]; (2) modeling the additional physics through adding or modifying terms in the pair of stochastic differential equations (Equations 5.37 and 5.38) for the Doi-Edwards model [74]; and (3) developing the reptation model by writing down the set of stochastic differential equations for the full chain motion [100]. In this section, some of the non-reptative relaxation mechanisms will be discussed, followed by a presentation of the incorporation of these physical ideas into a constitutive equation through the first and the second approaches.

5.3.3.1 Chain stretching

The idea in chain stretching idea is to replace the micromechanical model in the Curtiss-Bird model (Kramers chain) by a multi-bead-spring model. This idea was first proposed by Marrucci and Grizzuti [146] for predicting steady-state properties. In elongational flows, chain stretching gives rise to an expected upturn (strain-rate hardening) of the elongational viscosity. Surprisingly, the implementation of chain stretching by Marrucci and Grizzuti shows no effect for steady shear flows. In particular, the extended model does not improve the quality of the model prediction for the power-law index of the viscosity. The same type of model with chain stretching was studied by Pearson et al. [172] in transient situations. They found that both the shear stress and the first normal stress difference show overshoots in the startup of steady flows, and the times required to reach these maxima are independent of shear rate. Mead and Leal [156] and Mead, et al. [157] presented a comprehensive study of the DE model by including chain stretching

with a nonlinear finitely extensible spring law. Numerical predictions for steady two-dimensional flows with a continuously variable degree of extensional and shearing character revealed that significant steady state stretch is predicted as the flow becomes increasingly extensional in character.

Although chain stretching corrects some of the failings such as the lack of overshoot in the first normal stress coefficient, it does not solve a long-standing problem in the DE model of the excessive shear thinning of the viscosity at high shear rates. Part of the reason for this short-coming is the inappropriate set of assumptions used to incorporate chain stretching into a single segment theory. In the single segment theory, the chain stretching mechanism is incorporated with certain consistent-averaging and decoupling assumptions. Some of these assumptions smooth out the effect of constraint release due to stretched segments, and therefore the tube segments remain highly oriented in the flow direction and present a very low hydrodynamic resistance that leads to excessive shear thinning. Nevertheless, incorporation of the chain-stretching mechanism through the single-segment theory is essential for a computationally affordable constitutive model for complex flow calculations.

The single segment theory incorporates chain-stretching by introducing a new variable L which is the ratio of the averaged chain contour length to the equilibrium contour length. The equation that describes stretching or relaxation of the chain contour length is postulated to be a balance between a convective contribution and a dissipative contribution. An example of this postulated equation for the chain stretching mechanism is that proposed by Fang et al. [74].

$$\frac{dL}{dt} = \kappa : \langle \mathbf{u}\mathbf{u} \rangle L - \frac{1}{\tau_R} \frac{(1 - 1/L^2)}{(1 - L^2/L_{max}^2)} L \quad (5.49)$$

where τ_R is known as a “Rouse” relaxation time and L_{max} is the ratio of the maximum contour length to the equilibrium contour length. The first term in Equation 5.49 is the convective contribution and the second term is the dissipative contribution. Other postulated equations for chain stretching have been proposed by Pearson et al. [172] and Mead et al. [158]. All these equations share the same feature of convective-dissipative coupling.

5.3.3.2 Constraint release mechanism

Constraint release describes the extra relaxation induced by the relaxation or movement of the neighboring polymer molecules. In the context of the DE model, under fast flow conditions, the polymer molecules are generally aligned parallel to one another, and therefore the constraints or the number of entanglements should drop. This physical picture of the constraint release mechanism corresponds to a change in the postulated expression for the second moment of the momentum space distribution function in the kinetic theory. Two different constraint release mechanisms proposed so far are double reptation (DR) and convective constraint release (CCR).

Double reptation represents the relaxation mechanism for the tube that arises from the motion of the surrounding chains instead of motion of the primitive chain. In terms of kinetic theory this corresponds to the second moment of the momentum space distribution function being a superposition of the expressions for this quantity obtained from the equilibrium in momentum space and reptation approximations [20]. The incorporation of the double reptation leads to a correct mixing rule in the linear regime. Furthermore, it provides a simple mechanism for incorporating the effects of polydispersity which is common in polymer melt systems.

Incorporating the double reptation can be achieved out by introducing a stochastic contribution to the evolution of the tube deformation (Eqn. 5.37). Mathematically this results in second order derivatives with respect to $\mathbf{u}$ in the diffusion equation (Eqn. 5.39)

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \mathbf{u}} \cdot [\boldsymbol{\kappa} \cdot \mathbf{u} - \boldsymbol{\kappa} : \mathbf{u}\mathbf{u}\mathbf{u}]f + \frac{\epsilon_{Br}}{\lambda} \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial f}{\partial \mathbf{u}} + \frac{1}{\lambda} \frac{\partial^2 f}{\partial \sigma^2} \quad (5.50)$$

The stress tensor expression for the double reptation model derived from kinetic theory is

$$\begin{aligned} \frac{\boldsymbol{\tau}_p}{nNkT} = & - \left(\int_0^1 (1 + 3\epsilon_{Br}\sigma(1-\sigma)) \langle \mathbf{u}\mathbf{u} - \frac{1}{3}\boldsymbol{\delta} \rangle d\sigma \right. \\ & \left. + \lambda \epsilon_{Hyd} \boldsymbol{\kappa} : \int_0^1 \sigma(1-\sigma) \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle d\sigma \right) \end{aligned} \quad (5.51)$$

This incorporation of the double reptation effect into the stress tensor expression was suggested [113] to be inconsistent with a thermodynamic formulation of the time evolution equations for nonequilibrium systems developed by Jonschaap. It is hence inconsistent with thermodynamics.

Öttinger incorporated the effects of double reptation into the stress tensor expression through the viscous stress by introducing a new parameter ϵ_2 , which is related to ϵ_{Br} .

$$\begin{aligned} \frac{\boldsymbol{\tau}_p}{nNkT} = & - \left(\int_0^1 \langle \mathbf{u}\mathbf{u} - \frac{1}{3}\boldsymbol{\delta} \rangle d\sigma \right. \\ & \left. + De \mathbf{G}^T : \int_0^1 (\epsilon_{Hyd}\sigma(1-\sigma) + \epsilon_2) \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle d\sigma \right) \end{aligned} \quad (5.52)$$

However, in light of the GENERIC structure developed by Öttinger and Germela [170], Eqn. 5.51 is actually agree with the equation formulation by defining the osmotic pressure (Eqn. 122 of reference [170]) as the elastic stress (the first term in Eqn. 5.51). Hence, whether Eqn. 5.51 is consistent with thermodynamics is still debatable. However, it has been shown that the use of the stress tensor expression Equation 5.52 requires the use of a small value of ϵ_2 (with $\epsilon_{Hyd} = 0$) to achieve a monotonically increasing shear stress. This small value of ϵ_2 ensures better agreement with the stress-optical law as com-

pared with the Curtiss-Bird model or the general double reptation model with stress tensor evaluated by Equation 5.51.

The convective constraint release (CCR) mechanism was proposed by Marrucci [151] and Ianniruberto and Marrucci [105] for renewing the topological constraints on a probe chain through the relative motion among chains due to chain retraction. In kinetic theory terms, CCR can be considered as an attempt to incorporate the effect of molecular extension on the flow behavior into the evolution equation of the momentum space distribution function. In fast flow situations this mechanism enhances the relaxation of the chains and hence prevents the tube segments from becoming highly oriented in the flow direction.

This corresponds to introducing a flow depending ϵ_{Br} into the second order derivative with respect to $\mathbf{u}$ in the kinetic theory diffusion equation. Most implementations of the CCR mechanism, however, involve direct modification of λ in the constitutive equation for the DE model (Eqn. 5.44). This can be done by simply modifying the relaxation modulus $P(s)$, which in turn is the solution of an ordinary differential equation. In the limit of pure reptation, this ordinary differential equation is given by

$$\frac{\partial P}{\partial t} = -\frac{1}{\lambda}P \quad (5.53)$$

Incorporation of the CCR mechanism is then done by modifying λ in Equation 5.53. An example of the modified λ is proposed by Ianniruberto and Marrucci [105] is

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} + \beta \kappa : \langle \mathbf{u} \mathbf{u} \rangle \quad (5.54)$$

where λ_0 is the relaxation time for reptation motion under the absence of CCR, and β is a numerical factor. It should be noticed that the incorporation of CCR through the constitutive equation is fundamentally different from that through the diffusion equation or the pair of stochastic differential equations. This is because the incorporation of CCR through

the constitutive equation essentially modifies the relaxation time for the stochastic process σ , instead of the stochastic process u . As a result, the additional constraint relaxation from CCR actually comes from the relaxation of the primitive chain (*intramolecular* effect) instead of the relaxation of the tube, or the surrounding polymer molecule (*intermolecular* effect).

5.3.3.3 Independent alignment assumption

The independent alignment assumption (IA) arises in the DE model through neglecting the chain connectivity and hence results in a single segment model. Same implication on the resulting diffusion equation can be obtained through the “mild curvature assumption” in the kinetic theory, which leads to a large discrepancy between the model prediction and experimental data in a double step strain with flow reversal. The relaxation of this assumption in the DE model leads to which is sometimes referred to as “rigorous constitutive equation for the reptation model” [59]. In this approach the contour length of the primitive chain changes in response to follow the flow field. This change in contour length relaxes rapidly compared to the reptation process. Relaxing the independent alignment assumption corrects the previous discrepancy with the double step strain experiment. Marrucci [145] and Marrucci and Grizzuti [146] also showed that a reptation model without IA is capable of predicting the Weissenberg effect, which corresponds to a correct ratio between the first and second normal stress difference.

Mathematically, removing the independent alignment assumption a convective term with respect to σ in Equation 5.39 that leads to a coupling between the different modes in Equation 5.41. To conserve probability, a “first order reaction term” must be added to Equation 5.39 and the resulting diffusion equation is:

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \mathbf{u}}[\boldsymbol{\kappa} \cdot \mathbf{u} - \boldsymbol{\kappa} : \mathbf{u} \mathbf{u} \mathbf{u}]f + \frac{1}{\lambda} \frac{\partial^2 f}{\partial \sigma^2} - \frac{\partial}{\partial \sigma}(\boldsymbol{\kappa} : \hat{\boldsymbol{\tau}} f) + \boldsymbol{\kappa} : \bar{\boldsymbol{\tau}} f \quad (5.55)$$

here $\hat{\boldsymbol{\tau}}$ and $\bar{\boldsymbol{\tau}}$ are functions of σ . An example derived by Doi [59] for these two function is that,

$$\hat{\boldsymbol{\tau}} \equiv - \int_{\sigma}^{1/2} \mathbf{u} \mathbf{u} f(\mathbf{u}, s, t) d\mathbf{u} ds \quad \text{for } \sigma \leq 1/2 \quad (5.56)$$

and

$$\hat{\boldsymbol{\tau}} \equiv -\hat{\boldsymbol{\tau}}(1 - \sigma, t) \quad \text{for } \sigma > 1/2 \quad (5.57)$$

$\bar{\boldsymbol{\tau}}$ is then given by $\boldsymbol{\kappa} : \mathbf{u} \mathbf{u}$. Other expressions for $\bar{\boldsymbol{\tau}}$ that depend on the average orientation are possible. A comparison of different expressions for $\bar{\boldsymbol{\tau}}$ within a thermodynamic framework is offered by Beris and Öttinger [12].

A direct consequence of the mathematics of the alignment-coupling is that depending on the functions $\hat{\boldsymbol{\tau}}$ and $\bar{\boldsymbol{\tau}}$, the steady state contracted distribution function for σ may depends on σ . This distribution function $\tilde{f}(\sigma, t)$ is the projection of $f(\mathbf{u}, \sigma, t)$ onto (σ, t) , that is, $\tilde{f}(\sigma, t) = \int f(\mathbf{u}, \sigma, t) d\mathbf{u}$. For the DE model or other models with IA approximation, the governing contracted diffusion equation $\tilde{f}(\sigma, t)$ consists of only a diffusion term and at steady state, $\tilde{f}(\sigma) = C$. The governing diffusion equation for $\tilde{f}(\sigma, t)$ without IA assumption is a convective-diffusive equation with a homogeneous reaction contribution. This type of equation admits solution of $\tilde{f}(\sigma)$ that depends on σ . If $\tilde{f}(\sigma, t)$ is not a constant, then the distribution function gives the “monomer distribution” along the contour length. This provides information about the segment distribution along the tube surrounding the primitive chain.

To incorporate the alignment-coupling mechanism by starting from the constitutive equation of the DE model, one starts with the segmental relaxation modulus $p(\sigma, s)$,

which is related to the relaxation modulus $P(s)$ in through $P(t) = \int_0^1 p(\sigma, t) d\sigma$. The segmental relaxation modulus $p(\sigma, s)$ is the same as the monomer⁰ distribution function $\tilde{f}(\sigma, t)$. In the pure reptation limit, the governing equation for p is

$$\frac{\partial p}{\partial t} = \frac{1}{\lambda} \frac{\partial^2 p}{\partial \sigma^2} \quad (5.58)$$

The alignment-coupling mechanism is added into Eqn. 5.58 by introducing a convective term. The resulting equation is the same as the equation that governs the evolution of $\tilde{f}(\sigma, t)$. As a result, the implementation through the diffusion equation is the same as modifying the relaxation modulus in the constitutive equation.

5.3.3.4 Anisotropic tube cross section

The idea behind the anisotropic tube cross section is the deformation of an initially circular tube cross section into ellipse during flow. This concept is due to different orientations between the primitive chain and the tube surrounds the chain. Hence, the region that can be explored by the primitive chain at a given cross-section becomes elliptical instead of circular. This idea was first introduced by Ianniruberto and Marrucci [105]. They derived the corresponding expression for the stress tensor without a time evolution equation for the tube cross section in flow. An anisotropic tube cross section mainly influences the ratio of normal stress differences in shear flow, which can also be changed by other mechanisms such as removal of the independent alignment assumption.

Since anisotropic tube cross sections does not occur explicitly in the DE model, a new variable has to be introduced to describe this effect. Öttinger included anisotropic tube cross sections by introducing a new vector $\mathbf{Q}$, in addition to the tube orientation $\mathbf{u}$ and σ . He defined $\mathbf{Q}$ as the vector pointing from the centerline to the surface of the tube at the position σ along the primitive chain. Because this effect will not be studied in this thesis,

the details of the governing equation and the stress tensor expression are not be presented here.

Although the various non-reptative mechanism can be incorporated into the DE model through the pair of stochastic differential equations or the constitutive equation and produce decent agreement with experimental data, the theory is more descriptive than predictive for polymer behavior in entangled systems. Furthermore, the single-segment theory provides very limited information regarding the overall polymer configuration. Therefore, a full chain model derived from kinetic theory is desirable. One of such model has been proposed by Hua and Schieber [100]. Their model retains the notion of a polymer chain confined in a tube. The primitive chain is represented by a multibead-spring chain and a multi-segment, Kramers like chain model is used for the tube surrounding the chain. As a result, the overall configuration of the primitive chain is modelled explicitly and the various non-reptative mechanisms described in this section arise naturally from this formulation. However, they neglected the orientation of the elastic spings in the primitive chain and assumed the number of beads in the primitive chain is different from the number of segments in the tube. This leads to a imprecise definition of the segment orientation (defined as the vector from one bead to the other) along the primitive chain. Nevertheless, this full chain model provides an implementation of the reptation and non-reptative relaxation concepts for the prediction of nonlinear rheology of highly entangled polymer systems with a much better description of the primitive chain orientation and the interactions between the intra and intermolecular forces on the motion of the primitive chain.

Chapter 6

A wavelet-Galerkin method for simulating the Doi model with orientation dependent rotational diffusivity

6.1 Introduction

Molecular constituents and their configurations have proven to have significant impact on both the mechanical and transport properties of polymeric and liquid crystalline materials, and much research has recently been focused on combining molecular simulations and traditional fluid mechanics computations to study the transport phenomena of polymeric liquids. The ultimate goal is to optimize process design for achieving desirable product properties. To this end, kinetic theory is used as the primary framework for molecular modeling, because it is computationally more affordable than atomistic simulations of polymeric liquids. A hybrid simulation with kinetic theory models and conventional, continuum transport equations requires solution of the coupled set of the equations of change, the diffusion equation from kinetic theory, and the flux expressions for the macroscopic properties that link the molecular distribution function to macroscopic quantities. For a very limited class of molecular models, the diffusion equation and the flux expressions can be combined and simplified to yield closed-form constitutive equations; examples include the (upper) convected Maxwell model and the (upper) convected Jeffery model (Oldyold-B model). In general, constructing a constitutive equation from a kinetic theory model results in a hierarchy of closure problems. Although much effort has been focused on developing closure approximations, there is in general no guarantee that the resulting closed-form constitutive equations predict the same macroscopic behavior as the unapproximated diffusion equation and flux expressions. Moreover, the availability of robust and accurate hybrid simulation methods would greatly ease the incorporation of improve-

ments in molecular models into macroscopic simulations. Therefore, hybrid simulation algorithms that couple the equations of change and the diffusion equation have become a major research focus.

The most popular hybrid simulation strategy involves solving the equations of change by using the finite element method and simulating the contribution of the macromolecules to the stress tensor by using a Brownian dynamics technique [102, 122–224]. For simulating molecular models with a small number of degrees-of-freedom in a fixed, homogeneous flow field, direct simulation of the diffusion equation by a Galerkin method is more robust and powerful than a Brownian dynamics simulation. Because hybrid simulation algorithms are limited to molecular models with small numbers of degrees-of-freedom, direct simulation of the diffusion equation should show significant advantages over Brownian dynamics approaches for coupling with finite element methods. For a given accuracy, the total number of unknowns needed to represent a distribution function in a Galerkin method is always less than the total number of trajectories required to represent the probability density in a Brownian dynamics simulation. Furthermore, the convergence properties of Galerkin's method are superior to those of stochastic methods. Depending on the basis functions used, the order of convergence in Galerkin's method ranges from unity to exponential convergence, whereas that for a stochastic simulation is $1/2$. That is, doubling the number of trajectories in a stochastic simulation improves the estimate of an output functional by less than 0.5 [25]. Both the smaller number of unknowns and the superior order of convergence relative to Brownian dynamics methods recommend the Galerkin method as a numerical algorithm for low dimensional molecular models.

Critical elements for a successful Galerkin method are the choices of trial functions and a suitable operator splitting algorithm. Spherical harmonics have traditionally been used as the trial functions for simulating the diffusion equation in the polymer kinetic the-

ory for rod-like macromolecules idealized as rigid dumbbell models [204,207]. This choice is motivated by the fact that spherical harmonic functions are eigenfunctions for the Laplacian operator in spherical coordinates. Hence, an expansion in spherical harmonic functions can be optimal for representing the distribution function for the rigid dumbbell model when the associated diffusion equation is diffusion dominated.

In a previous publication [2,161], we simulated the steady state behavior of a dilute suspension of rigid dumbbells in a steady, homogeneous shear flow by solving the diffusion equation with a wavelet expansion. The accuracies of the viscosity and first normal stress coefficient predicted by the wavelet expansion are comparable to those obtained by using spherical harmonics (at low shear rates) or Brownian dynamics (at high shear rates). In this paper, we extend the use of the wavelet-Galerkin method for simulating molecular models to more complex descriptions of polymeric liquids. In particular, we simulate the exact Doi model for a monodomain, lyotropic liquid crystalline polymer solution [58,59].

The Doi model can be considered as a modification of the kinetic theory of dilute solutions of polymers idealized as rigid dumbbells [15]. Molecules of a liquid crystalline polymer system are modeled as a collection of rigid rods or rigid ellipsoids with *infinite* aspect ratio, and the interactions between the rods are described by a mean-field intermolecular interaction potential. This mean field intermolecular interaction potential leads to a nonlinear diffusion equation for the distribution function that is extremely difficult to solve. Much effort has been devoted to simplifying the governing equation of the Doi model so as to make it mathematically more tractable. For example, various modifications to the nonlinear diffusion equation and closure approximations for moment equations of the diffusion equation have been studied [34,35,107]. Much of the progress in developing closure approximations prior to 1995 has been summarized in [34]. Approximations made to the nonlinear diffusion equation in the Doi model include reducing the configuration space

dimensions from two to one, using a self-consistently averaged or constant anisotropic drag coefficient or rotational diffusivity, and replacing the Onsager potential by a separable Maier-Saupe potential.

The most interesting nonlinear dynamics for the Doi model have been found for homogeneous, simple shear flow. The first simulation of a simplified Doi model was presented by Marrucci and Maffettone [148], who assumed that molecules only evolve within the flow plane¹ and derived a one-dimensional² version of the Doi model with a constant, anisotropic drag coefficient and with the intermolecular interaction described by the Maier-Saupe potential. This work provided the first demonstration of time periodic behavior at moderate shear rates and of the suppression of time periodic behavior at high shear rates. Larson [123] used spherical harmonics as basis functions for the distribution function for simulating a simplified Doi model with the Onsager potential and a self-consistently averaged anisotropic drag coefficient in the first two-dimensional numerical simulation of a simplified Doi model. A self-consistently averaged anisotropic drag coefficient was employed, such that the resulting diffusive operator in the diffusion equation is a spherical Laplacian operator with a time-dependent coefficient. In subsequent publications [124,125], the Doi model was shown to be capable of capturing the extraordinary behavior of liquid crystalline polymers, such as various time periodic states and two sign changes of the first normal stress difference as shear rate increases.

Larson and Öttinger [125] have qualitatively studied the effects of initial conditions on the various time-dependent states of the simplified Doi model by using both spherical harmonics and stochastic simulations. Stochastic simulations were further used to simulate

1. The flow plane is defined as the plane formed by the flow direction and the velocity gradient direction.

2. By one dimensional, we refer to the dimension of the configuration space. In their publication, Marrucci and Maffettone refer to the simulation as two-dimensional in reference to the physical space dimensions.

the behavior of the exact Doi model without simplification. However, due to computational limitations, the simulation of the exact Doi model was very inaccurate. A much improved numerical algorithm for Brownian dynamics simulations of the Doi model was proposed by Bell [9,10], in which the stochastic differential equation was decoupled into a linear stochastic differential equation and an interpolate for the mean-field potential. The interpolate was represented with an expansion in spectral polynomials. This reduces the order of computation from N^2 to N , where N is the number of trajectories in the stochastic simulation. In addition to the Doi model with the Onsager potential and self-consistently averaged anisotropic drag coefficient, Bell, *et al.* have simulated the exact Doi model with the Onsager potential and an anisotropic drag coefficient. These authors reported an aperiodic feature in the time-dependent states of the Doi model at high De . A similar feature of the time dependent states has also been observed by Larson and Öttinger [125] and Hua and Schieber [98] by using the order N^2 method, although these authors attributed the aperiodic feature to limited ensemble size (maximum ensemble size was only 10000). Bell, *et al.* employed a much larger ensemble (up to 500000 trajectories) with a smaller time step size (on the order of 0.001), and hence they believed that the aperiodic behavior was real physical feature of the model. However, the aperiodic behavior observed was insensitive to the initial conditions and, hence, failed this classical criterion for chaotic dynamics¹. Furthermore, the Doi model does not fit a standard description of stochastic resonance. Therefore, it is questionable whether the dynamical behavior observed by these authors represents predictions of the nonlinear diffusion equation or simply failure of the Brownian dynamics numerical algorithm to describe the highly anisotropic drift and diffusion terms. We believe the wavelet-Galerkin method can resolve this question.

1. Chaotic dynamics, however, has been observed by various researchers by simulating the Doi model at the parameter window where both nematic and isotropic phase and at a shear rate sufficiently small that periodic doubling occurs within the kayaking state. These conditions are very different from that observed by Bell, *et al.*

The rest of this chapter is organized as follows. A description of the kinetic theory model is presented in Section 6.2 where the Doi model is interpreted based on the diffusion equation derived by Bhawe, *et al.* [15]. This treatment also leads to the natural inclusion of the viscous contribution to the stress tensor and allow a more systematic development and extension of the kinetic theory for liquid crystalline polymers. The numerical method for simulating this kinetic theory model is the focus of Section 6.3. In Section 6.4, the accuracy and convergence of the wavelet-Galerkin method is demonstrated by studying the numerical solution of a nematic state of the equilibrium problem and simulating a time-dependent state during steady-state shear flow. The time-dependent problem involving both a large inter-molecular potential strength U and a large flow strength, De , $(U, De) = (12, 30)$, is specifically chosen for the convergence study, as this facilitates direct comparison between the wavelet-Galerkin simulation results and those from the prior stochastic simulations. The nonlinear dynamics of the exact Doi model is presented in Section 6.5. In particular, the existence of the periodic solution is traced to a supercritical bifurcation at $De = De_{\text{Hopf}}$, which further suggests only periodic solutions occur in the range of De that Bell, *et al.* have investigated. The predictions of the evolution of the distribution function in the various dynamic regions are described in depth. Finally conclusions are offered in Section 6.6.

6.2 Kinetic theory of liquids of rigid rod-like polymers

Molecules of a liquid crystalline polymer solution are traditionally modeled as ellipsoids or cylinders (of length ℓ and diameter d) with a specific intermolecular interaction. In the limit of large aspect ratio, $\ell/d \gg 1$, these micromechanical models can be mathematically represented with the rigid dumbbell model. By assuming that each molecule evolves in a statistically similar manner, the dynamics of a large ensemble of molecules is formulated in the framework of a configuration space or phase space kinetic theory. Fol-

lowing the developments in Bird, *et al.* [20] and Bhawe, *et al.* [15], a governing equation for the evolution of the orientation distribution function is derived based on a projected Liouville equation and a torque balance on a single molecule. The resulting equation is called a diffusion equation and the dimensionless form is

$$\frac{\partial f}{\partial t} = -De \frac{\partial}{\partial \mathbf{u}} \cdot [\boldsymbol{\kappa}^* \cdot \mathbf{u} - \boldsymbol{\kappa}^* : \mathbf{u} \mathbf{u} \mathbf{u}] f + \frac{\partial}{\partial \mathbf{u}} \cdot \sigma \left[\frac{\partial f}{\partial \mathbf{u}} + U \left(\frac{\partial}{\partial \mathbf{u}} \Phi^* \right) f \right] \quad (6.1)$$

The first term on the right side accounts for the effects of hydrodynamic forces on the evolution of the distribution function. The second term is the Brownian motion contribution, and the last term is the contribution due to polymer-polymer interactions. Time is made dimensionless by the relaxation time λ associated with the Brownian motion. The two main dimensionless groups in the diffusion equation are Deborah number (De) and U . De is defined as the ratio of λ to a characteristic flow time. U is normally interpreted as the dimensionless concentration. Alternatively, U can be interpreted as the ratio of the relaxation times associated with intermolecular and Brownian forces. The symbol $\boldsymbol{\kappa}^*$ denotes the transpose of the dimensionless velocity gradient tensor scaled by the flow time scale.

In Eq. 1, the drag on a bead is assumed to be anisotropic as a way to describe the reptation-like movement of the liquid crystalline polymers in a concentrated solution or melt. This anisotropic hydrodynamic drag on the beads is described by a modified Stokes' law in which the drag coefficient is a tensor $\boldsymbol{\zeta}$ rather than a scalar ζ . The tensor $\boldsymbol{\zeta}$ is defined by $\boldsymbol{\zeta}^{-1} = \boldsymbol{\zeta}^{-1} \{ \sigma \boldsymbol{\delta} + (1 - \sigma) \mathbf{u} \mathbf{u} \}$ and the scalar parameter σ accounts for the anisotropy; for $\sigma = 0$, Stokes' law is recovered. The three most commonly used expressions for the anisotropic drag coefficient are the orientation dependent form due to Doi [58] (Eq. 6.2), the self consistently averaged form of Larson [124] (Eq. 6.3), and constant form ($\sigma = \sigma_0$).

$$\sigma_{OD} = \left(\frac{\Phi(f)}{\Phi(f_{iso})} \right)^{-2} = \left[(4/\pi) \int \sin(\mathbf{u}, \mathbf{w}) f(\mathbf{w}, t) d\mathbf{w} \right]^{-2} \quad (6.2)$$

$$\sigma_{\text{sc}} = \left(\frac{A^{\text{Ex}}(f)}{A^{\text{Ex}}(f_{\text{iso}})} \right)^{-2} = [(4/\pi) \iint \sin(\mathbf{u}, \mathbf{w}) f(\mathbf{w}, t) f(\mathbf{u}, t) d\mathbf{w} d\mathbf{u}]^{-2} \quad (6.3)$$

Here, Φ is the intermolecular interaction potential and A^{Ex} is the excess Helmholtz free energy.

Before discussing the form of the intermolecular potential in detail, an important result is obtained from Eq. 6.1, namely a self-consistent solution at equilibrium ($\text{De} = 0$) which is *independent* of the functional form of σ

$$f(\mathbf{u}) = J_{\text{eq}} \exp(-U\Phi^*(\mathbf{u})) \quad (6.4)$$

where J_{eq} is the normalization constant. Equation 6.4 shows that the equilibrium solution of the diffusion equation is independent of σ . Therefore, it is an ideal benchmark for evaluating the accuracy of the wavelet-Galerkin method by comparing the equilibrium solution for an orientation-dependent anisotropic drag coefficient with the calculations by Larson [124] for a self-consistently averaged anisotropic drag coefficient. The simulation results for this benchmark problem are presented in Section 6.4.1.

6.2.1 Intermolecular interaction potential

The most popular intermolecular potentials for describing isotropic-nematic transitions in liquid crystal systems are those derived from the Onsager [164] and the Maier-Saupe [144] theories. Whereas the Onsager theory is based on a *short*-range, hard core intermolecular potential, the Maier-Saupe theory assumes a *long*-range, orientation-dependent attractive intermolecular interaction. Although these two potentials have very different fundamental origins, the functional forms of the resulting potentials are very similar. In fact, Doi and Edwards [59] interpret the Maier-Saupe potential as a linear approximation to the Onsager potential. Below, a brief account of the Onsager mean-field potential is given.

In the Onsager theory, a liquid crystalline polymer system is modeled as a multicomponent mixture in which each component corresponds to a collection of molecules whose orientation is parallel to a specific orientation, $\mathbf{u}$. The resulting Helmholtz free energy A for this multicomponent system can be written as a virial expansion with each virial coefficient derived by using the Mayer-Mayer expansion. By assuming that the underlying micromechanical models are infinitely long, thin rigid rods and that number density of the molecules is small, the Mayer-Mayer expansion is truncated at the second order. By defining the mean-field intermolecular potential between a test molecule of orientation $\mathbf{u}$ and the other liquid crystal polymer molecules as the functional derivative of the excess Helmholtz free energy, the mean-field intermolecular potential is as follows.

$$\Phi(\mathbf{u}) = \frac{\delta \beta A^{\text{Ex}}}{\delta f} = 2nd\ell^2 \int f(\mathbf{w}) \sin(\mathbf{u}, \mathbf{w}) d\mathbf{w} = U \langle \sin(\mathbf{u}, \mathbf{w}) \rangle_{\mathbf{w}} \quad (6.5)$$

The prefactor $2nd\ell^2$ is interpreted as the potential strength U . Equation 6.5 is the original Onsager potential. A major assumption in the development of the Onsager potential is that the solution is sufficiently dilute that only a second virial coefficient is required. It is therefore inappropriate to apply this potential to a concentrated liquid crystalline polymer solution or melt, as treated in the Doi model,

Modification of the Onsager theory is necessary before applying it to the Doi model. Ultimately, higher virial coefficients should be included in the Helmholtz free energy and a new mean-field potential derived. This is possible, but very complicated and computationally intensive. An alternative approach is to use a decoupling approximation by mapping the high-order virial coefficients onto the variation of low-order virial coefficients and the virial coefficients of a reference system. A standard second-order approximation involves mapping high-order virial coefficients onto the second-order virial coefficient. One of the most popular reference systems for computational simplicity is a hard sphere

system of equivalent volume. For this choice the excess Helmholtz free energy can be obtained by summing all the virial coefficients, and the resulting potential strength U is

$$U = \frac{\eta(4-3\eta)3\ell}{(1-\eta)^2 \pi d} \quad (6.6)$$

where η is the packing or volume fraction of the system and is defined as $n\nu_0$ with ν_0 being the molecular volume. For ellipsoids, $\nu_0 = \ell d^2 \pi / 6$. This potential strength is significantly different from that of the second-order virial coefficient expansion. Because the functional dependence of the potential on U does not change for a homogeneous solution, U can be taken as a parameter in the model and should not affect the dynamics of the model. However, for a realistic system in which the polymer concentration is not homogeneous, this expression provides a more accurate estimate of the effect of local concentration on the dynamics of the liquid crystalline polymer molecules than that of the linear representation.

6.2.2 Structure tensor and structure parameters

It is widely assumed in the liquid crystal literature that the birefringence can be related to a structure parameter, which in turn is related to a structure tensor. A commonly used structure tensor is the deviation of the second moment of the distribution function from that of an isotropic distribution, or

$$\mathbf{S} \equiv \langle \mathbf{u}\mathbf{u} \rangle - \frac{1}{3} \delta = \int \mathbf{u}\mathbf{u} (f - f_{\text{iso}}) d\mathbf{u} \quad (6.7)$$

The first expression in Eq. 6.7 is the traditional definition for the structure tensor. In the second expression, the structure tensor is written as the second moment of the deviation of a distribution function from an isotropic distribution function. The unit vector pointing along the major axis of the ellipsoid that characterizes $\mathbf{S}$ is defined as the director $\mathbf{n}$. Mathematically, the director is proportional to the eigenvector of the structure tensor corre-

sponding to the eigenvalue with the largest magnitude. In situations in which the structure tensor is characterized by an oblate structure, the director corresponds to the eigenvector with a unique eigenvalue.

Scalar structure parameters are traditionally defined in terms of either invariants or eigenvalues of the structure tensor. Because the vector $\mathbf{u}$ is a unit vector, $\text{tr}(\mathbf{S})$ is zero. A standard choice is to define two structure parameters based on the two nonzero scalar invariants $\text{tr}(\mathbf{S} \cdot \mathbf{S})$ and $\text{tr}(\mathbf{S} \cdot \mathbf{S} \cdot \mathbf{S})$ such that at equilibrium they have the same magnitude as the eigenvalue with the largest magnitude. These two structure parameters are

$$S_2 = \sqrt{\frac{3}{2} \text{tr}(\mathbf{S} \cdot \mathbf{S})} \quad (6.8)$$

$$S_3 = \sqrt[3]{\frac{9}{2} \text{tr}(\mathbf{S} \cdot \mathbf{S} \cdot \mathbf{S})} \quad (6.9)$$

The structure parameter S_2 varies from 0 to 1 as the liquid crystal structure ranges from isotropic to perfect prolate order, and S_3 ranges from -0.5 to 1 as the structure varies from perfect oblate ordering to perfect prolate ordering. In experiments, a structure parameter is customarily defined as the ensemble average of the second Legendre polynomial with θ defined to be the angle between the molecules and a reference axis. The mathematical form of this structure parameter is identical to $(3/2)S_{33}$.

Because S_2 and S_3 are derived from scalar invariants, they contain no information about the direction of the average molecular orientation. Additional structure parameters are required to represent information about the director orientation. For example, Larson defined a structure parameter as $S_{22} - S_{33}$. At equilibrium, this structure parameter is equal to S_2 if the director points in the x_2 direction; it is equal to $-S_2$ if the director points along the x_3 direction; and it vanishes if the director points along the x_1 direction.

6.3 Numerical methods

The governing equation for the distribution function of the Doi model is a highly nonlinear, integro-differential equation. Linearization methods for the nonlinear operator are required for developing an algorithm for simulation. Whereas most linearizations are based on a Taylor expansion around a fixed point, we approximate the nonlinear operator by rewriting the diffusion equation in the form

$$\frac{\partial f}{\partial t} = D(f, \Xi) \quad (6.10)$$

where

$$\Xi(\mathbf{u}) = \langle \sin(\mathbf{u}, \mathbf{w}) \rangle_{\mathbf{w}} \quad (6.11)$$

Equation 6.10 is subject to periodic boundary conditions and the normalization condition

$$\int f(\mathbf{u}, t) d\mathbf{u} = \int \int f(\theta, \phi, t) \sin \theta d\theta d\phi = 1 \quad (6.12)$$

Although the diffusion equation itself is a conservation equation, we find improved numerical stability when the normalization condition is incorporated explicitly. The reformulation of the diffusion equation allows a decoupled simulation strategy by updating Ξ explicitly and calculating $f(\mathbf{u}, t)$ implicitly. Equation 6.10 can be solved numerically by projecting the equation onto a subspace spanned by a set of test functions, $\{\varphi_i, i=1..N\}$, by using a Galerkin method. The normalization condition for f is implemented with a Lagrange multiplier. Adding the Lagrange multiplier, $\lambda \sin \theta$, gives the final discretized equation set as

$$\begin{bmatrix} M & 0 \\ 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \frac{d\hat{f}}{dt} \\ \frac{d\lambda}{dt} \end{bmatrix} = \begin{bmatrix} \hat{D}(\hat{\Xi}) & SI^T \\ SI & 0 \end{bmatrix} \cdot \begin{bmatrix} \hat{f} \\ \lambda \end{bmatrix} \quad (6.13)$$

where M is the mass matrix, $\hat{D}(\hat{\Xi})$ is the Jacobian of the discrete diffusion equation, and SI is the Jacobian of the discrete normalization equation. Equation 6.13 is a set of differential-algebraic equations (DAE's) that approximates the continuous Doi model. The numerical algorithm is completed by specifying sets of trial and test functions, a temporal discretization algorithm, and a numerical method for solving the linear algebraic problem resulting from both the spatial and temporal discretizations. We first describe the use of wavelet approximations as trial and test functions, followed by discussions of the temporal discretization method and the numerical method for solving the linear algebraic problem.

6.3.1 Trial and test functions

The success of a numerical method depends strongly on the choice of the approximation functions. Typical choices of basis functions include low order, piece-wise continuous polynomials, as used in the finite element method, and spectral polynomials such as spherical harmonics and Chebyshev polynomials. Whereas the piece-wise polynomials are of low order, they have compact support in the physical domain¹. Because of the compact support property, the stiffness matrix resulting from the use of piece-wise polynomials would lead to a sparse matrix structure. Spectral approximations are higher order polynomials and have compact support in the Fourier domain. Furthermore, spectral polynomials are usually eigenfunction of a specific differential operator. Spectral approximations suffer the drawback of possessing global support, which leads to dense stiffness matrices for operators such as $D(f, \hat{\Xi})$ in Eq. 6.10. To approximate accurately the various sharply peaked distribution functions and nonlinear operators requires many basis functions, which in turn increases the computational cost.

1. A function has compact support in a specific space if it is nonzero only over a limited region of that space.

We take an alternative approach. The distribution function is approximated by using the scaling functions in wavelet theory. In particular, we use the scaling functions introduced by Daubechies [48]. These scaling functions are generated by translation and dilation of a single function, known as the mother function, in an independent variable x as

$$\varphi_{j,m}(x) = \varphi(2^j x - m) \quad (6.14)$$

where j denotes the scale of dilation and m corresponds to the translation. Equation 6.14 is generic for all first generation wavelets. For Daubechies wavelets, the mother function φ in Eq. 6.14 is defined *recursively* by a dilation equation

$$\varphi(x) = 2 \sum_{k=1}^N h_0(k) \varphi(2x - k) \quad (6.15)$$

The coefficient in this equation, $h_0(k)$, is known as the k -th filter coefficient of the dilation equation; these coefficients were first derived from filter bank theories in signal processing [209]. The number N of the filter coefficients in Eq. 6.15 is known as the length of the filter coefficient. The wavelets and scaling functions derived from the filter bank theories are considered as the first generation wavelets. New, second generation wavelets do not employ the translation and dilation properties as well as the requirement of a single mother function. This gives flexibility for generating wavelets on manifolds, M -channel wavelets, multi-dimensional wavelets, and many others. Readers are referred to the article by Swelden [215] for more information about second generation wavelets. First generation wavelets, the Daubechies wavelets in particular, are used in this work because of their thoroughly studied and verified mathematical and computational aspects. Daubechies scaling functions have been used for a wide variety of problems such as simulation of Burger's equation [129], Helmholtz equation [176], traffic control models [227], population balance equations [141], and many others. When compared with traditional basis

functions, Daubechies wavelets have the advantage of possessing localization and compact support in *both* the spatial and Fourier domains. This is due to the smoothness of the wavelets and their vanishing polynomial moments. The smoothness of the wavelets leads to the rapid decay at high frequencies in the Fourier domain, and the vanishing polynomial moment property corresponds to the rapid decay at low frequencies in the Fourier domain.

Applying the Daubechies wavelets in simulations requires calculation of the filter coefficients $h_0(k)$, the connection coefficients (inner products of the scaling functions) [129], and definition and extension of the one-dimensional scaling functions to higher dimensions. Most of the computations that employ wavelets make use of the recursive relationship in Eq. 6.15 and formulate the unknowns (such as filter coefficients or connection coefficients) as an eigenvalue problem. These computational approaches for wavelets have been described extensively and various software packages have been written to compute these coefficients. Therefore, we will not repeat a discussion of these methods. Instead, we show some common Daubechies scaling functions and the corresponding power spectrum in Fourier space (Figs. 6.1). One should notice the span across x coordinate as the number of filter coefficients increases. As the length of the filter coefficients increases, the scaling function loses compact support but gains better approximation ability. Therefore, choosing an appropriate length for the filter coefficients is a trade off between the sparsity of the stiffness matrix and the approximation properties of the basis functions. Testing increasingly larger sets of filter coefficients is analogous to studying the convergence behavior of polynomials with increasing order, or p -convergence. The only limitation in choosing the length of the filter coefficient is that the resulting scaling function should not overlap onto itself in the mesh. This limits the length of the filter coefficient to less than or equal to the number of grid points on the mesh. In addition to using

different length filter coefficients, we can also use higher resolution scaling functions by increasing j in Eq. 6.14. This is equivalent to mesh refinement, or h -convergence.

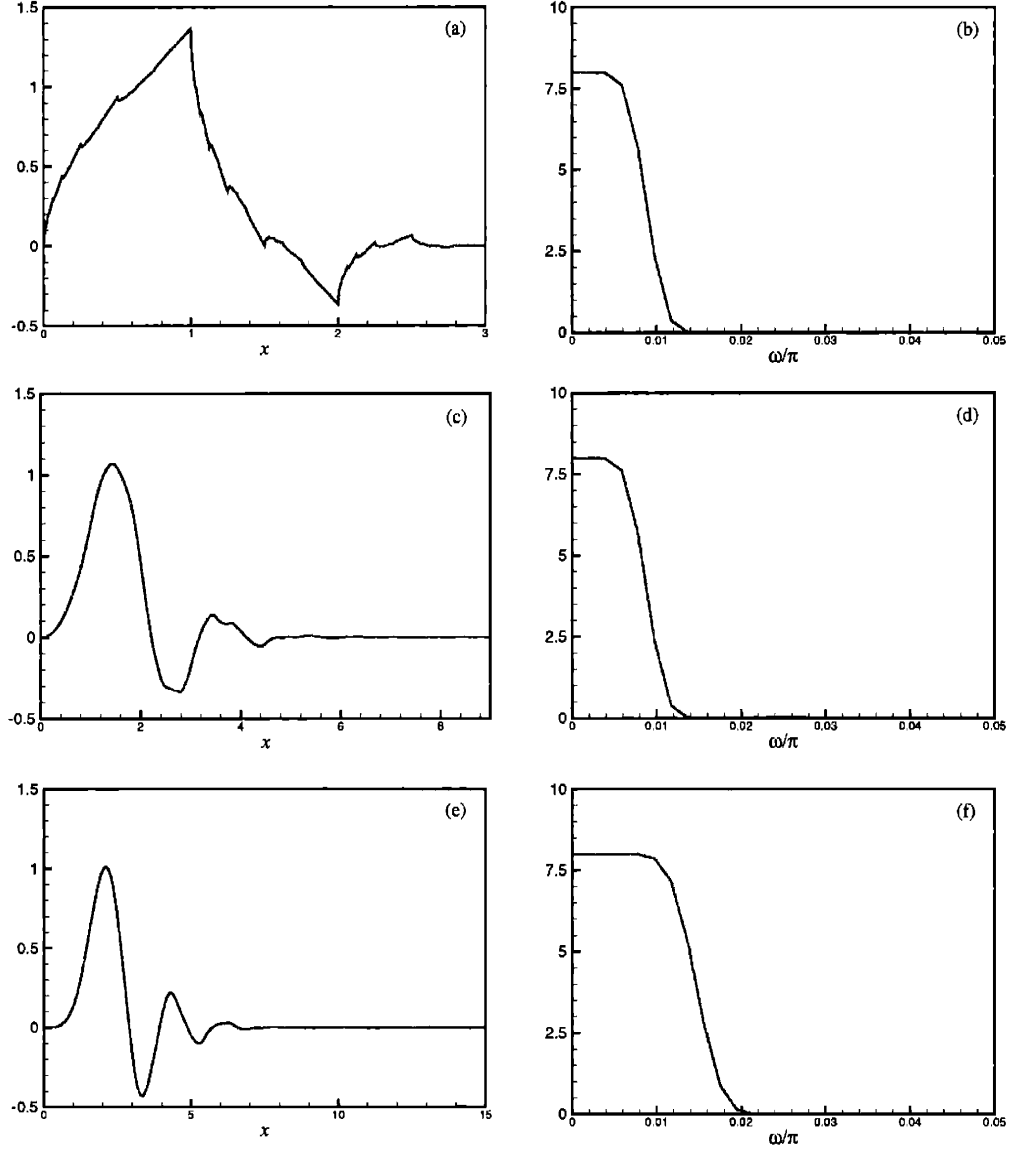


Figure 6.1: Typical Daubechies scaling functions in physical space and their power spectra. (a) First-order Daubechies scaling function with four coefficients in h_0 ; (b) power spectrum of the first-order Daubechies scaling function; (c) fourth-order Daubechies scaling function with 10 coefficients in h_0 ; (d) power spectrum of the fourth-order Daubechies scaling function (e) 7th-order Daubechies scaling function and wavelets with 16 coefficients in h_0 ; (f) power spectrum of the 7th-order Daubechies scaling function.

Extension of the one-dimensional wavelets and scaling functions to higher dimensions can be performed by using dyadic products, i.e. $\Phi(x, y) = \varphi(x)\varphi(y)$. If we use the same

number of basis functions along each dimension, then the dimension of the stiffness matrix for a two-dimensional problem is the square of that of a one-dimensional problem. The computational cost will therefore increase exponentially with the number of degrees of freedom. Hence, alternative multidimensional wavelets, such as spherical wavelets or their variants, have to be explored before adapting wavelets to simulate the diffusion equations with large numbers of internal degrees of freedom.

6.3.2 Time integration method

The wavelet-Galerkin discretization of the diffusion equation gives rise to a large, non-linear DAE set. Because of the normalization condition for the distribution function, the DAE set has index two and requires an implicit time integration scheme for numerical stability. Classical implicit time integration schemes such as Adams-Moulton or implicit Runge-Kutta methods [86] require iterative solution of nonlinear algebraic equations at each time step; solution of these equations at each time step is computationally expensive. Furthermore, the integral operator in the intermolecular potential and in the anisotropic drag coefficient lead to a dense matrix. In order to obtain an efficient simulation strategy, we generalize the linearized time integration scheme of Simo and Arneo [196] and develop a linearly extrapolated time integration scheme for temporal discretization.

The DAE set in Eq. 6.13 has the form

$$\mathbf{M} \cdot \frac{d}{dt} \hat{\mathbf{x}} = \mathbf{A}(\hat{\mathbf{x}}) \cdot \hat{\mathbf{x}} \quad (6.16)$$

For the time interval $[t_n, t_{n+1}] \subset \mathbb{R}$, a one-step time stepping method involves a finite difference approximation to Eq. 6.16 as

$$\mathbf{M} \cdot \frac{\hat{\mathbf{x}}_{n+1} - \hat{\mathbf{x}}_n}{\Delta t} = \mathbf{A}(\hat{\mathbf{x}}^*) \cdot \hat{\mathbf{x}}_{n+\theta} \quad (6.17)$$

where $\hat{\mathbf{x}}_{n+\theta} \equiv \hat{\mathbf{x}}(t_{n+\theta})$, $t_n \leq t_{n+\theta} \leq t_{n+1}$ and $\hat{\mathbf{x}}^*$ is defined later in this Section. The value $\hat{\mathbf{x}}_{n+\theta}$ is defined by the interpolation formula

$$\hat{\mathbf{x}}_{n+\theta} = \theta \hat{\mathbf{x}}_{n+1} + (1 - \theta) \hat{\mathbf{x}}_n \quad (6.18)$$

where $\theta \in [0,1]$. If $\hat{\mathbf{x}}^* = \hat{\mathbf{x}}_{n+\theta}$, this algorithm corresponds to both the first order implicit Euler method for $\theta = 1$ and the second order Crank-Nicholson method for $\theta = 0.5$. However, these are nonlinear schemes that require iterative methods such as Newton's method to solve for the solution at each time step. In order to achieve a linear scheme and hence improve the efficiency of the time stepping method, we choose $\hat{\mathbf{x}}^*$ to be evaluated independently of $\hat{\mathbf{x}}_{n+1}$. An obvious choice is $\hat{\mathbf{x}}^* = \hat{\mathbf{x}}_n$, which leads to a first order algorithm for all θ . In the interest of developing a higher order time integration scheme, we consider a specific choice of $\hat{\mathbf{x}}^*$ introduced by Simo and Armero [196], where $\hat{\mathbf{x}}^*$ is expressed in a linear, multi-step form as

$$\hat{\mathbf{x}}^* = a_0 \hat{\mathbf{x}}_n + a_1 \hat{\mathbf{x}}_{n-1} + a_2 \hat{\mathbf{x}}_{n-2} + a_3 \hat{\mathbf{x}}_{n-3} + \dots \quad (6.19)$$

where the a_i , $i = 0,1,2,\dots$ are coefficients that define the algorithmic approximation. These coefficients must sum to unity for consistency.

To determine all of the coefficients a_i , we consider the Taylor series of $\hat{\mathbf{x}}_{n-i}$ around $\hat{\mathbf{x}}_{n+\theta}$,

$$\hat{\mathbf{x}}_{n-i} = \hat{\mathbf{x}}_{n+\theta} - (i + \theta) \frac{d\hat{\mathbf{x}}}{dt} \Big|_{n+\theta} + \frac{(i + \theta)^2}{2} \frac{d^2\hat{\mathbf{x}}}{dt^2} \Big|_{n+\theta} + \dots \quad (6.20)$$

Assuming that $\hat{\mathbf{x}}$ is sufficiently smooth, Eq. 6.20 can exactly represent $\hat{\mathbf{x}}_{n-i}$ up to order m . For the choice $\theta = 1/2$, which corresponds to a second order time integration scheme, we have considered $\hat{\mathbf{x}}^*$ up to second or third order accurate. In order for $\hat{\mathbf{x}}^*$ to be second order accurate with $\theta = 1/2$, only two terms are required. By substituting Eq. 6.20 into Eq.

6.19 and by forcing the coefficient of $\hat{x}_{n+\theta}$ to be unity and all other coefficients to be zero, we obtain a set of equations for a_0 and a_1 :

$$\begin{pmatrix} a_0 + a_1 = 1 \\ a_0 + 3a_1 = 0 \end{pmatrix} \quad (6.21)$$

The solution for (a_0, a_1) can be trivially obtained as $(1.5, -0.5)$. It should be noticed that only this pair of coefficients results in second order accuracy of the linearized scheme. Any other combination of these two coefficient automatically leads to a first-order scheme. Although, theoretically, higher order accuracy in $\hat{x}^*$ should not lead to a higher order time integration scheme as the order of accuracy is defined by θ , we show in Section 6.4.2 that the accuracy of the linearly extrapolated Crank-Nicholson method can be improved by using a third-order accurate $\hat{x}^*$. Because the linearized time integration scheme is performed by using a linear extrapolate, we called this method the linearly extrapolated Crank-Nicholson method. The procedure described above can also be used to calculate the coefficients for $\hat{x}^*$ with higher order accuracy. For convenience, a list of the sets $\{a_i\}$ that correspond to $\hat{x}^*$ of accuracy up to third order is shown in Table 6.1.

Order of accuracy	a_0	a_1	a_2
1	1.0	0.0	0.0
2	1.5	-0.5	0.0
3	3.0	-3.0	1.0

Table 6.1: Values of $\{a_i\}$ in the linearly extrapolated Crank-Nicholson method for a given order of accuracy.

6.3.3 Solution method for the linear algebra problem and computational issues

The spatial and temporal discretization results in a large dimension, linear algebraic problem with a *sparse* matrix structure due to the compact support properties of the wavelets. This strongly suggests the use of either a sparse direct solver or a Krylov subspace based iterative algorithm. A sparse direct solver, such as the banded Gaussian solver,

requires a narrow bandwidth matrix structure, which is not present here because of the periodic boundary conditions. Therefore, a Krylov subspace based iterative solver is the natural choice for solving the linear algebra problem. In particular, we choose the generalized minimum residual (GMRES) method with the dual threshold, incomplete LU factorization preconditioner with pivoting by Saad and Schultz [186,187] as the iterative solver in this chapter. Both the GMRES algorithm and the ILUTP preconditioner are implemented by using SPARSKIT2 [189].

The computations in Sections 6.4 and 6.5 were performed on dual Pentium III 500MHz processors workstations. The number of basis functions used in a calculation is limited by the memory requirement for computing $\langle \sin(\mathbf{u}, \mathbf{w}) \rangle$, which corresponds to $\sum_j [\sin(\mathbf{u}, \mathbf{w}) \sin \theta]_{i,j} \hat{f}_j(\mathbf{w})$ upon discretization with the scaling functions. The matrix, $[\sin(\mathbf{u}, \mathbf{w}) \sin \theta]_{i,j}$, is a full matrix; and the storage requirement for it with 64×128 basis functions along the θ and ϕ directions, respectively, is 512 Megabytes. A subsequent mesh refinement that doubles the number of basis functions along the θ and ϕ directions would increase the memory requirement to 2 Gigabytes. By using a Daubechies 16 scaling function expansion, the total memory requirement is 633 Megabytes. Therefore if $[\sin(\mathbf{u}, \mathbf{w}) \sin \theta]_{i,j}$ were not stored, the total memory usage would be about 120 Megabytes even for this fine mesh. This is particularly attractive for calculations with traditional polymer kinetic theory models, because the diffusion equation for most models is linear in $\hat{f}$; and, hence, only a limited resolution is required for accurate simulations. For example, for a dilute solution of rigid polymers modeled as rigid rods, only 16×32 basis functions are required for converged simulation results. This corresponds to only 15 Megabytes of memory for storing the stiffness matrix and other necessary vectors. This suggests that the wavelet-Galerkin method is suitable for use in complex flow simulations when used in combination with a macroscopic simulation method such as the finite element method.

The dominant computational expense is rebuilding the stiffness matrix at each time step because $\sin(\mathbf{u}, \mathbf{w}) = \sqrt{1 - (\mathbf{u}\mathbf{u}:\mathbf{w}\mathbf{w})}$ is a nonlinear function of the $\mathbf{w}\mathbf{w}$ tensor. For a simulation of the Doi model with a mesh of 32×64 Daubechies 16 scaling functions, the computation time for assembling the stiffness matrix is about 55 cpu-seconds per time step, whereas that for solving the linear algebraic problem is less than 0.5 cpu-seconds. In the case of a traditional polymer kinetic theory model, such as FENE dumbbell or reptation models, the corresponding diffusion equation is *linear* with respect to the distribution function and hence the stiffness matrix can be assembled only once at the beginning of the simulation. Therefore, for these traditional models our numerical method should perform more efficiently than when used for simulating the Doi model. The speed-up for those problems will be approximately two orders of magnitude.

6.4 Convergence study

The accuracy and convergence characteristics of the wavelet-Galerkin numerical method are demonstrated with three different measures. First, the discretization error of the wavelet expansion is examined by using a scaling function expansion to represent the Onsager trial function [see Eq. 6.22 below]. This test shows the error and convergence of a wavelet expansion in approximating a sharply peaked function. Then the accuracy and convergence of the method are demonstrated by long time integration to steady state for the equilibrium problem ($De = 0$) at a given U . The goal of this test is two fold: (1) to test the sensitivity of the accuracy and convergence of the method to the director orientation when computing the equilibrium distribution function, and (2) to test the effects of the different forms of anisotropic drag coefficient on the accuracy of the method. We believe that the accuracy of the wavelet-expansion, and other numerical methods, for discretizing the diffusion equation will be strongly affected by the form of the anisotropic drag coefficient, even though a self-consistent equilibrium solution is independent of the form of the aniso-

tropic drag coefficient. Lastly, accuracy and convergence of the wavelet-Galerkin method are shown by time integration of a periodic state. We specifically choose $U = 12$ and $De = 30$ for this final study for two reasons. First, this state corresponds to a highly convective state; the large magnitude of the dimensionless groups makes the resulting distribution function and the stiffness matrix difficult to resolve. Demonstrating convergence for this state strongly suggests that convergence also is achieved for states for which the dimensionless groups are smaller. Second, aperiodic behavior was observed around this state by using a stochastic simulation method [9,10,98,125]. Showing convergence at this state is essential for determining whether or not this aperiodic behavior is a consequence of the physical model or a numerical artifact.

6.4.1 Steady state simulations with $De = 0$

Onsager's trial function is widely used as an *approximation* to the equilibrium problem. It has only one adjustable parameter, α , and has the following form

$$f(\mathbf{u}, \alpha) = \frac{\alpha}{4\pi} \frac{\cosh(\alpha \mathbf{n} \cdot \mathbf{u})}{\sinh \alpha} \quad (6.22)$$

where $\mathbf{n}$ is the director orientation. With Onsager's trial function, the structure parameter, S_2 , for a given α is expressed as

$$S_2 = 1 - \frac{3}{\alpha} \coth \alpha + \frac{3}{\alpha^2} \quad (6.23)$$

Although Onsager's trial function is *not* a solution to the equilibrium problem, it generates a distribution function that can be used as an initial guess for the equilibrium problem or an initial condition for the time-dependent problem. Furthermore, S_2 is a known function of α ; and, therefore, one can directly compute the discretization error of S_2 for a given basis function set.

We have used two types of measures to study the accuracy of the scaling function expansion approximation. First, the accuracy of the scaling function expansion is studied by comparing the exact nodal values of a distribution function against the nodal values of the same distribution function calculated from its scaling function projection. Specifically, a two-norm is considered for the difference between the exact and approximate values as shown in Eq. 6.24:

$$\|f - \hat{f}\| \equiv \frac{1}{N} \left(\sum_{i=1}^N (f_i - \hat{f}_i)^2 \right)^{0.5} \quad (6.24)$$

The result for Onsager's trial function with $\alpha = 14.2$ is shown in Fig. 6.2. Results of four sets of scaling functions, Daubechies sets (D4, D6, D10, and D14)¹ are shown in this figure. The mother functions for these four scaling functions can exactly represent polynomials up to orders 1, 2, 4, and 6, respectively. The orders of accuracy, as measured by Eq. 6.24, for the various Daubechies scaling functions are 3, 4, 6, and 7.5, respectively.

1. Here DN corresponds to the Daubechies scaling function with N filter coefficients in h_0 .

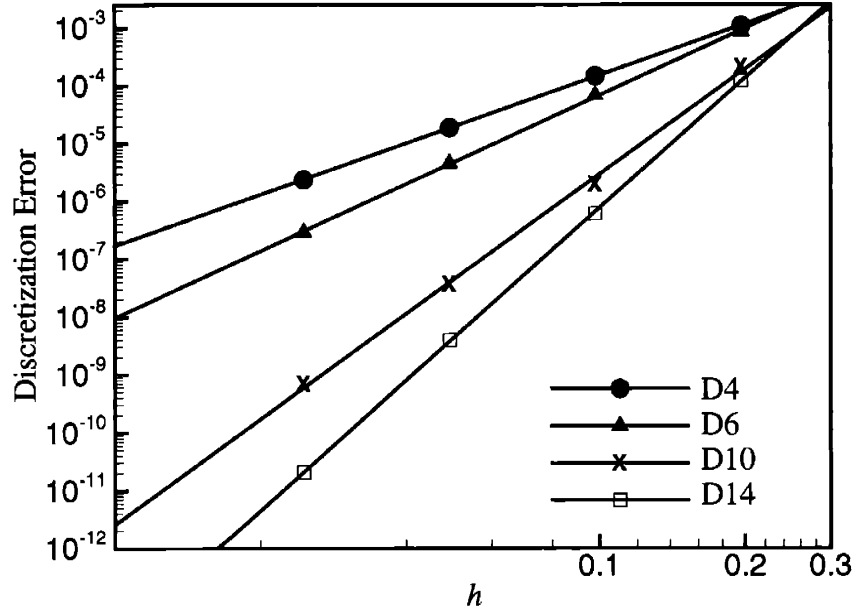


Figure 6.2: Convergence properties of the discretization error for various scaling functions. Discretization error is defined as the L_2 norm of the difference between the nodal value of Onsager's trial function with $\alpha = 14.2$ and the nodal value of the same function calculated from the projection of the scaling function expansion. The convergence rates for various Daubechies scaling functions are (from top to bottom): 2.95 for D4, 3.85 for D6, 6.05 for D10, and 7.48 for D14.

In addition to studying the L_2 norm, we study the accuracy of the wavelet expansion by measuring the functional, S_2 . In particular, we estimate the error by calculating S_2 for Onsager's trial function with $\alpha = 14.2$. The approximation error is defined as the deviation of the value of S_2 obtained from the wavelet expansion from the value of S_2 calculated by using Eq. 6.23. The value of S_2 given by Eq. 6.23 for $\alpha = 14.2$ is 0.8039. The results for the four sets of scaling function approximations are shown in Fig. 6.3. The order of convergence, independent of the type of the basis function, is two. Furthermore, except for the D4 basis functions, all other basis functions have the same error estimate. The error estimate for a relatively coarse mesh with 16×32 D6 scaling functions along the θ and ϕ directions is already better than 1 percent. Onsager's trial function with $\alpha = 14.2$ is a sharply peaked function, and hence we believe the scaling function expansion should be

able to represent accurately sharply peaked distribution functions that result from solution of the diffusion equation.

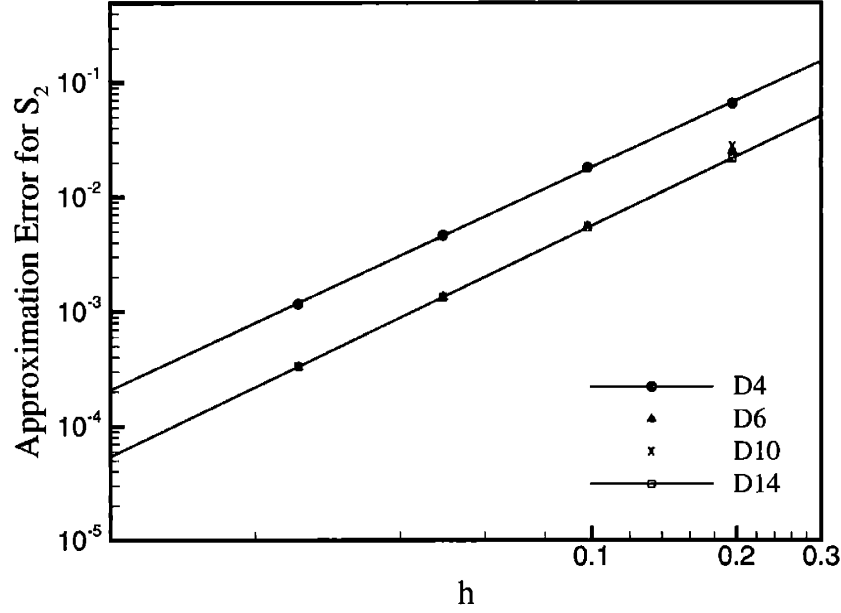


Figure 6.3: Convergence properties of the approximation error in representing S_2 of Onsager's trial function with $\alpha = 14.2$ by using various Daubechies scaling functions, D4, D6, D10, and D14. The reference value of S_2 is calculated from Eq. 6.23.

Next, the accuracy and convergence properties of the wavelet-Galerkin method are examined by calculating the equilibrium solution with the Doi model. As discussed previously, the number of basis functions used per interval of π is limited by the dimension of the matrix $[\sin(\mathbf{u}, \mathbf{w}) \sin \theta]_{i,j}$. As a result, there are only three different number of scaling functions that can be used for simulation with the scaling of metric sets (16×32 , 32×64 , 64×128). Because only three resolutions are used to study the accuracy of the scaling function expansion, there are insufficient data to extrapolate the order of convergence or the simulation result to the limit $h \rightarrow 0$.

As mentioned in Section 6.2, for a given U , the equilibrium solution ($De = 0$) for the Doi model is independent of the form of σ . Therefore, the numerical solution of Larson [125] is used to compare the accuracy of our numerical method for estimating S_2 at a

given U . The estimates for S_2 for a number of different values of U for the numerical solution with an in-plane configuration are listed in Table 6.2. For an in-plane configuration, the director of the distribution function lies in the plane $\theta = \pi/2$.

Scaling Functions	$U = 10.67$	$U = 12.0$	$U = 14.0$
32×64 D6	0.7915	0.8560	0.9086
16×32 D10	0.7915	—	—
32×64 D10	0.7936	0.8582	0.8558
64×128 D10	0.7922	0.8558	0.9042
32×64 D14	0.7930	0.8563	0.9044
16×32 D16	0.8063	—	—
32×64 D16	0.7931	0.8566	0.9055
64×128 D16	0.7922	0.8558	0.9043
Reference results in	0.7922	0.8555	0.9042

Table 6.2: Convergence study for the structure parameter S_2 at equilibrium ($De = 0$) for various U with the nematic director taken to point in the x_1 direction. Because of under resolution, no converged results were obtained for entries represented by dashes.

The results of Larson and Öttinger for $U = 14$ only serve as a guide for the range of S_2 because they did not demonstrate convergence for this parameter value. For the reference results for $U = 10.67$ and $U = 12$, they have shown convergence by increasing the number of spherical harmonics. For the values of U that we considered, the wavelet-Galerkin results are within one percent of the simulation results by Larson and Öttinger, who employed the self consistent σ , which numerically is much more stable and much easier to simulate than the anisotropic σ we use here.

When the director points along the vorticity axis, the shape of the distribution function is dramatically different from that corresponding to the director's pointing along x_1 direction. The distribution function for this situation is referred to as out-of-plane in the litera-

ture. The accuracy of the scaling function expansion for simulating S_2 at equilibrium is shown in Table 6.3.

Scaling Functions	S_2	Error
16×32 D10	0.5251	0.2671
32×64 D10	0.7121	0.0801
64×128 D10	0.7933	0.0011
16×32 D16	0.6455	0.1467
32×64 D16	0.7931	0.0009
64×128 D16	0.7928	0.0006

Table 6.3: Convergence study of the structure parameter S_2 at equilibrium for $U=10.67$ with the director pointing along the x_3 direction. Error is defined as $|S_2 - 0.7922|$.

The error in approximating the structure parameter, S_2 , was larger than 10% with 16 D10 basis functions per interval of π . To explore the origin of this inaccuracy, we examined the computed distribution function for various numbers of D10 basis functions; these results are shown in Fig. 6.4. For an out-of-plane distribution function at equilibrium, the distribution is one dimensional and is independent of ϕ . Hence, we only show the variation of the distribution function in the θ direction. In Fig. 6.4, the presence of a thin bound-

ary layer close to $\theta = 0$ and $\theta = \pi$ is apparent. This boundary layer corresponds to a sharp peak in the distribution function around $\theta = 0$.

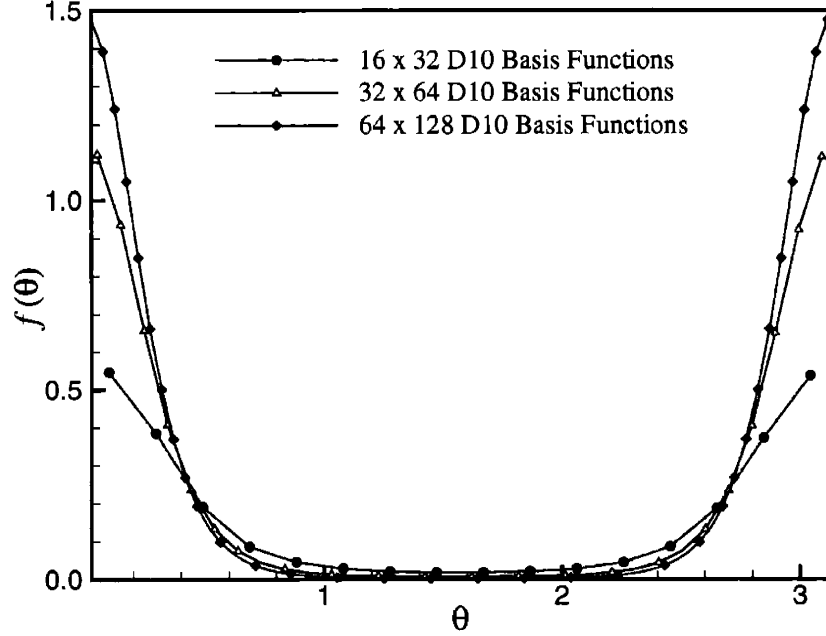


Figure 6.4: Effect of mesh refinement on the computation of the distribution function in the equilibrium problem with $U = 10.67$ and the director pointing along the x_3 direction. D10 scaling functions are used as the basis functions. Successive meshes correspond to 16, 32, and 64 basis functions per interval of π .

Despite the inaccurate estimate of S_2 for a sharply peaked distribution function with director pointing along the x_3 direction, the D10 scaling function expansion does not introduce any alias into the numerical solution. Aliasing is a common problem in spectral methods when insufficient resolution is used to compute a numerical solution. The absence of aliasing in the present calculation is a direct result of the compact support property of the scaling functions in the spatial domain.

As seen from Figs. 6.2 and 6.3, the scaling function expansion can accurately represent a sharply peaked distribution function. In Figs. 6.2 and 6.3, the sharply peaked distribution function is Onsager's trial function with the director oriented in the x_1 - x_2 plane; the value of S_2 for this distribution is 0.8. However, when the director points along the x_3 direction,

as demonstrated in Fig. 6.4, the scaling function expansion does not resolve the boundary layer, and hence the sharp peak near $\theta = 0$ and $\theta = \pi$. As a result, the scaling function expansion underestimates the equilibrium value of the structure parameter. Therefore, we suspect that the failure to resolve the rapidly varying region of the out-of-plane distribution function is due to the fact that the action of the operator $D(f, \Xi)$ on a scaling function is poorly resolved by the scaling function expansion. In order to check this hypothesis, the behavior of the Doi model is simulated for constant σ and for two anisotropic expressions for σ with a scaling function expansion that uses 32 D10 functions per interval of π at $U = 10.67$. The simulation results for S_2 are listed in Table 6.4.

σ	S_2	Error = $ S_2 - 0.792 $
constant	0.7892	0.003
$\left(\frac{4}{\pi} \cdot \langle \sin(u, w) \rangle_w\right)^{-2}$	0.7121	0.080
$\left(\frac{4}{\pi} \cdot \langle \sin(u, w) \rangle_w\right)^{-4}$	0.3041	0.488

Table 6.4: Effect of anisotropic σ on the accuracy of the numerical solution of the equilibrium problem.

Following the results from Section 6.2, Eq. 6.4, S_2 should be independent of σ for a given U . Therefore, the numerical solutions for different σ should be identical. The results in Table 6.4 suggest that as σ becomes more anisotropic, the action of $\hat{D}(\hat{\Xi})$ on a basis function becomes more difficult to resolve by the basis function expansion; and, hence, the error of estimating S_2 by a given set of basis functions becomes larger. Furthermore, anisotropic σ also limits the numerical stability of the calculation. For constant σ and the first choice for anisotropic σ , i.e., the first two rows in Table 6.4, the time-dependent simulation is stable with $\Delta t = 0.01$; our numerical method is only stable for $\Delta t \leq 10^{-5}$ for the third choice for σ in this table. This suggests that the anisotropy of σ is responsible for reducing both the accuracy and stability of the numerical method for simulating the diffu-

sion equation of the Doi model. We believe that anisotropy in σ also will lead to difficulty in simulating stochastic trajectories with a Brownian dynamics approach.

6.4.2 Convergence studies for time-dependent simulations

The accuracy and stability of the numerical method for simulating time-periodic behavior is the focus of this section. The time-periodic behavior for $De = 30$ and $U = 12$ is studied by varying the number of basis functions (mesh or h -refinement), the type of basis function (p -refinement), and Δt . This particular choice of Deborah number and intermolecular potential strength was made in order to match the state where stochastic simulations were used to simulate the dynamics of the Doi model. This allows us to compare the time-dependent states obtained by using our deterministic method with those predicted by the stochastic method.

The temporal evolution of S_3 simulated by using 16×32 , 32×64 , and 64×128 D10 basis functions with $\Delta t = 0.01$ is shown in Fig. 6.5. The initial condition for these simulations is an isotropic distribution function. h -convergence is shown by the superposition of the evolution of S_3 for the 32×64 and 64×128 D10 scaling function expansions.

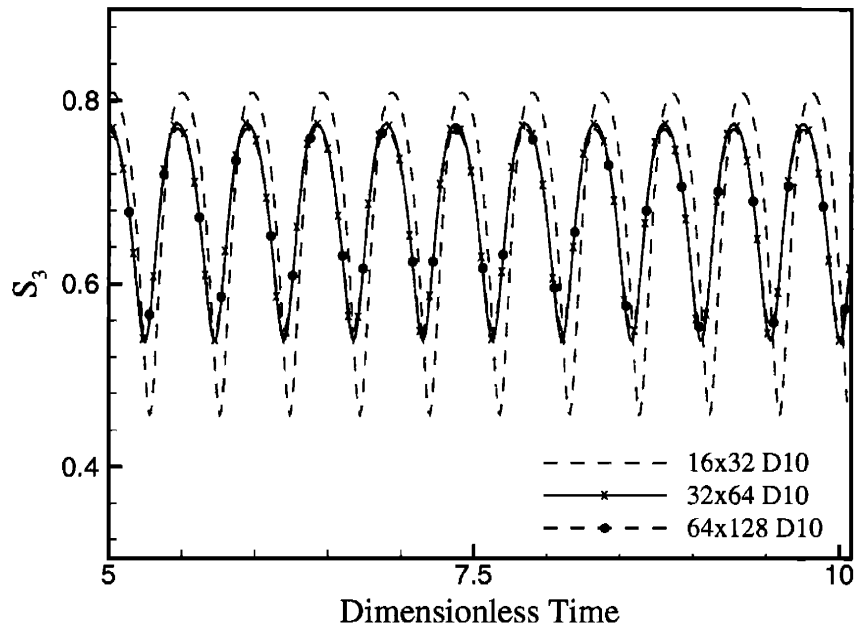


Figure 6.5: Effect of h -refinement on the convergence of a time-periodic state of the Doi model ($De = 30$, $U = 12$); $\Delta t = 0.01$. D10 scaling functions are used as basis functions. Successive meshes correspond to 16, 32, and 64 basis functions per interval of π .

The p -convergence of the wavelet-Galerkin method is demonstrated in Fig. 6.6. In this figure, four different scaling functions, (D6, D10, D14, D16), were used to simulate the evolution of S_3 beginning from the value for the isotropic distribution function; for each of scaling functions, the same time step, $\Delta t = 0.01$, was used. These four different scaling functions, (D6, D10, D14, D16), can exactly approximate polynomials of order 2, 4, 6, and 7 respectively. Whereas the simulation of S_3 evolution by the D6 scaling function expan-

sion underestimates the amplitude and overestimates the period of the oscillations in S_3 , the results obtained with (D10, D14, D16) overlap and demonstrate p -convergence.

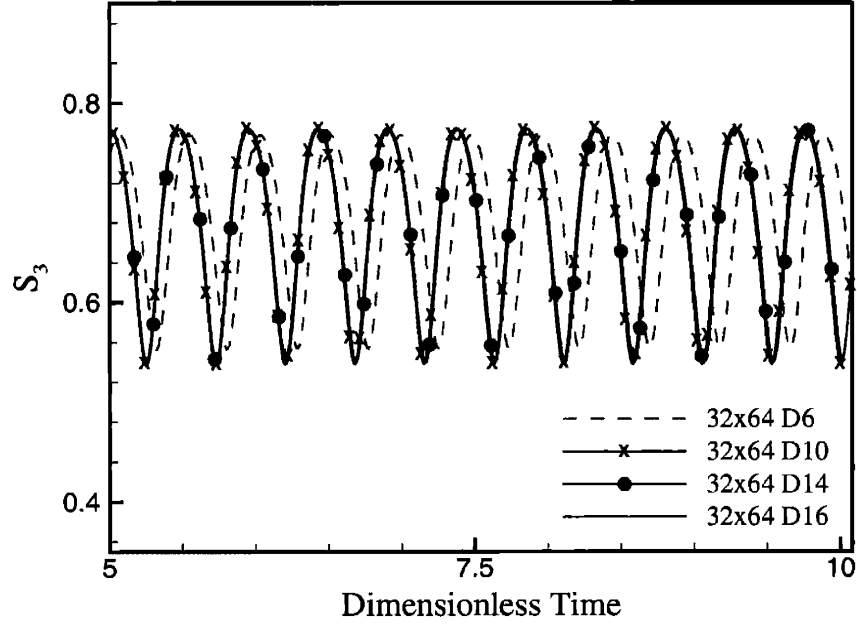


Figure 6.6: Effect of p -refinement on the convergence of a time-periodic state of the Doi model ($De = 30$, $U = 12$); $\Delta t = 0.01$. 32 basis functions are used per interval of π . D6, D10, D14, and D16 scaling functions are used in the simulation.

Convergence with Δt is illustrated by simulating the evolution of S_3 with a series of time steps (0.001, 0.005, 0.01, 0.03). Figure 6.7 shows that whereas the simulation with $\Delta t = 0.03$ overestimates the amplitude of evolution, the evolution of S_3 predicted by the other choices for Δt overlap, thereby confirming Δt convergence.

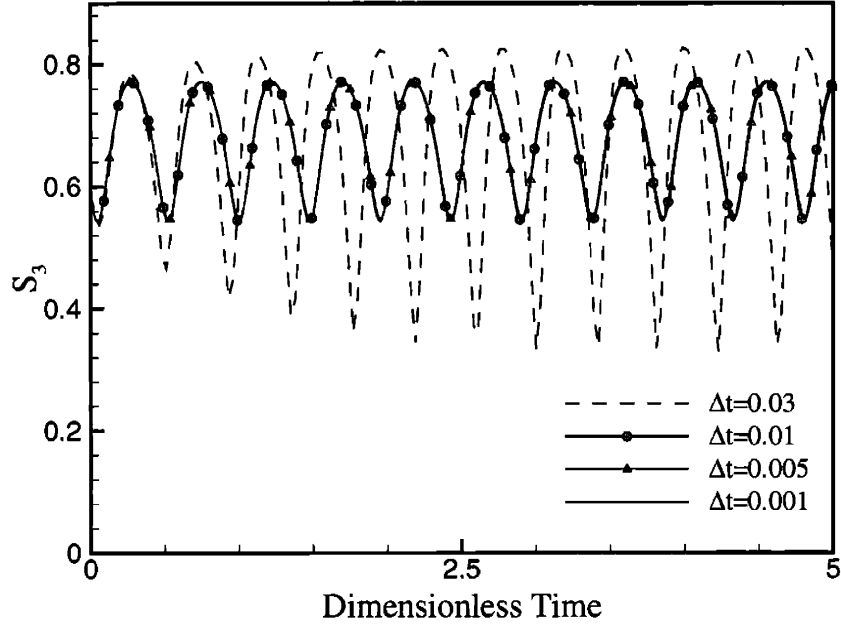


Figure 6.7: Convergence study for the time integration scheme with different Δt by simulating the time-periodic state of the Doi model at ($De = 30$, $U = 12$). 32 D10 basis functions are used per interval of π . The four values of Δt used in the simulations are 0.03, 0.01, 0.005, and 0.001. Except for $\Delta t = 0.03$, all of the simulation results superpose.

To further examine the convergence properties of our time integration scheme, the linearly extrapolated Crank-Nicholson method with second- and third-order interpolates for S were investigated. The error estimate used for the comparison is the magnitude of the difference between the computed S_3 at $t = 2.0$ and an extrapolated value obtained for a series of simulation results using a linearly extrapolated Crank-Nicholson algorithm with a second-order interpolate. The simulation results are presented in Fig. 6.8. Whereas the linearly extrapolated Crank-Nicholson scheme with a second-order interpolate converges quadratically, the convergence rate for the linearly extrapolated Crank-Nicholson scheme with a third-order interpolate is approximately 3.5. Although the power law regime for the third-order interpolate scheme is narrow (spans only from 5×10^{-3} to 0.03), the error

induced by the linearly extrapolated Crank-Nicholson scheme with a third-order interpolate is always smaller than that with a second-order interpolate for any given Δt

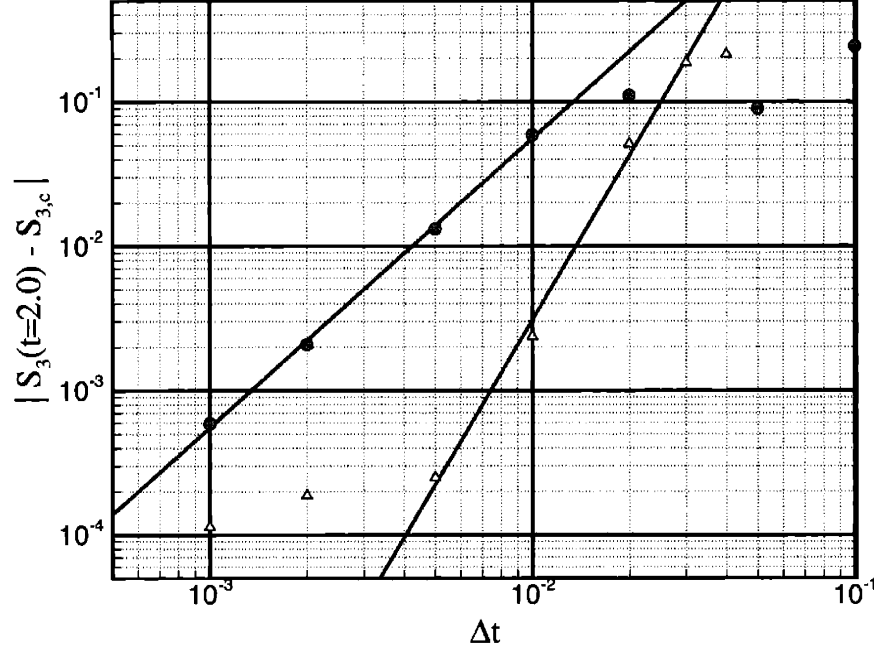


Figure 6.8: Convergence study for the time integration scheme with different Δt and different interpolates ($\mathbf{x}^*$ in Eq. 6.17). The circle symbols correspond to the simulation results for a second-order interpolate and the diamond symbols correspond to the simulation results for a third-order interpolate. The reference point is the structure parameter at dimensionless time equal to 2 during the start-up of simple shear flow from an isotropic initial distribution function of the Doi model with $De = 30$, $U = 12$. 32 D10 basis functions are used per interval of π . The convergence rate for the second-order interpolate is 2, and the convergence rate for the third-order interpolate is 3.5.

6.5 Nonlinear dynamics of the exact Doi model

6.5.1 Dynamics at low De

At low shear rates, the evolution of the director and the average ordering of the molecules depend strongly on the initial condition. The evolution of $S_{22} - S_{33}$ and S_3 at $U = 10.67$ and $De = 7$ are shown in Figs. 6.9a and 6.9b, respectively. In these calculations, the distribution function is given initially by Equation 6.22, with α is calculated to match the equilibrium structure parameter for $U = 10.67$ and initial director angles are chosen ranging between 0° to 90° . The initial director angle is defined as the angle measured from the

vorticity axis (x_3) towards to the velocity gradient axis (x_2). An initial director angle of 0° corresponds to a director orientation along the vorticity axis, and an initial director angle of 90° corresponds to a director orientation along the velocity gradient axis. As shown in Section 6.2.2, S_3 is an invariant of the structure tensor; and, hence, there is no information about the director orientation in S_3 . The trajectories of S_3 for various time-dependent states are therefore similar except for their amplitudes. The evolution of $S_{22} - S_{33}$, on the other hand, clearly demonstrates difference between various time-dependent and steady states for different initial director orientations.

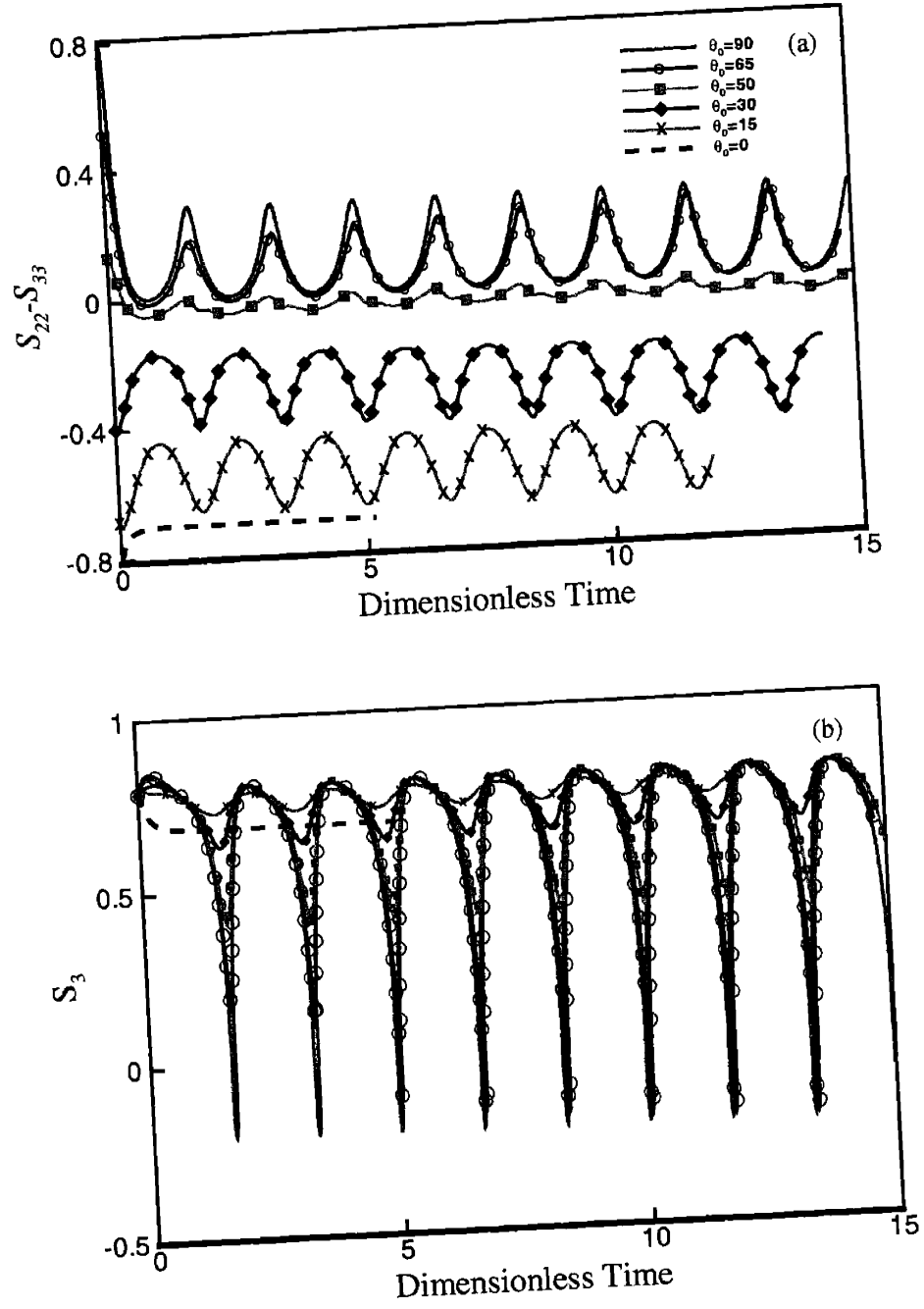


Figure 6.9: Effect of initial director orientation on the dynamics of (a) $S_{22} - S_{33}$ and (b) S_3 for $U = 10.67$ and $De = 7$. The simulations employ 32×64 D10 scaling functions with $\Delta t = 0.01$. For a given initial director angle, the corresponding initial distribution function is calculated by using the Onsager's trial function. The initial director angles from bottom to top are $0^\circ, 15^\circ, 30^\circ, 50^\circ, 65^\circ$, and 90° in part (a).

The time-dependent behaviors shown in Fig. 6.9 are classified as tumbling and kayaking states [125]. A tumbling state is a two-dimensional periodic state in which the director rotates in the plane perpendicular to the vorticity axis; this behavior is depicted by the top lines in Fig. 6.9a and the evolution with the largest amplitude in Fig. 6.9b. Details of the distribution function evolution during tumbling can be seen in Fig. 6.10, which shows a sequence of contour plots in configuration space for approximately one period of tumbling. The two peaks shown in each of the contour plots correspond to a symmetric structure such that $f(\mathbf{u}) = f(-\mathbf{u})$. Whereas the director rotates in the x_1 - x_2 plane during tumbling motion, the dynamics of the distribution function is apparently much more complicated. The nonlinear dynamics of the distribution function is a result of the balance between the Brownian force, hydrodynamics force, and intermolecular force. The hydrodynamic force aligns molecules along the flow direction. The Brownian force randomizes the orientations of the molecules and hence makes the distribution function more homogeneous. The intermolecular force tends to align molecules with respect to one another in the direction of the director, but it does not favor a specific director orientation. Depending on the relative orientation of the director to the flow direction, the intermolecular force can align *constructively* or *destructively* with the hydrodynamic force and, hence, produce a resulting stronger or weaker convective force as compared to the hydrodynamic force alone. This net convective force, together with the Brownian force, determines the overall shape of the distribution, such as the location and intensity of the peak, as well as the broadness and skewness of the distribution. For moderately high shear rates such as $De = 7$ shown in Fig. 6.9b, the molecules may even form an oblate structure.

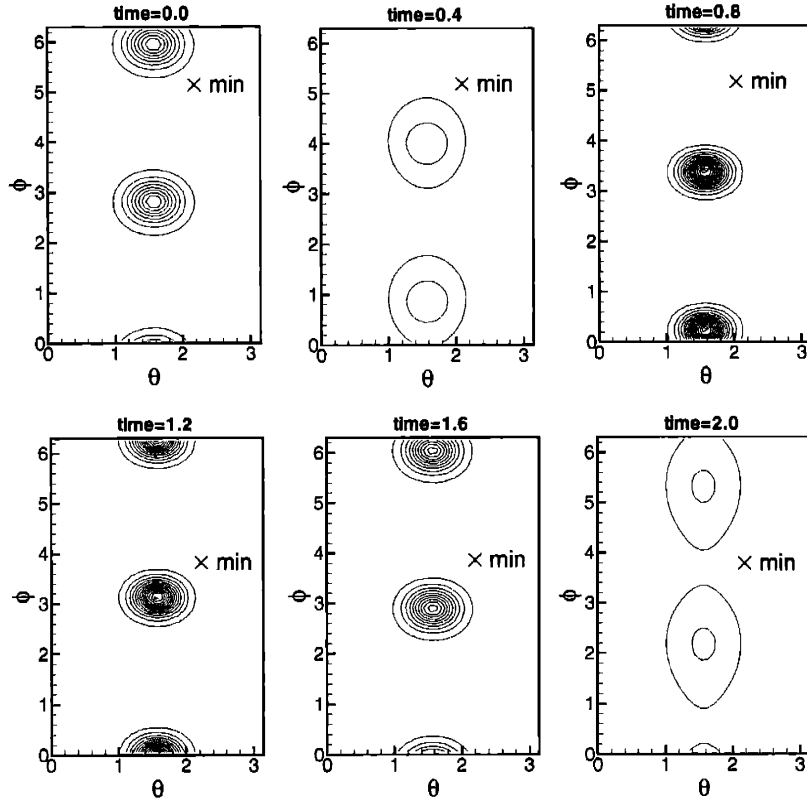


Figure 6.10: Dynamics of the distribution function of the Doi model for tumbling motion with $U = 10.67$ and $De = 7$. The simulations employ 32×64 D10 scaling functions with $\Delta t = 0.01$. Time is made dimensionless by λ . The period of this tumbling state at $De = 7$ is 1.8. The location of minimum value is denoted by “ $\times$ ” and the increment of each contour line is 0.1 with the first contour line value equal to 0.1. The location and magnitude of the peak of the distribution function as well as its breadth depend on time. This suggests that the dynamics of the distribution function is much more complicated than the description given by director or structure tensor theories.

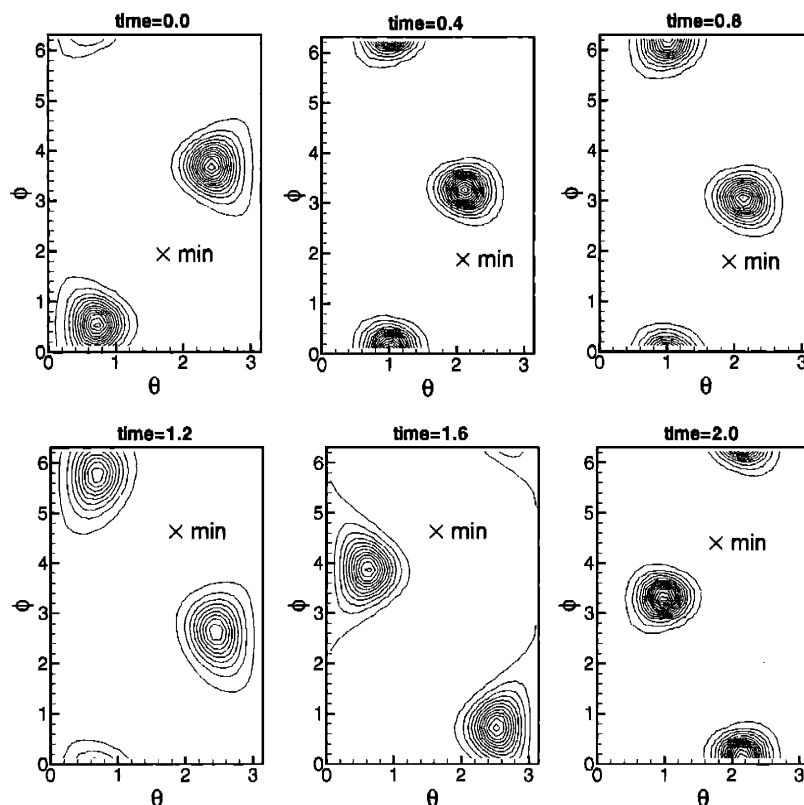


Figure 6.11: Dynamics of a distribution function of the Doi model for kayaking motion with $U = 10.67$ and $De = 7$. The simulations employ 32×64 D10 scaling functions with $\Delta t = 0.01$. Time is made dimensionless by λ . The period of this kayaking state at $De = 7$ is 1.8. As in Fig. 6.10, the location of minimum value is denoted by “x”; and the increment between each contour line is 0.1, with the value of the first contour line equal to 0.1. The location and the magnitude of the peak, breadth, and even the skewness of the distribution function all depend on time.

Kayaking is a three-dimensional time-periodic state, represented by the collection of trajectories in the middle of Fig. 6.9. A detailed sequence of the evolution of the distribution is shown in Fig. 6.11. The rotational motion of the molecules within $x_1 - x_2$ is dominated by the hydrodynamic force. Because the initial condition of the distribution function accumulate a high concentration of molecules with an out-of-plane orientation, the intermolecular force tends to align molecules with the overall distribution function to be out of plane. This leads to a rich two-dimensional dynamics as compared with the tum-

bling motion (Figure 6.11) It should be noted that the peak structure parameter value for the tumbling and kayaking states are the same, as shown in Fig. 6.9b, but the shapes of the corresponding distribution functions are completely different.

The steady behavior of $S_{22} - S_{33}$ and S_3 , observed in Figs. 6.9a and 6.9b, is known as the log-rolling state [125]. Here, the majority of the molecules point along the vorticity axis. When a molecule is parallel to the vorticity axis, there is no hydrodynamic force acting on it. The molecules aligned near the vorticity axis experience only a weak hydrodynamics force that would change their orientation. As a result, the overall distribution function for the molecular orientation remains similar to the equilibrium distribution function (Fig. 6.4), where the distribution function is independent of ϕ and is sharply peaked around $\theta = 0$ and $\theta = \pi$. The independence of the distribution function from ϕ indicates that molecules are oriented randomly in the cone of fixed θ with the highest density of molecules oriented along the vorticity axis.

6.5.2 Dynamics at high De

The evolution of $S_{22} - S_{33}$ at a moderately high De is shown in Fig. 6.12 for $U = 10.67$ and $De = 12$. Under these conditions the hydrodynamic force is stronger than the rotational forces from the Brownian and intermolecular forces; and, hence, the long-time behavior of the unapproximated Doi model is independent of initial conditions. For any initial director angle, there is only one stable, time-periodic state. This time-periodic state is known as the wagging state, in which the director vibrates within the flow (x_1 - x_2) plane around a mean director orientation. The evolution of the complete distribution function is illustrated in Fig. 6.13. Similar to the tumbling state, the peak of the distribution function is localized along $\theta = \pi/2$. However, the structure of the distribution function does not change significantly due to the large De and, hence, strong hydrodynamic force.

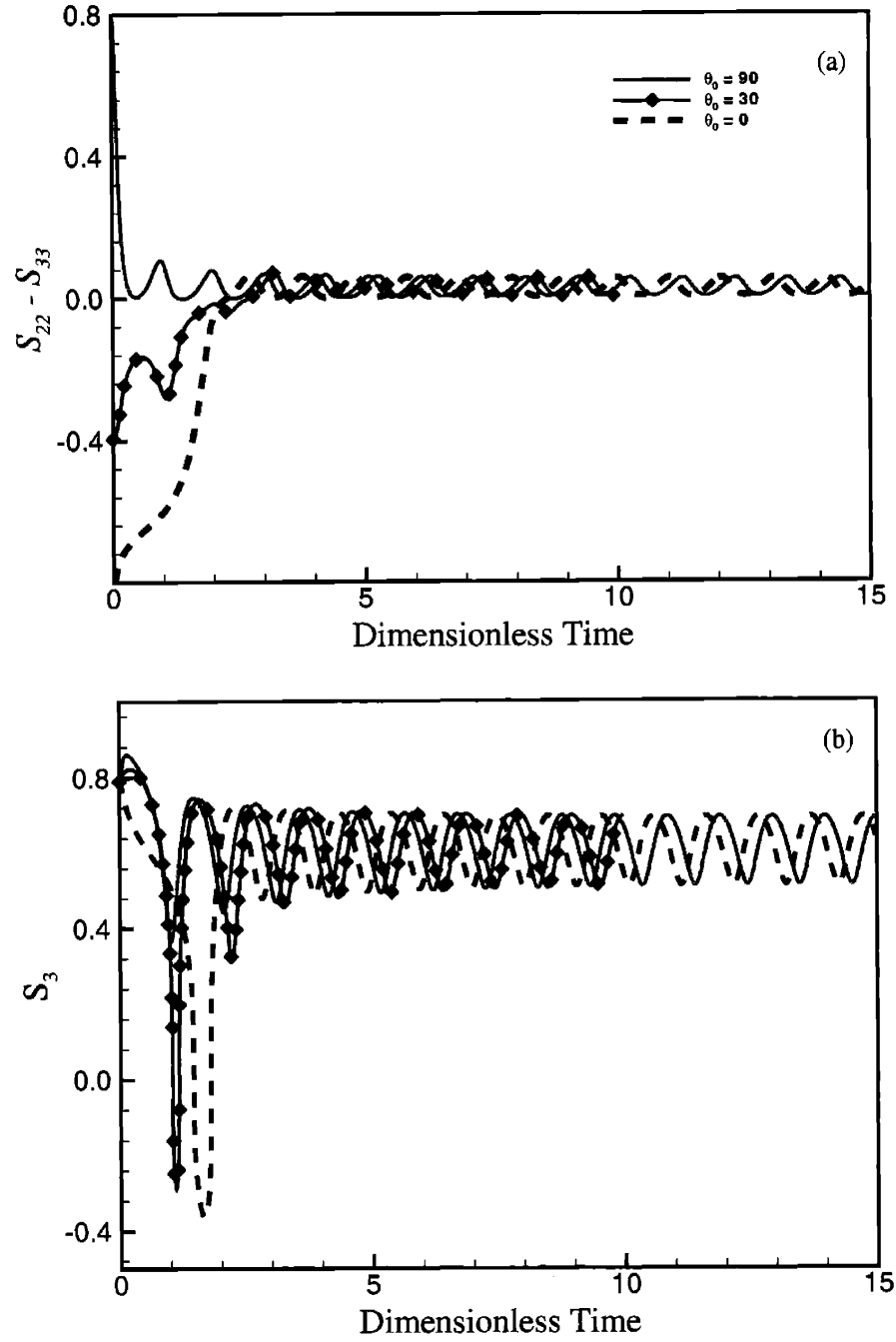


Figure 6.12: Effect of initial director orientation on the dynamics of (a) $S_{22} - S_{33}$ and (b) S_3 for $U = 10.67$ and $De = 12$. The simulations employ 32×64 D10 scaling functions with $\Delta t = 0.01$. The initial director angle is set by using Onsager's trial function. The initial director angles from bottom to top are 0° , 30° , and 90° in part (a).

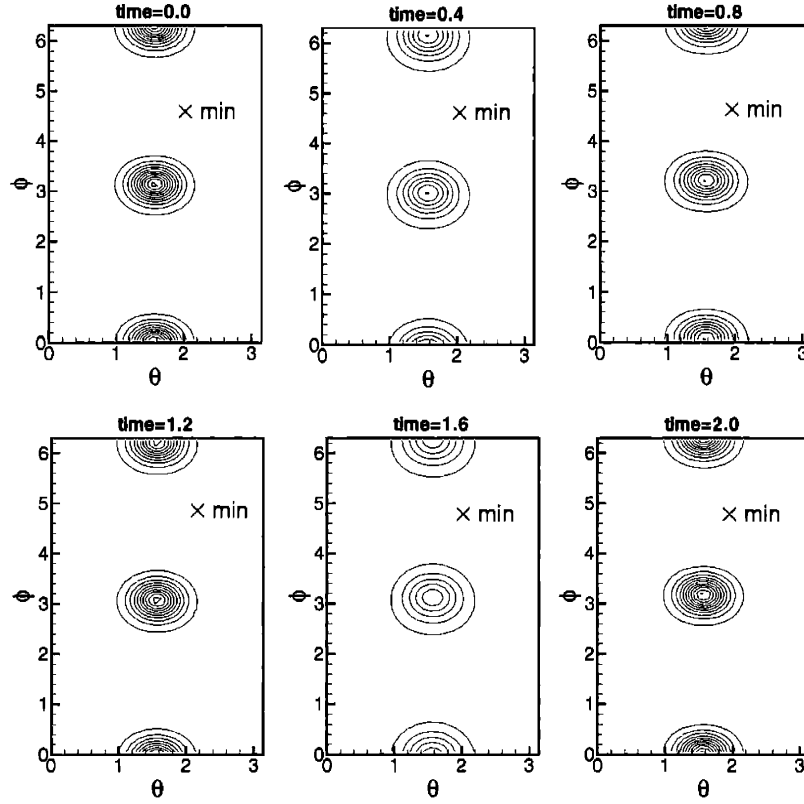


Figure 6.13: Dynamics of the distribution function of the Doi model in a wagging motion with $U = 10.67$ and $De = 12$. The simulations employ 32×64 D10 scaling functions with $\Delta t = 0.01$. Time is made dimensionless by λ . The period of the wagging state at $De = 12$ is 0.90. As in Fig. 6.10 the location of minimum value is denoted by “x”; and the increment of each contour line is 0.1, with the value for the first contour line set to 0.1. The location, peak magnitude, and breadth of the distribution function all depend on time.

At higher values of De , the hydrodynamic and intermolecular forces dominates over the Brownian forces. As a result, the amplitude of the wagging motion decreases and the distribution function reaches a steady state known as the flow aligning state. The steady-state structure parameter of this flow aligning state is in general larger than that predicted by the rigid rod model in a dilute solution. This is due to the additional aligning force of the intermolecular force. The nonlinear stability of the transition between the wagging and flow aligning states is explored below.

6.5.3 Nonlinear stability analysis for the exact Doi model during transitions between in-plane states

Direct numerical simulation of the unapproximated Doi model has shown much of the nonlinear dynamics due to the presence of the mean-field intermolecular potential and anisotropic drag coefficient. In this section, we continue to probe the in-plane dynamics of the unapproximated Doi model by examining the transitions between various states.

We characterize the various transitions by the amplitude, $A = A(\text{De}, U) = S_{3,\text{max}} - S_{3,\text{min}}$, of the oscillations in S_3 in a time-periodic state. The amplitude variation for different De at $U = 10.67$, $A(\text{De}, U = 10.67)$, is shown in Fig. 6.14. A distinctive feature in this figure is the prominent maximum in amplitude at $\text{De} \approx 8$. This maximum can be used to define the transition between the tumbling and wagging states.

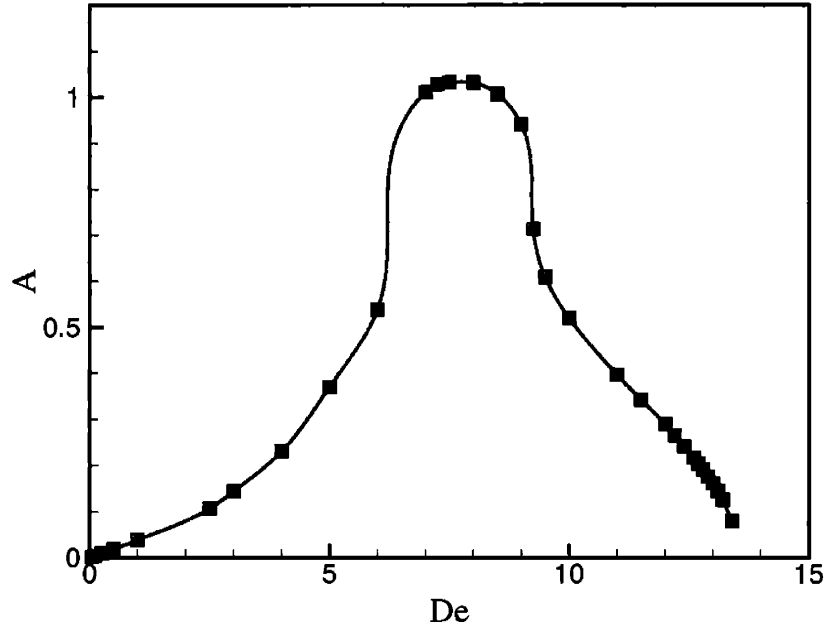


Figure 6.14: The amplitude, A , of the periodic, in-plane motion of S_3 for $U = 10.67$ and various De . The simulations employ 32×64 D10 scaling functions with $\Delta t = 0.01$. The maximum at $\text{De} = 7.5$ corresponds to the transition between the tumbling state and the wagging state.

As De increases beyond approximately 8, the amplitude of the wagging state decreases; and, at a critical De , the transition between the time-periodic, wagging state and

the steady, flow aligning state occurs. To understand the nature of this latter transition, we fit the amplitude dependence on De as $A = A_0(De_c - De)^\alpha$. This is shown in Fig. 6.15, and the expression for the nonlinear fit is

$$A = 0.228 \cdot (13.52 - De)^{0.5} \quad (6.25)$$

The fact that $\alpha = 0.5$ suggests that the transition from the wagging state to the flow aligning state is a Hopf bifurcation that occurs at $De = 13.52$ for $U = 10.67$. In order to determine whether this Hopf bifurcation is subcritical or supercritical, the critical point is estimated both from above (from time-periodic state to steady state) and below (from steady state to time-periodic state). The amplitude plot in Fig. 6.15 is used to estimate the critical point from below, and the disturbance plot in Fig. 6.16 is used to determine the critical point from above. To construct a disturbance plot, a steady-state distribution is first calculated by setting $\partial f / \partial t = 0$. Then a random disturbance was added to the steady-state solution, which in turn is used as an initial condition for a time-dependent simulation. The growth or decay of the disturbance is monitored by using the L_2 -norm of the difference between the distribution at time t and the steady-state distribution function, $\|f(t) - f_{ss}\|$. The long-time growth rate of the disturbance corresponds to the real part of the largest eigenvalue of the stiffness matrix, which can also be obtained by solving the generalized eigenvalue problem in a linear stability analysis. Disturbance plots for various De around the transition between the wagging and flow aligning states at $U = 10.67$ are shown in Fig. 6.16. The insert in Fig. 6.16 interpolates the long-time decay rates to determine the location of the Hopf bifurcation point, which is found at a critical De equal to 13.52 for $U = 10.67$. This is exactly the same value as that found from the amplitude plot (Fig. 6.15). Due to the fact that the critical De values estimated from above and below the bifurcation are exactly the same, the bifurcation occurring between the wagging and flow aligning states is a *supercritical* Hopf bifurcation. Therefore, no hysteresis will occur.

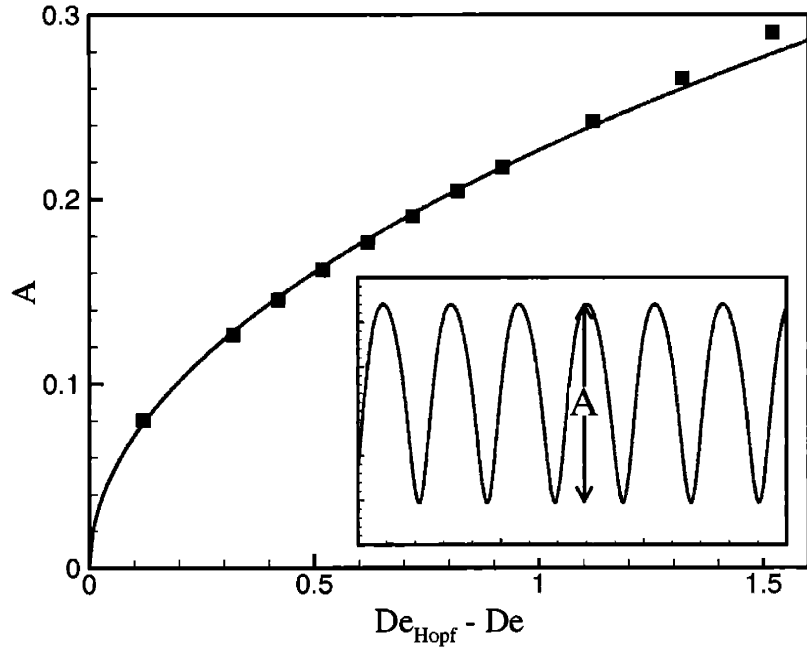


Figure 6.15: The amplitude plot for $U = 10.67$. The simulations employ 32×64 D10 scaling functions with $\Delta t = 0.01$. Numerical data are fit to the equation, $A = A_0(De_c - De)^\alpha$; and α and De_c are found to be 0.5 and 13.52, respectively. The insert provides the definition for A in the time-periodic state.

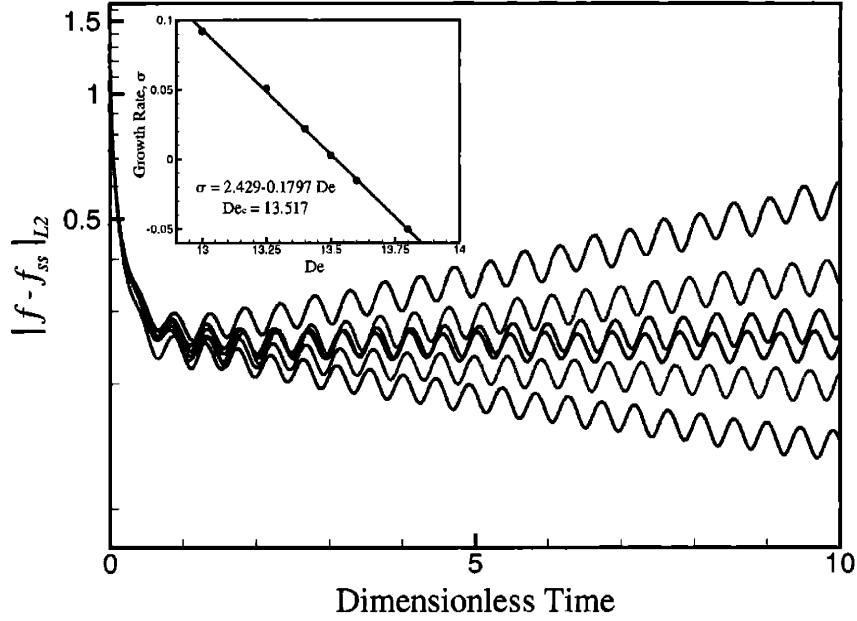


Figure 6.16: Disturbance plots for $U = 10.67$. The simulations employ 32×64 D10 scaling functions with $\Delta t = 0.01$. The measure of the disturbance is the L_2 norm of the deviation of the distribution function from the steady-state distribution function. The curves ranging from the bottom to top in the figure correspond to $De = 13.8, 13.6, 13.5, 13.4, 13.25$, and 13.0 . The insert shows the interpolation for the critical De from the growth rates of the disturbance plots. The curve fit is given by $\sigma = 2.429 - 0.1797 De$. The critical De , which corresponds to $\sigma = 0$, is 13.52 .

Much information and insight can be obtained from a phase diagram, which is a correlation between the two independent dimensionless parameters, U and De , for a given bifurcation. Figure 6.17 compares the phase diagrams for the supercritical Hopf bifurcation between the wagging and flow aligning states for the unapproximated Doi model and the Doi model with the Maier-Saupe potential and constant σ . The results for the Doi model with the Maier-Saupe potential and constant σ were obtained by Nayak [161] with an arc-length continuation technique. Both sets of data are found to be described by a proportionality between De and $(U - U_c)^\alpha$, where α is a fitting parameter and U_c is the limit point encountered in the nematic branch [75,161]. It is found that $U_c = 8.38$ for the

Onsager potential [124] and $U_c = 4.49$ for the Maier-Saupe potential [75,161]. The curve in Fig. 6.17 for the unapproximated Doi model is approximated by

$$De_{\text{Hopf}} = 2.757 \cdot (U - 8.38)^{1.97} \quad (6.26)$$

and that for the Doi model with Maier-Saupe potential and isotropic drag coefficient is given by

$$De_{\text{Hopf}} = 3.367 \cdot (U - 4.49)^{1.22} \quad (6.27)$$

The difference in the scaling between the exact Doi model and that with the Maier-Saupe potential and isotropic drag coefficient can be attributed to differences in an effective potential in these two models. In the exact Doi model, the anisotropic environment experienced by the molecules is affected by the Onsager potential and the localized anisotropic drag coefficient. In the simplified Doi model, the anisotropic drag coefficient is constant, and thus the anisotropic environment experienced by the molecules in this model is solely dependent on the Maier-Saupe potential. The Onsager potential is proportional to $\langle \sin(\mathbf{u}, \mathbf{w}) \rangle$, whereas the Maier-Saupe potential is proportional to $\langle (\sin(\mathbf{u}, \mathbf{w}))^2 \rangle$. For the same distribution function, the square dependence in the Maier-Saupe potential leads to a smoother potential than the Onsager potential and makes the effective environment more homogeneous. Therefore, a given fractional increment in $U - U_c$ for the Doi model with the Maier-Saupe potential induces a smaller fractional increment in De_{Hopf} . Thus the slope of the correlation serves as a means for identifying the anisotropic environment generated by a given mean field intermolecular potential.

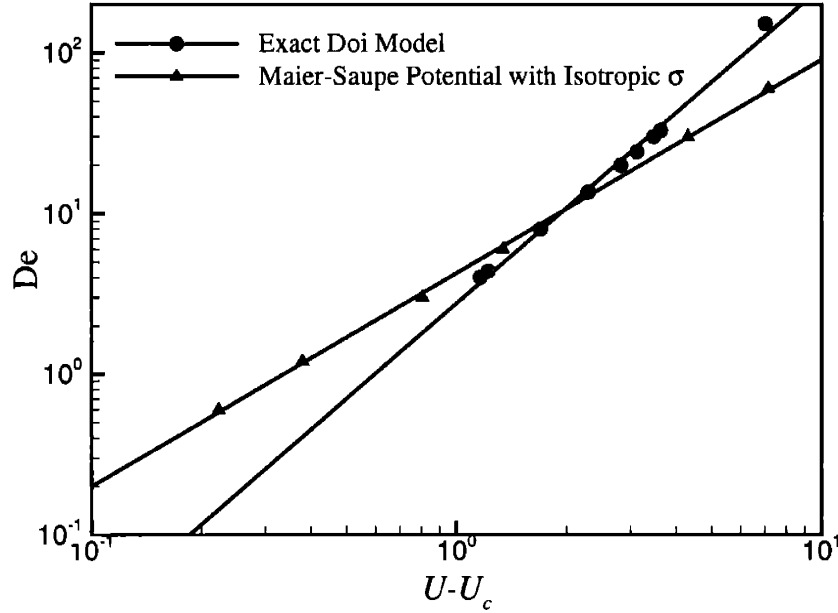


Figure 6.17: Phase diagram of the critical De in the wagging to flow aligning state transition for the Doi model with (a) the Onsager potential with anisotropic drag (circular symbols) and (b) the Maier-Saupe potential with isotropic drag (triangular symbols). The data for (b) are from Nayak [161].

6.6 Conclusions

A wavelet-Galerkin method is presented for direct simulation of molecular models from polymer kinetic theory. The exact Doi model with the Onsager mean-field potential and an orientation-dependent rotational diffusivity was simulated to illustrate the accuracy and robustness of the numerical method. The convergence studies presented in this chapter confirm that the numerical method converges with mesh refinement (h -convergence), order refinement (p -convergence), and time step (Δt -convergence) at high De ($De = 30$) and large U ($U = 12$). In contrast to results obtained by stochastic simulations, the wavelet-Galerkin method predicts a time-periodic state for this particular set of parameters.

We have also studied the evolution of the distribution function during various time-dependent states for the Doi model. Unlike stochastic simulations or other particle based

techniques, the dynamics revealed in the simulations presented here is purely distributional; and, hence, the evolution behavior is directly related to the macroscopic properties. At low De , the dynamics of the distribution function is determined through the interplay between the hydrodynamic force and the intermolecular force. This gives rise to a wide range of behavior such as tumbling, wagging, and log-rolling states for the Doi model. The long-time behavior also is dependent on the initial condition. At high De , the hydrodynamic force dominates the force balance, and the dynamics of the Doi model becomes independent of the initial condition.

The nonlinear dynamics of the exact Doi model is examined in detail, in particular the transition or bifurcation from the time-dependent wagging state to the steady, flow aligning state. Together with the convergence analysis shown earlier, we have shown that the wavelet-Galerkin method predicts no aperiodic behavior over a range of De close to the supercritical Hopf bifurcation point. Because an orientation-dependent σ acts as a rescaling factor for the Brownian and intermolecular force terms in the diffusion equation relative to the hydrodynamic force term, we believe that the aperiodic, time-dependent response for the unapproximated Doi model that is computed with stochastic methods is a numerical artifact associated with the poor convergence properties of the stochastic simulation method for a system with multiplicative, mean-field interacting noise. Power-law behavior of the locus for the supercritical Hopf bifurcation between the wagging and flow aligning states in the parameter space (U, De) is demonstrated. The slope of the power law reflects the anisotropy of the effective intermolecular potential. The exact Doi model is much more anisotropic than the simplest Doi model formulated with the Maier Saupe potential and constant, isotropic drag coefficient.

The wavelet-Galerkin method appears to be a powerful approach for computing rheological dynamics and viscoelastic flows with constitutive descriptions based directly on

diffusion equations from kinetic theory. This approach is generalizable to fully two-dimensional flows, as described in [2] and in Chapters 7-9.

Chapter 7

Complex flow simulations of Doi model

7.1 Introduction

The inability to predict and control the complicated microstructure formation in a fabrication process has limited the large-scale, commercial application of liquid crystalline polymers. This is because the rich rheological dynamics such as director tumbling and sign-change of normal stresses disrupt orientation order, which results in a proliferation of orientation defects known as disclination. The key to solving these problems is to understand the relationship between the microstructure and the transport properties and to develop numerical software that is capable of describing the transport phenomena based on the constitutive modeling of the microstructure. Thus, the modeling and calculation of the transport processes and microstructure evolution are essential and play a central role in facilitating the use of liquid crystalline polymers in large scale production and applications.

Modeling the complex structure of liquid crystalline polymers, however, is extremely difficult. Little progress has been made despite the considerable attention devoted to the development of models for liquid crystalline polymers. This is because of the vast range of length and time scales involved in the transport processes in liquid crystalline polymers. Typical modeling of liquid crystalline polymers requires resolution of at least four different length scales. At the molecular length scale ($O(10nm)$) [29], excluded volume interactions between the molecules in the system lead to various structural phases such as nematic or even smectics phases. The length scale of the disclination or defects in the microstructure ($O(0.1\mu m)$) is much larger than the molecular scale. The interactions between disclinations or defects leads to various nonuniform morphologies in liquid crys-

talline polymer samples. The length associated with these interactions, in turn, is an order of magnitude larger than the size of the defects. The last length scale is that for the fabrication process. In a typical rheological experiment, the length scale is of order 1mm. Even in a roll cell experiment, the typical length scale is order 100 μ m. Hence, the length scale from a microdevice to the molecular length scale spans four to five orders of magnitudes. A comprehensive theory that describes dynamics over then span of this large length scale difference, however, has not yet been developed. Most models or theories involve one or two of these length scales in detail and either ignore the contribution from the other length scales. Although this assumption may be valid, it still requires a numerical method with extremely high spatial resolution and simulation of these models is quickly limited by the available computational resources.

Three different strategies have been applied to the constitutive modeling of liquid crystalline polymers rheology. A purely continuum approach such as the Leslie-Ericksen theory is based on the extension of an evolution equation for an isolated, rigid ellipsoid and couples its evolution with elasticity theory. A stress tensor expression is then derived from elasticity theory. Although it is capable of predicting instabilities such as roll-cell formation in a weak shear flow, it is not applicable to processing flows where elastic effects are significant. This is because the Leslie-Ericksen theory is essentially the linear limit of molecular theory near equilibrium. During a typical processing flow, the molecular distribution is distorted far from equilibrium and hence the linear approximation is no longer valid.

At the other end of the spectrum lies the molecular approach. The most detailed molecular theory involves modelling each liquid crystalline polymer molecule explicitly by a micromechanical model such as ellipsoid. The dynamics of the molecules are then simulated by using nonequilibrium molecular dynamics. Mean-field theory has also been

applied in the modeling of liquid crystalline polymers. One of the most common molecular theories for homogeneous, monodomain liquid crystalline polymers in the Doi model. It models a liquid crystalline polymer solution as a suspension of *infinitely* thin rods suspended in a Newtonian solvent acted on by Brownian motion forces, hydrodynamic forces, and a mean-field intermolecular potential. Both Maier-Saupe and Onsager potential have been widely used in the Doi model to account for the isotropic-nematic transition, which is the signature phenomena of a lyotropic liquid crystalline polymers. This Doi model has been generalized in a phase space kinetic theory development by Bhawe et al. [15]. They demonstrated that the presence of the viscous stress contribution is due to the constraint of constant length of the micromechanical model. Extensions of the Doi model to include distortional elasticity have been made by Marrucci and Greco [150], Bhawe [14], and others [77]. Most of these attempts involve modification of the mean-field intermolecular potential to include spatial variations in the distribution function. Feng, et al. [77] have modified the stress tensor expression for the Doi model with Marrucci-Greco potential by using a virtual work argument.

Mesoscopic approaches in between the molecular theory (such as the Doi model) and continuum approach (such as the Leslie-Ericksen model) involve both modifying the moment equation of the Doi model and *ad hoc* modeling that combines aspects of both the Doi model and the Leslie-Ericksen theory. Marrucci and Maffettone [149] and Larson and Doi [126] assume a polydomain structure with microstructural evolution of each domain modelled by the Doi model. The overall structure and rheological properties are then defined by averaging over each of these domains. While such approach is descriptive for steady state, homogeneous flow, it is incapable of modeling complex flows. This is because of the lack of an explicit, spatial dependence in the microstructure evolution. An alternative approach employed by Edwards, et al. [63] and Tsuji and Rey [220] used the

second moment equation derived from the Doi model in which replace the intermolecular potential is replaced by a mean-field intermolecular potential derived from a Landau-de Gennes potential. Formally, such an approach is only valid near the isotropic state because the Landau-de Gennes expansion is essentially an expansion around the isotropic state. Furthermore, the phenomenological nature of this model limits its usefulness for understanding the molecular effects beyond a mesoscopic length scale. Therefore, we focus on the modeling of liquid crystalline polymer by using the kinetic theory described in Chapter 5. In contrast to the common practice in extending the Doi model, we focus on the simulation of the Doi model incorporating the effects of the concentration fluctuation. This also introduces a spatial-gradient contribution to the diffusion equation.

Numerical simulation of liquid crystalline polymer flows that use the Doi model have thus far been limited by the need to use a closure approximation to make the calculations affordable. The only notable simulations that solve the distribution function are due to Ramalingam and Armstrong for one-dimensional fiber-spinning flow [181], Grosso et al. [92] for a decoupled simulation of the Doi model in an eccentric cylinder with an assumed Newtonian flow field, and Nayak [161] for a fully two-dimensional, coupled simulation of the Doi model. For pressure-driven, planar channel flow, Nayak found disclination formation. This is due to the range of different tumbling/wagging frequencies at different shear rates and distance from the centerline to the wall of the channel flow. Due to the lack of an intrinsic length scale, the disclinations refine to an extremely small length scale. When the length scale of the disclination becomes similar to that of the mesh, the code terminates.

It is the focus of this chapter to study the effect of introducing an intrinsic length scale to this disclination refinement. The simplest implementation of this length scale is through the incorporation of the concentration fluctuation effect. The outline of the rest of this chapter is as follows. The governing equations and the mathematical formulation of the

model are presented in Section 7.2, where we give the diffusion equation and stress tensor expressions. The numerical method for simulating the Doi model, in particular with the concentration fluctuations, is the focus of Section 7.3. Then in Section 7.4, calculations of the Doi model in pressure-driven, planar channel flow are shown. We first reconfirm the instability observed by Nayak and study the effect of flow rate on the results. Then, we show the effect of concentration fluctuations on the flow calculation. Finally, conclusions are offered in Section 7.5.

7.2 Governing Equations

7.2.1 Equation of change

In the inertialess limit, the equation of motion and the equation of continuity are

$$\eta_s \nabla \cdot \{ \nabla \mathbf{v} + \nabla \mathbf{v}^T \} - \nabla \cdot \{ \boldsymbol{\tau}_p + p \boldsymbol{\delta} \} = 0 \quad (7.1)$$

$$\nabla \cdot \mathbf{v} = 0 \quad (7.2)$$

where η_s is the solvent viscosity, $\mathbf{v}$ and p are the velocity and pressure, and $\boldsymbol{\tau}_p$ is the polymeric contribution to the extra stress. Generally, $\boldsymbol{\tau}_p$ can be split into contributions of elastic stress and viscous stress, that is, $\boldsymbol{\tau}_p = \boldsymbol{\tau}_p^E + \nabla \mathbf{v} : \boldsymbol{\tau}_p^V$. Here the viscous stress is a fourth order tensor and is given by $\langle \mathbf{u} \mathbf{u} \mathbf{u} \mathbf{u} \rangle$ for rigid rod models. Other typical sources of viscous stress contribution arises from the constraint in the micromechanical model for the polymer molecule.

In the numerical computations presented in this chapter, the equations of change (Eqs. 7.1 and 7.2) are solved in dimensionless forms selected to be appropriate for each test problem. Setting a velocity scale V , a length scale L , a time scale L/V , and a pressure and stress scale $\eta_0 V/L$ leads to a set of dimensionless equations. Rewriting these equations in the DEVSS-G formulation [139] gives rise to the following set of equations

$$\nabla \cdot \{ \nabla \mathbf{v} + \nabla \mathbf{v}^T \} - \nabla \cdot \{ \boldsymbol{\tau}^E + \mathbf{G}^T : [\boldsymbol{\tau}^V + (1 - \beta) [\mathbf{I} + \mathbf{I}^T]] + p \boldsymbol{\delta} \} = 0 \quad (7.3)$$

$$\nabla \cdot \mathbf{v} = 0 \quad (7.4)$$

where $\beta \equiv \eta_s/(\eta_s + \eta_p)$ is the dimensionless solvent viscosity, $\mathbf{I}$ is a fourth order isotropic tensor with components $I_{ijkl} = \delta_{ik}\delta_{jl}$ and $\mathbf{G}$ is the velocity gradient tensor defined as $\mathbf{G} \equiv \nabla \mathbf{v}$.

Traditionally, the viscoelastic contribution to the stress tensor is expressed by a closed form constitutive equation. In this work, the stress tensor is written in terms of moments of a distribution function, whose evolution is in turn calculated directly from a configuration space distribution function. The evolution of this configuration distribution function is governed by a diffusion equation from kinetic theory. This chapter considers the Doi model for a monodomain liquid crystalline polymer system and a modified Doi model that includes the effects of concentration fluctuations.

7.2.2 Doi model with concentration fluctuation

One of the simplest ways to introduce an intrinsic molecular length scale is to incorporate the effect of concentration variations. By using standard kinetic theory and assuming that the location of the center of mass of a molecule is under the influence of macroscopic velocity and Brownian motion, the diffusion equation for the configuration space distribution function is found to be

$$\begin{aligned} \frac{\partial f}{\partial t} = & -\mathbf{v} \cdot \nabla f + \nabla \cdot \mathbf{D}_{tr} \nabla f \\ & - \text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u} \mathbf{u} \mathbf{u}] f + \frac{\partial}{\partial \mathbf{u}} \cdot \sigma \left[\frac{\partial f}{\partial \mathbf{u}} + \frac{\partial \Phi}{\partial \mathbf{u}} f \right] \end{aligned} \quad (7.5)$$

where

$$\mathbf{D}_{tr} = \frac{1}{4} \left(\frac{\ell}{L} \right)^2 [\sigma \delta + (1 - \sigma) \mathbf{u} \mathbf{u}] \quad (7.6)$$

with a normalization condition of

$$\int \int f(\mathbf{r}, \mathbf{u}, t) d\mathbf{r} d\mathbf{u} = N \quad (7.7)$$

While more interesting boundary conditions may be used to incorporate the effects of wall anchoring, we assume natural boundary conditions to be implemented at the solid wall surface and the line of symmetry.

For the developments in later sections, it is convenient to define an operator $\mathcal{L}(\mathbf{G}, f)$ for the orientation variation as,

$$\mathcal{L}(\mathbf{G}, f) \equiv -\text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u} \mathbf{u} \mathbf{u}] f + \frac{\partial}{\partial \mathbf{u}} \cdot \sigma \frac{\partial \Phi}{\partial \mathbf{u}} f \quad (7.8)$$

For simplicity, we assume $\sigma = 1$ and Φ takes the form of the Maier-Saupe potential

$$\Phi = -\frac{3}{2} U(n) \mathbf{u} \mathbf{u} : \mathbf{S} \quad (7.9)$$

where $U(n)$ is dimensionless and depends on the local number density n ; $\mathbf{S}$ is the structure tensor defined as

$$\mathbf{S} \equiv \langle \mathbf{u} \mathbf{u} - \frac{1}{3} \delta \rangle \quad (7.10)$$

We note that the normalization condition (Eqn. 7.7) requires a coupling of the distribution over both the complete physical space and the configurational space. This is computationally impossible. A strategy to decouple the calculation involves introduction of a new equation for the number density of the macromolecules, $n(\mathbf{r})$. The number density equation is derived by integrating the diffusion equation over the configuration space. For the diffusion equation 7.5, the resulting number density equation is,

$$\frac{\partial n}{\partial t} + \text{Dev} \cdot \nabla n = D_{tr} \nabla^2 n \quad (7.11)$$

and the associated normalization condition for the diffusion equation becomes

$$\int f(\mathbf{r}, \mathbf{u}, t) d\mathbf{u} = n(\mathbf{r}) \quad (7.12)$$

For pressure-driven, planar channel flow, Eqn. 7.11 will lead to a uniform number density profile for all velocity profiles. In order to study the influence of concentration fluctuations, we need to add in a perturbation. One simple form of perturbation is to make use of the intermolecular potential and postulate the number density equation as

$$\frac{\partial n}{\partial t} + \text{De} \mathbf{v} \cdot \nabla n = D_{tr} \nabla^2 n - 1.5 D_{tr} \nabla \cdot [\nabla U(n) \mathbf{S}] : \mathbf{S} \quad (7.13)$$

In the limit of $\ell/L \rightarrow 0$, the diffusion equation (Eqn 7.5) reduces to the Doi model for a monodomain liquid crystalline polymer and the normalization condition (Eqn 7.7) becomes $\int f(\mathbf{r}, \mathbf{u}, t) d\mathbf{u} = 1$.

The stress tensor for the Doi model with concentration fluctuation is the same as the the homogeneous Doi model, that is

$$\boldsymbol{\tau}_p = -\frac{(1-\beta)}{\text{De}} \left\{ 3 \langle \mathbf{u}\mathbf{u} - \frac{1}{3} \boldsymbol{\delta} \rangle - \langle \mathbf{u} \frac{\partial \Phi}{\partial \mathbf{u}} \rangle + 6 \text{De} \mathbf{G} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle \right\} \quad (7.14)$$

where the prefactor, $(1-\beta)/\text{De}$, is equal to $n_0 kT/(\eta_0 V/L)$. For the Maier Saupe potential, $\Phi = -(3/2) U \mathbf{u}\mathbf{u} : \mathbf{S}$, the stress tensor becomes

$$\boldsymbol{\tau}_p = -\frac{(1-\beta)}{\text{De}} \{ (3 - U(n)) \mathbf{S} - 3 U(n) [\mathbf{S} \cdot \mathbf{S} - \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle : \mathbf{S}] + 6 \text{De} \mathbf{G} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle \} \quad (7.15)$$

The corresponding stress tensor expressions for the viscous stress $\boldsymbol{\tau}^v$ and the elastic stress $\boldsymbol{\tau}^E$ can be identified as

$$\boldsymbol{\tau}^v(f) = -6(1-\beta) \int \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} f(\mathbf{r}, \mathbf{u}, t) d\mathbf{u} = -6(1-\beta) \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle \quad (7.16)$$

$$\boldsymbol{\tau}^E(f, n) = -\frac{(1-\beta)}{\text{De}} \{ (3 - U(n)) \mathbf{S} - 3 U(n) [\mathbf{S} \cdot \mathbf{S} - \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle : \mathbf{S}] \} \quad (7.17)$$

7.3 Numerical method

Spatial approximation of the computational domain of the physical space is performed by using a mixed finite element method. The physical domain Ω is divided in to a collection

of N_e non-conforming elements T_e in the shape of both rectangles and triangles. We define V_h as the space spanned by biquadratic Lagrangian polynomials ($\mathbb{Q}_2(\Omega)$ as the space for biquadratic polynomials for quadrilaterals and $\mathbb{P}_2(\Omega)$ as the space for quadratic polynomials for triangles) and S_h as the space spanned by bilinear Lagrangian polynomials ($\mathbb{Q}_1(\Omega)$ as the space for bilinear polynomials for quadrilaterals and $\mathbb{P}_1(\Omega)$ as the space for linear polynomials for triangles). These functional spaces will be used to discretize the physical space for the equations of change and the diffusion equation, as described below.

7.3.1 Finite element approximation to the equations of change

The discretized equations of change (Eqns. 7.3 and 7.4) describe a modification of the standard elliptic saddle point problem for $\mathbf{v}$ and p . The pair of finite element basis functions for interpolating these two variables is chosen to be compatible for the solution of the Stokes problem with the polymeric stress taken as data. In particular, the Taylor-Hood element is chosen (i.e. $\mathbf{v}_h \in V_h$ and $p_h \in S_h$). Bilinear basis functions are used to approximate $\mathbf{G}$ and $\boldsymbol{\tau}_p$; this choice gives compatibility with p . Unlike the typical DEVSS-G formulation, the viscous stress consists of the additional contribution from the polymer. The resulting linear-algebra problem is solved by using a frontal solver. Because the viscous stress from the polymer contribution changes after each time step, a full LU decomposition is necessary. Alternative strategies for explicitly updating the polymeric viscous stress introduce numerical instabilities that require a reduction in time step size.

7.3.2 Wavelet-Galerkin/Finite element method

The diffusion equation (Eqn. 7.5) is discretized by using a mixed wavelet-Galerkin/finite element method. Before going into the details of the implementation, we point out that the physical space of the diffusion equation is discretized by a discontinuous Galerkin finite element method, as will be explained in the next section. The configuration space discretization is performed by using an expansion in Daubechies scaling functions. These

scaling functions are determined by an index DN and a set of scaling parameters $\{h_0(k): 0 \leq k \leq DN\}$ known as the filter coefficients that define the “mother” function $\varphi(x)$ through a “two-scale” relationship

$$\varphi(x) = 2 \sum_{k=1}^{DN} h_0(k) \varphi(2x - k) \quad (7.18)$$

This equation is also known as the dilation equation. For $j \geq 0$, various orders of scaling function can be defined for $0 \leq m \leq 2^j$ as

$$\varphi_{j,m}(x) = \varphi(2^j x - m) \quad (7.19)$$

Let V_j be the space spanned by the scaling functions $\{\varphi_{j,m}(x): 0 \leq m \leq 2^j\}$. One can show that $V_0 \subset V_1 \subset \dots \subset \mathbb{L}^2[0, 1]$. This provides a rigorous approach for a systematic refinement procedure. The diffusion equation in the configuration space is then discretized at scale j determined by the resolution of the space V_j . This is done by a mixed Galerkin-collocation procedure. The spatially varying (in configuration space) coefficients are evaluated and formed by a collocation method, and are then projected onto the scaling function space. The implementation detail has already been described in Chapter 6 and will not be repeated here.

7.3.3 Local discontinuous Galerkin method

The physical space of the diffusion equation is discretized by a discontinuous Galerkin (DG) method. To incorporate the diffusion operator of the diffusion equation, a local discontinuous Galerkin method is required. The local discontinuous Galerkin (LDG) method is a generalization of the DG method for solving general convection-diffusion equations [6, 7, 37]. By introducing an auxiliary variable for the flux, the elliptic differential equation is written as a pair of hyperbolic equations, which in turn is solved with the standard DG method. Cockburn et al. [37] proved that the LDG method for a scalar equation is stable in the $\mathbb{L}_2$ norm and that the LDG method converges as $O(h^k)$ when k -th order approx-

imation polynomials are used in space. This order of accuracy is suboptimal; for a linear elliptic boundary value problem, the order-of accuracy of the LDG method is $O(h^k)$ and $O(h^{k+1})$ for odd and even values of k , respectively. Thus the accuracy is $O(h)$ for bilinear approximation polynomials.

The weak formulation for the LDG method applied to the diffusion equation for the distribution function of the modified Doi model is presented below. Let ψ_{DG} be the discontinuous basis function. The LDG formulation is defined through introducing an auxiliary variable $\mathbf{q} \equiv -D_{ir}\nabla f$ within each element T_e

$$\begin{aligned} \int_{\Omega} \left(\frac{\partial f}{\partial t} \psi_{DG} - [\mathbf{v}f + \mathbf{q}] \cdot \nabla \psi_{DG} \right) dA + \int_{\partial\Omega} (\mathbf{n} \cdot \mathbf{v}) f \psi_{DG} dl + \int_{\partial\Omega} (\mathbf{n} \cdot \mathbf{q}) \psi_{DG} dl \\ = \int_{\Omega} \left(\mathcal{L}(\mathbf{G}, f) + \frac{\partial^2 f}{\partial u^2} \right) \psi_{DG} dA \end{aligned} \quad (7.20)$$

$$\int_V \mathbf{q} \psi_{DG} dA = \int_V D_{ir} f \nabla \psi_{DG} dA - \int_{\partial V} \mathbf{n} D_{ir} f \psi_{DG} dl \quad (7.21)$$

Intuitively, one might expect certain compatibility criteria for the functional space for discretizing f and $\mathbf{q}$. However, as shown by Shu, et al. [195], same functional space may be employed for both f and $\mathbf{q}$ without leading to numerical instability. In this chapter, the physical space of both f and $\mathbf{q}$ is represented by bilinear Lagrangian polynomials.

7.3.4 Time integration algorithm

The mixed wavelet-Galerkin/LDG-finite-element discretization for the diffusion equation and the mixed finite element formulation for the equations of change results in a large set of differential-algebraic equations for the time-dependent coefficients in both the finite element and scaling function expansions. In this chapter, a semi-implicit Euler method is used for the temporal discretization. Although fully explicit, higher order time integration schemes can be implemented, we notice a significant drop in numerical stability with

these higher order time integration methods and therefore we focus on the use of the semi-implicit Euler method. This time integration method makes use of an operator-splitting method that decouples the calculation of the polymer stress (by solution of the diffusion equation for the Doi or the modified Doi model) from the temporal updating of the velocity and pressure field (by solution of a generalized Stokes problem). Following the standard presentations of time-splitting methods for partial differential equation, the semi-implicit Euler method is written in terms of the original equation set even though it is applied to the discretized equation in the weak formulation. We denote x_n as the discrete variable x evaluated at the n -th time step, given by $t_n = n\Delta t$, where Δt is the time step size.

The solution update from t_n to t_{n+1} begins with the update of the kinematic variables with the polymeric stress evaluated from the previous time step

$$\nabla^2 \mathbf{v}_{n+1} - \nabla \cdot \{ \mathbf{G}_{n+1} : [\boldsymbol{\tau}_n^V + (1 - \beta)[\mathbf{I} + \mathbf{I}^T]] + p_{n+1} \} = \nabla \cdot \boldsymbol{\tau}_n^E \quad (7.22)$$

$$\nabla \cdot \mathbf{v}_{n+1} = 0 \quad (7.23)$$

$$\mathbf{G}_{n+1} - \nabla \mathbf{v}_{n+1} = 0 \quad (7.24)$$

Then, the updated velocity field and velocity gradients, as well as the auxiliary variable $\mathbf{q}$ for the distribution gradient evaluated from the previous time step, are used to advance the distribution function with the constraint from t_n to t_{n+1} as

$$f_{n+1} - \Delta t \left(\frac{\partial^2 f_{n+1}}{\partial u^2} + \lambda_{n+1} \sin \theta \right) = f_n - \Delta t (\mathbf{v}_n \cdot \nabla f_n + \nabla \cdot \mathbf{q}_n - \mathcal{L}(\mathbf{G}_{n+1}, f_n)) \quad (7.25)$$

$$\Delta t \int f_{n+1}(\mathbf{r}, \mathbf{u}, t) d\mathbf{u} = \Delta t n_n \quad (7.26)$$

Lastly, the distribution gradient and the stress tensor are calculated from the updated distribution function and the number density equation is updated

$$\mathbf{q}_{n+1} = -D_{lr} \nabla f_{n+1} \quad (7.27)$$

$$n_{n+1} + \Delta t(\mathbf{v}_{n+1} \cdot \nabla n_{n+1} - D_{tr} \nabla^2 n_{n+1}) = n_n - \Delta t \frac{3}{2} \nabla \cdot \nabla [U(n_n) \mathbf{S}_{n+1}] : \mathbf{S}_{n+1} \quad (7.28)$$

$$\boldsymbol{\tau}_{n+1}^V = \boldsymbol{\tau}^V(f_{n+1}) \quad (7.29)$$

$$\boldsymbol{\tau}_{n+1}^E = \boldsymbol{\tau}^E(f_{n+1}) \quad (7.30)$$

The stress thus calculated are then used as input for the kinematic update for the next time step.

7.3.5 Solution strategy for solving for the nodal values of the distribution function

The typical dimension of the scaling function expansion is about 16 basis functions for the θ space and 32 basis function for the ϕ direction. Depending on the shape of the element (quadrilateral or triangle), the number of DG basis functions scales as $4N_e$ for quadrilateral element and $3N_e$ for triangular elements, where N_e is the total number of element in the mesh. Although the DG discretization allows an element-by-element decomposition strategy, the elements are coupled through the inflow boundary integrals unless the elements are ordered in a sequence that moves downstream from an inflow boundary. Hence, the typical dimension for the discrete version of the diffusion equation of a flow problem with 1000 elements is on the order of 500,000 unknowns for the Doi model. Solution of a problem of this size with a direct method is infeasible, and with an iterative method it would be very difficult even with an appropriate preconditioner. Therefore, we use a semi-implicit time-stepping method for the diffusion equations in which the orientation diffusion is treated *implicitly* and all other operators are treated *explicitly*.

Although this strategy allows an element-by-element decomposition, the stiffness matrix for each elemental matrix (of order 2,000 unknowns) has to be either stored or computed at each time step unless the Jacobian of the mass matrix in Ω^{2D} is a constant [161]. This greatly restricts the types of elements and problems that can be simulated with the hybrid method. By taking advantage of the tensorial product nature of the basis functions used in each subspace, we construct a node-by-node decomposition strategy to fur-

ther decrease the number of unknowns in each subproblem and allow the stiffness matrix for each subproblem to be the same at each node. This strategy is described in Chapter 4 and is summarized below:

Consider an entry in the mass matrix,

$$\begin{aligned} M_{\mu\nu} &\equiv \int \Phi_\mu \Phi_\nu d\Omega \\ &= \iint (\Psi_i \varphi_m)_{\mu = \mu(i, m)} (\Psi_j \varphi_n)_{\nu = \nu(j, n)} d\Omega^{2D} d\Omega^{\text{ori}} \end{aligned} \quad (7.31)$$

where $\mu(i, m)$ is the mapping from the i -th basis function in Ω^{2D} and m -th basis function in Ω^{ori} to the μ -th basis function in the space of $\Omega^{2D} \cup \Omega^{\text{ori}}$. By factoring out the integration over Ω^{2D} from that over Ω^{ori} , the stiffness matrix for a quadrilateral element can be represented as:

$$\begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \quad (7.32)$$

where S_{ij} is product of the i - j component of the mass matrix of the physical space and the mass matrix of the orientational space, i.e. $S_{ij} \equiv (\int \Psi_i \Psi_j d\Omega^{2D}) (\int \varphi_m \varphi_n d\Omega^{\text{ori}})$. We first apply the inverse of the mass matrix (M^{-1}) in Ω^{2D} to Eqn 7.32 and then solve each stiffness matrix in Ω^{ori} independently. This method can be shown schematically as,

$$\begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \rightarrow \begin{bmatrix} M_{1j}^{-1} S_{j1} & 0 & 0 & 0 \\ 0 & M_{2j}^{-1} S_{j2} & 0 & 0 \\ 0 & 0 & M_{3j}^{-1} S_{j3} & 0 \\ 0 & 0 & 0 & M_{4j}^{-1} S_{j4} \end{bmatrix} \rightarrow \begin{bmatrix} I & 0 & 0 & 0 \\ 0 & I & 0 & 0 \\ 0 & 0 & I & 0 \\ 0 & 0 & 0 & I \end{bmatrix} \quad (7.33)$$

The mass matrix in Ω^{2D} is of dimension three (for triangles) and four (for quadrilaterals) and therefore can be easily stored or even computed at each time step for each element. This strategy thus allows us to use or study a large variety of meshes and problems

where the mass matrix in Ω^{2D} is different from element-to-element. Some of these include the use of quadrilateral elements and the study of axisymmetric flow geometries.

The stiffness matrix in Ω^{ori} has only 513 unknowns. Both LU decomposition solvers (DGETRF/DGETRS in LAPACK) and iterative solvers (GMRES with ILUTP preconditioner) have been tested. Depending on the complexity of the stiffness matrix, iterative solvers perform at least as fast as the LU decomposition solver.

7.4 Simulation Results for a Planar Pressure-driven Channel Flow

In this section, simulation results for a planar pressure-driven channel flow are presented. We first simulate the flow of the Doi model with no intrinsic length scale in the model. This will recapture and confirm the results observed by Nayak that infinitesimal structure refinement occurs for all De . Then, the effect of spatially nonuniform concentration is explored.

The computation domain is set such that the length of the channel is 10 times longer than the width, which is chosen to be the characteristic length scale of the geometry. Periodic conditions are assigned to the inflow and outflow surface and hence the flow rate is set by fixing the pressure gradient. The line $y = 0$ corresponds to a the line of symmetry, and $y = 1$ corresponds to a zero velocity boundary. The finite element mesh used to discretize this domain consists of 300 quadrilateral elements. The viscosity ratio β is set to 0.1, and a time step size of $\Delta t = 0.005$ is used. Two Deborah numbers, $De = 1$ and $De = 5$, are investigated. The local dimensionless shear rate for the Newtonian velocity profile varies from zero at the centerline to two at the wall.

7.4.1 Doi model

For the homogeneous Doi model, the potential (strength) parameter U is set to 6. This value is chosen to ensure a nematic solution throughout the domain. Nayak [161] and Grosso et al. [93] show that various time-dependent states (tumbling at low De , wagging at

medium De and flow aligning at high De) are present for the range of dimensionless shear rates in the pressure-driven channel flow for a Newtonian fluid. The different frequencies in the time dependent states lead to a variation in structure parameter and director orientations in the cross-stream direction. Sharp gradients in structure will form and translate across the channel width. In the absence of interaction between streamlines, this texture exists with its structure varies with time. Furthermore, because extremely long period oscillations are present in this flow, new oscillatory modes will continuously be introduced into the interior of the channel, resulting in an increase in the number of sharp cross-stream gradients with time. Thus, as time increases, the texture length scale should continuously decrease. We refer this decrease of texture length scale as *texture refinement* even though the director field, defined as the eigenvector corresponding to the dominant eigenvalue of the structure tensor, points more or less uniformly along the flow direction.

The evolution of the centerline velocity with time for the channel flow problem at $De = 1$ and $De = 5$ is shown in Figure 7.1.

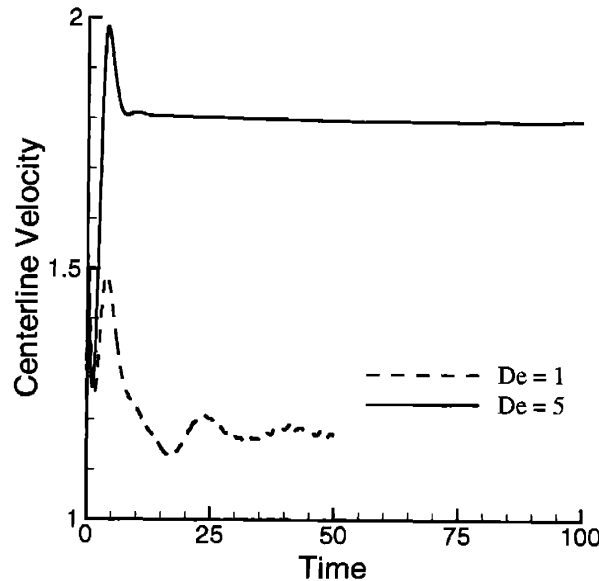


Figure 7.1: Time evolution of centerline velocity for pressure driven channel flow of the Doi model with $U = 6$. Blue solid line corresponds to the calculation with $De = 1$, and the red solid line corresponds to the calculation with $De = 5$

For $De = 1$, the time evolution of the centerline velocity eventually becomes erratically oscillatory after a smooth initial period. The onset of this oscillatory behavior is attributed to the refinement of texture beyond the degree that can be resolved by the mesh. This is confirmed by examining a time sequence of the cross-stream structure parameter profile. Figures 7.2 shows texture refinement at six different dimensionless times, $t = 0, 5, 15, 25, 35, 45$.

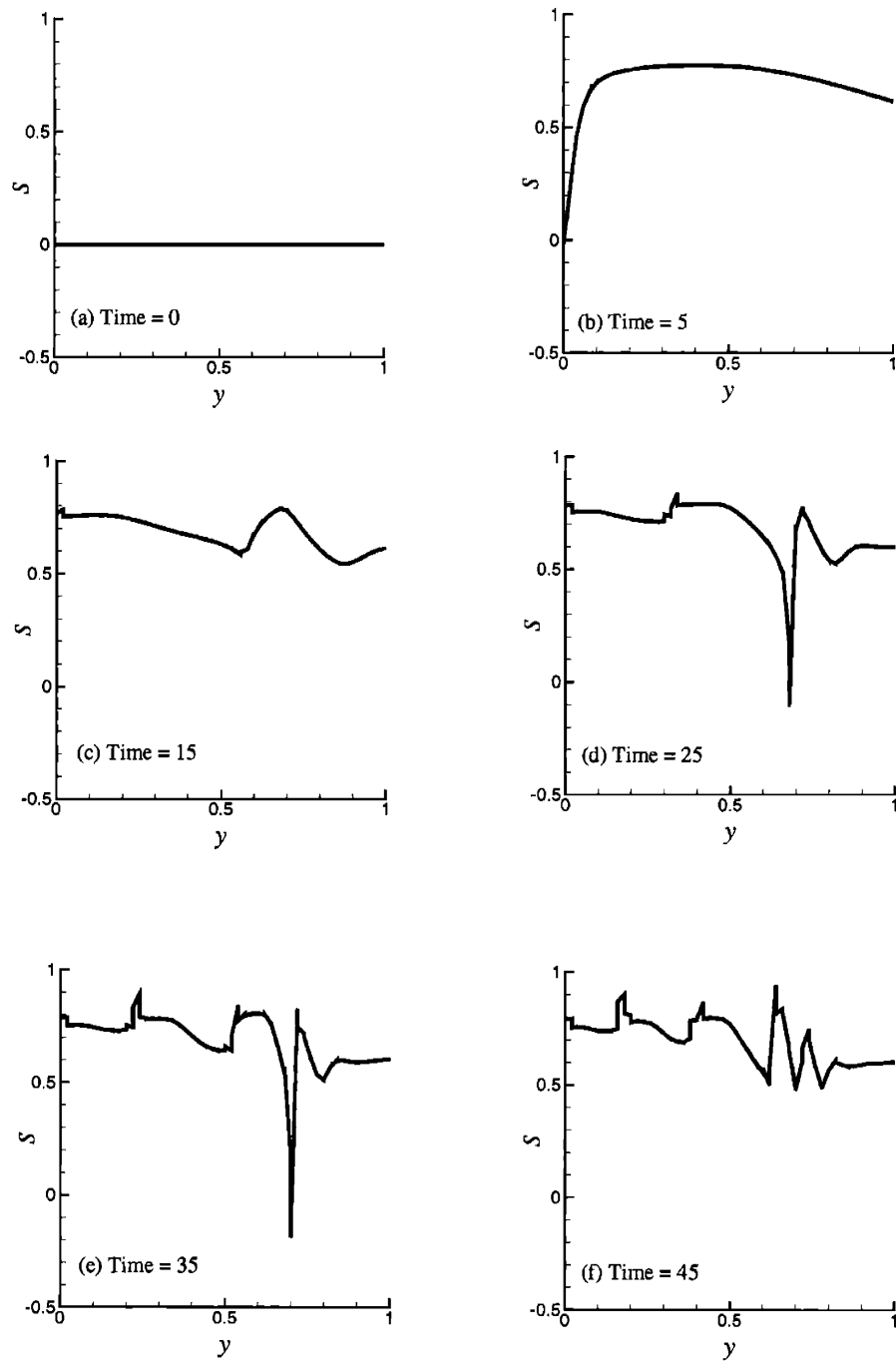


Figure 7.2: Time evolution of the cross-stream structure profile in pressure-driven channel flow at $De = 1$ and $U = 6$. Mesh contains of 60 elements cross-stream. Results are shown at dimensional times of (a) 0, (b) 5, (c) 15, (d) 25, (e) 35, (f) 45 relaxation times.

At $t = 15$, two abrupt changes in the structure parameter have developed across the channel width. Such abrupt changes created by sharp gradients in structure are conceptually close to the idea of *disclinations*. The difference is that conventional disclinations correspond to abrupt changes in director orientation, rather than structure. At this value of time, the smoothness of the 60 element result has begun to erode. By $t = 25$ the buildup of texture shows a discontinuity, due to the poor resolution of the finite element mesh. A more refined mesh has been used, but the discontinuity is still observed, albeit at a later time. 'Waves' in the director orientation are created near the wall due to the fast tumbling/wagging motion, and then move towards the centerline. These 'waves' are generated by the local periodic motion of a particular director orientation state in the cross-stream direction. Because the director at the center streamline will never tumble, the 'waves' generated by the tumbling in the interior of the channel concentrate as they approach the centerline, and texture refinement will be infinite. This is a direct result of fact that the period of the oscillations rises towards infinity as the centerline is approached. In a real liquid crystalline polymer system, such infinite buildup of texture is prevented or smoothed by cross-streamline interactions through the velocity field, molecular diffusion, or the so-called distortional stress. In the absence of these effects, the Doi model predicts infinite buildup of texture.

The comparison of the steady centerline velocity profile shown in Figure 7.1 for $De = 5$ at long times with the unsteady centerline velocity evolution for $De = 1$ suggests that at high De the flow aligning state may actually stabilize disclination refinement. However, a careful analysis of the time sequence of the structure profile across the channel (as shown in Figure 7.3) suggests that the rapid disclination formation and refinement does occur, and one should anticipate the centerline velocity would start to oscillate after a long period of time, on the order of 100 or even 200 relaxation times. At $De = 5$, the build-up or

structure refinement is actually very slow. After $t = 20$, the first discontinuity in the structure profile is observed. This texture and its refinement appear in a small region ($0 < y < 0.3$) of the flow domain. The size of this small region is in accord with the local shear rates, which correspond to the shear rates for the time periodic motions driving the texture formation. Even after 100 relaxation times, the presence and refinement of structure is still evident only in a small region near the wall.

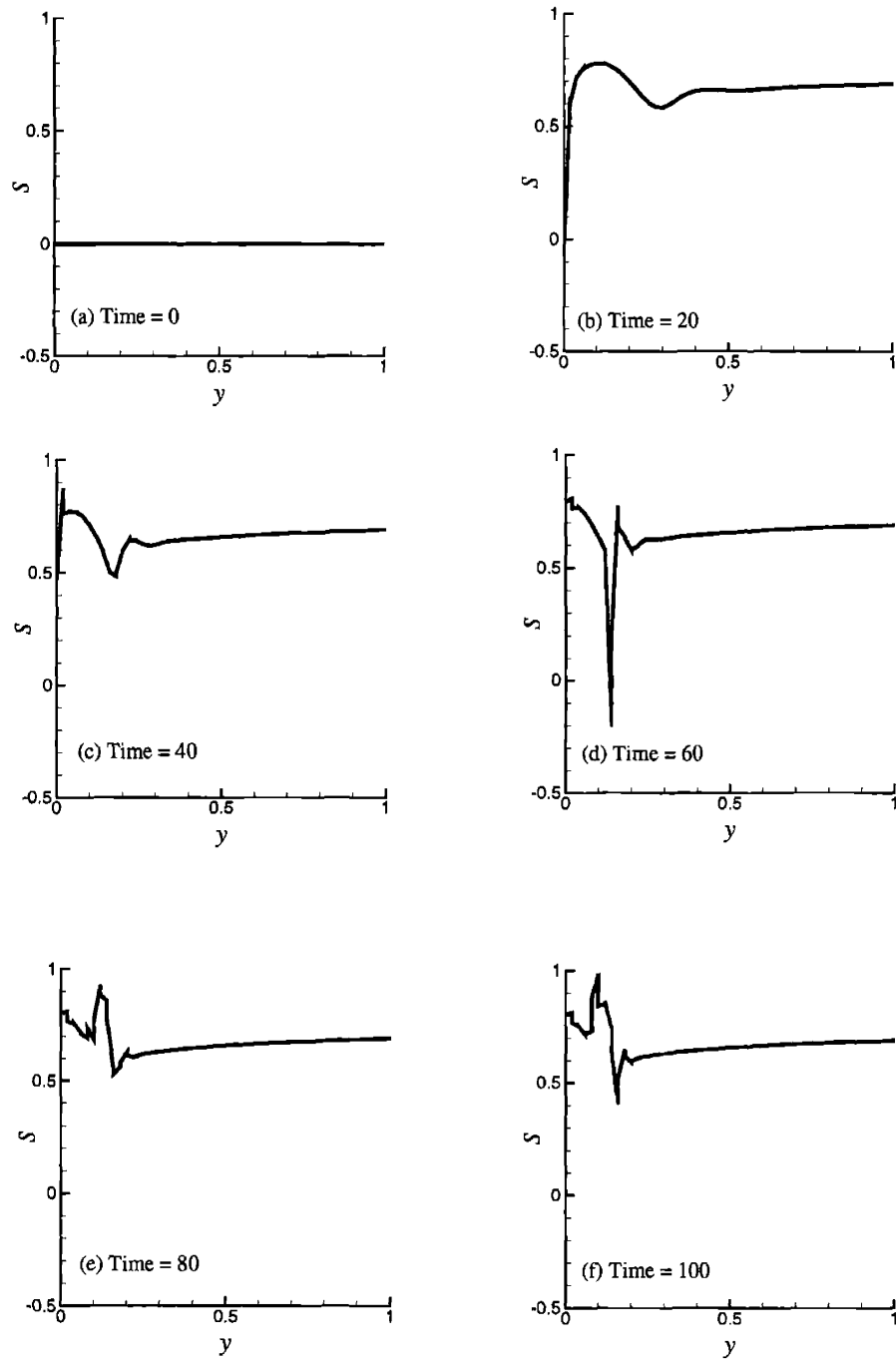


Figure 7.3: Time evolution of the cross-stream structure profile in pressure-driven channel flow at $De = 5$ and $U = 6$. Mesh contains of 60 elements cross-stream. Results are shown at dimensional times of (a) 0, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100 relaxation times.

We notice a significant slowing of the refinement dynamics in our calculations as compared with the disclination refinement dynamics computed by Nayak [161]. This is because of the different types of elements used in this study and by Nayak. Our calculations are performed with quadrilateral elements, and Nayak's results are obtained by using triangular elements. At any specific node in the space, the number of adjacent nodes for the discontinuous Galerkin method is different for quadrilateral and triangular elements. Because the disclination refinement is a numerical artifact for the monodomain model, the additional "communication" between the nodes leads to more rapid refinement dynamics.

7.4.2 Effect of spatial concentration nonuniformities

In this section, simulation of the Doi model with spatially varying concentration (Eqns 7.5 and 7.7) is performed. For simplicity, we set $U(n) = U = 6$, $\sigma = 1$, and $D_{tr} = 0.04$. Similar to the monodomain model, sharp gradients in structure will form and dissipate across the channel width under flow conditions for which time-periodic states are the stable states. However, this texture should be stabilized by cross-streamline diffusion and, hence, a stable structure profile observed. Number density fluctuations will also "smooth out" the extremely long period oscillations present in this flow, and a smooth structure profile is expected. The key issue here is whether spatially varying concentration will lead to formation of disclinations or defects that is similar to that observed in experiments or predicted by models with distortional stresses.

Figure 7.4 shows the evolution of the centerline velocity for both $De = 1$ and $De = 5$ for this model. After a overshoot of the centerline velocity, the velocity reaches steady state after approximately 50 relaxation times. This steady state centerline velocity is larger for $De = 5$ than for $De = 1$. Confirmation of the steady state profile can be done by looking at the structure profile across the channel. This is shown in Figures 7.5 (for $De = 1$) and 7.6 (for $De = 5$).

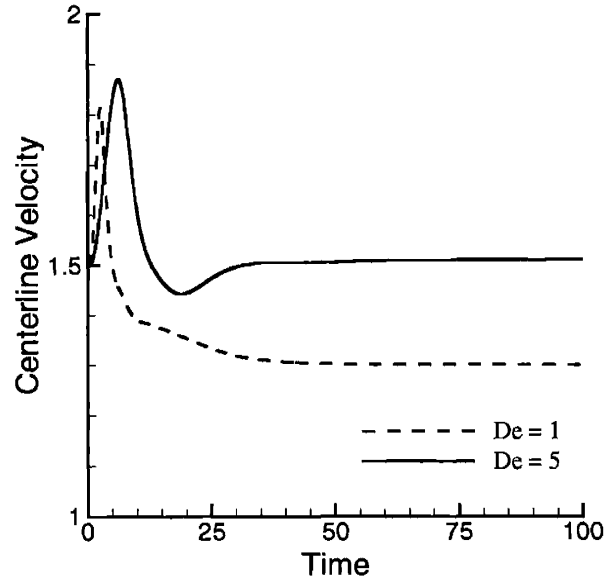


Figure 7.4: Time evolution of centerline velocity for pressure driven channel flow for the liquid crystalline model that allows for spatially varying concentration. We take $U = 6$, $\sigma = 1$ and $D_{lr} = 0.04$

Figure 7.5 shows a sequence of pictures of the structure profiles across the channel at intervals of 10 relaxation times. The structure profile has two peaks, one at the centerline with $S \approx 0.7$ and the other at the wall surface with $S \approx 0.65$. After a fast transient state, the structure profile is relatively unchanged after $t = 20$. This is consistent with the steady state centerline velocity profile for $De = 1$ in Figure 7.4.

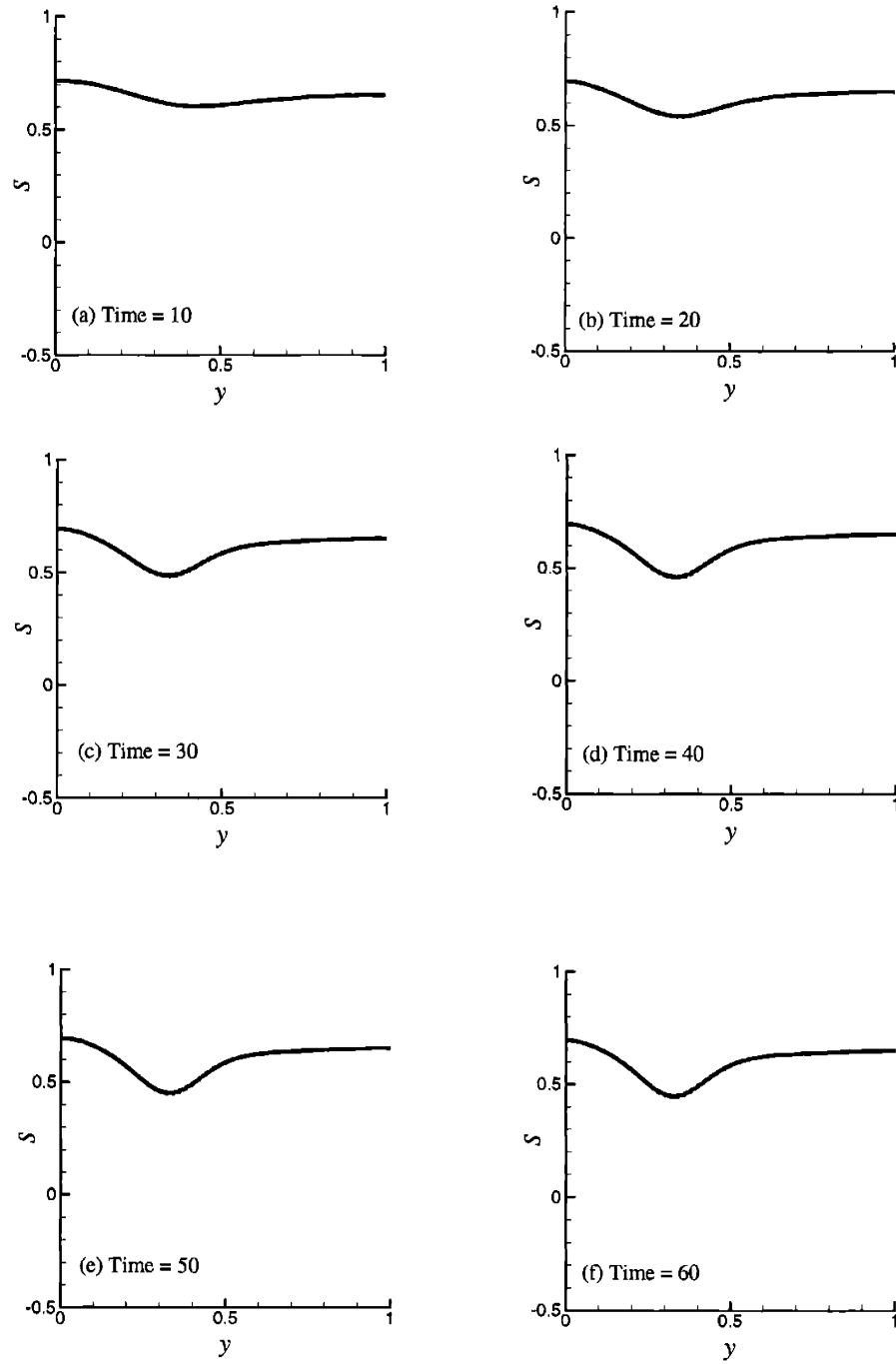


Figure 7.5: Time evolution of the cross-stream structure profile in pressure-driven channel flow at $De = 1$ and $U = 6$. Mesh contains 60 elements in the cross-stream. Results are shown at dimensional times of (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, and (f) 60 relaxation times. A steady structure profile is achieved after 40 relaxation times.

Figure 7.6 shows snapshots of the structure profile evolution for $De = 5$. The time interval between each snapshot is five relaxation times. After a short transient period, a steady state structure profile is formed after only 10 relaxation times.

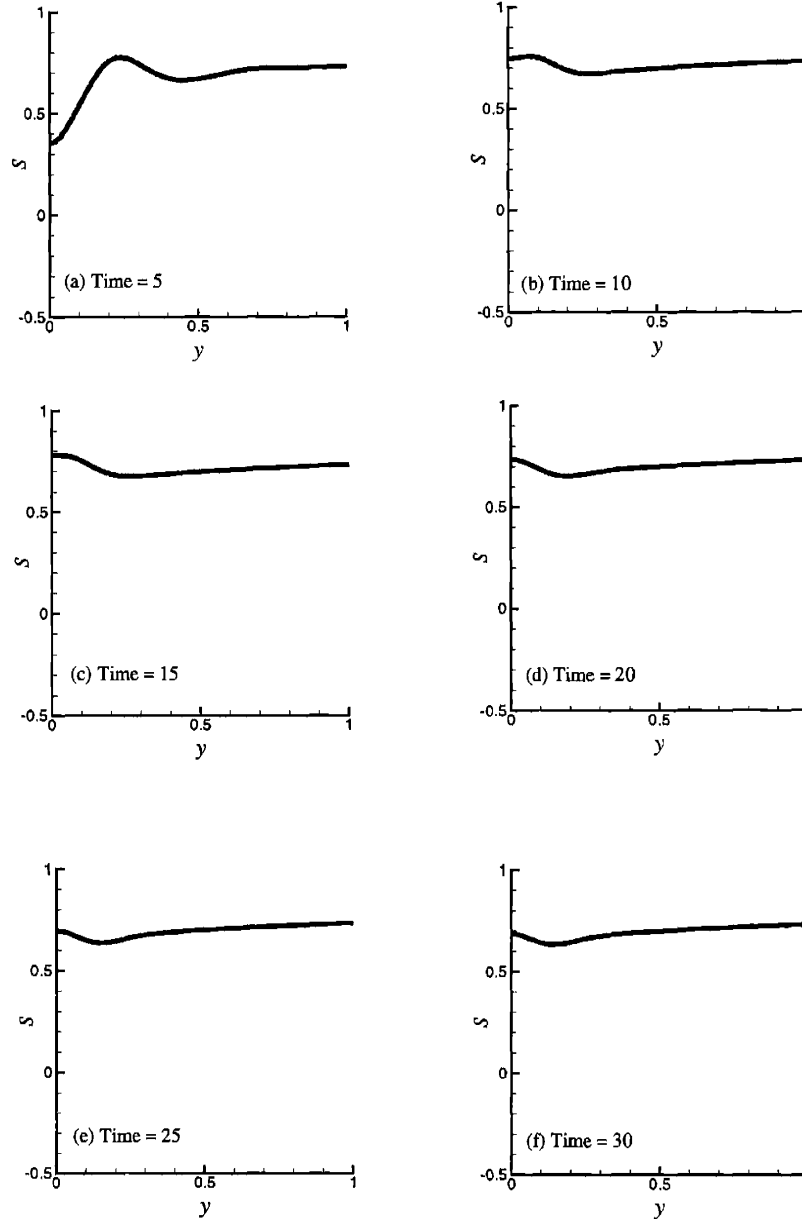


Figure 7.6: Time evolution of the cross-stream structure profile in pressure-driven channel flow at $De = 5$ and $U = 6$. Mesh contains 60 elements in the cross-stream direction. Results are shown at dimensional times of (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, (f) 30 relaxation times. A steady state structure profile is achieved after 20 relaxation times.

Finally, the steady state structure profile and the number density profile for $De = 1$ and 5 are compared and contrasted in Figure 7.7. In agreement with the predictions of the homogeneous Doi model, strong flows (high De) align molecules and hence reduce spatial structure variations. Whereas the monodomain Doi model leads to structure refinement to a small length scale that is smaller than the resolution of the finite element analysis, the inclusion of spatially dependent concentration stabilizes this refinement, and hence a steady state is achieved. Both the structure and the number density variations are smaller for $De = 5$ than $De = 1$. The maximum variation for the number density across the channel is less than 20 % for $De = 1$ and about 5% for $De = 5$.

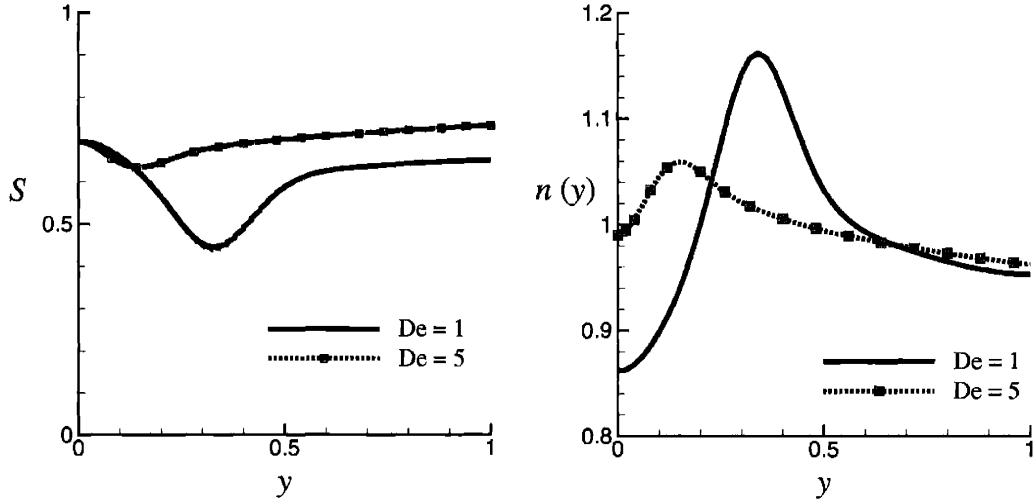


Figure 7.7: Steady state profiles of the structure parameter and the number density for two different values of De .

7.5 Conclusion

In this chapter, we simulate the Doi model in a nonhomogeneous flow by using a mixed numerical method that allows viscoelastic flow calculations with constitutive description based directly on the diffusion equation from kinetic theory. In this numerical approach, scaling function expansions are used to discretize the configuration space of the distribution function at every node in a complex flow, and the spatial variation of the distribution is then computed by using a mixed finite element discretization. For the monodomain Doi

model, The standard discontinuous Galerkin method is applied. The local discontinuous Galerkin method is employed to include the effects of spatial concentration variations. A novel two-stage, node-by-node decomposition strategy is devised to decouple the solution for the spatial variation of the distribution function from its dependence on the configuration space. This leads a significant speed-up over the implementation of Nayak. More importantly, the node-by-node decomposition allows the use of finite element with non-constant Jacobians for the transformation between the physical and isoparametric spaces, as well as the study of fluid mechanics problems that are expressed in coordinate systems other than Cartesian coordinates. The application of this strategy to molecular models with larger number of degrees-of-freedom (such as the reptation model) will be described in detail in the next two chapters.

Simulation of the homogeneous Doi model is first performed to review and confirm the simulation by Nayak [161]. Although the homogeneous Doi model is a monodomain model in the sense that there is no interaction between the different nodes in a physical space, it can predict the texture formation and refinement due to the presence of a span of frequencies for the time periodic motion in the inhomogeneous flow field that produces “waves” of time periodic motions across the channel width. This is in agreement with the simulation result by Nayak. Because the texture refinement is artificial and depends largely on mesh resolution, we expect different types of meshes will lead to different texture refinement dynamics. The simulation results in this chapter show slower refinement dynamics than the simulation results of Nayak. We attribute this difference to the artificial dynamics of the texture refinement. Our calculations are performed with quadrilateral elements, and Nayak’s results are obtained by using triangular elements. At any specific node in the space, the number of adjacent nodes for the discontinuous Galerkin method is dif-

ferent for quadrilateral and triangular elements. We believe that the additional “communications” between the nodes leads to a faster refinement dynamics.

One of the simplest way to introduce an intrinsic length scale is by introducing translational diffusion. We postulate a diffusion equation that includes the effects of translational diffusion and spatially nonuniform concentration. Although the resulting molecular model consists of *ad hoc* elements, it nevertheless shows that the presence of an intrinsic length scale can stabilize the dynamics of the disclination refinement observed in an inhomogeneous flow of the monodomain Doi model. The resulting steady state structure and number density profiles do not vary significantly for the parameter range studied in this chapter. The resolution of these profiles appears to be related to De , with a sharper structure observed at low De . The steady-state nematic director profile points more or less along the flow direction. This suggests that the structure observed spatially nonuniform concentration is different from that commonly referred to as a disclination, which is defined based on spatially varying director orientation. We attribute this to the lack of a distortional stress in the model. Because of this deficiency, extension of the calculation to complex geometries will not yield any useful information.

Incorporation of new physics and concepts such the distortional stress and other inhomogeneous phenomena are necessary to advance the understanding and modeling of transport phenomena in liquid crystal polymers. This can be done by using the kinetic theory approach described in Chapters 2 and 5. While rigorous theories at molecular level yields models that are capable of describing the dynamics of liquid crystalline polymers, the requirement of using a high order polynomial expansions to represent the inhomogeneous mean-field potential and lack of precise mathematical characteristics of the resulting diffusion equation prohibit the calculation with an advanced theory. Much work is needed in this area, but there appears to be no easy route to progress in this problem.

Chapter 8

A Mixed Finite-Element/Wavelet-Galerkin Method for Multiscale Simulations of Viscoelastic Flows with Reptation Models for Concentrated Polymer solutions and Melts

8.1 Introduction

One of the most important goals in computational rheology is to provide a tool for systematic analysis of effects of various process conditions on the properties of a final product. These properties in turn depend largely on the underlying molecular orientation and alignment. Hence, a successful computational rheology model has to be able to describe the effect of polymers on macroscopic flow fields and to be able to provide qualitative or quantitative descriptions about the underlying molecular arrangements. As a result, multiscale simulations of viscoelastic flows that directly couple a kinetic theory model with macroscopic flow calculations have become the center of attention in computational rheology for the last decade. Many of these advances are reviewed by Suen et al. [210] and Keunings et al. [115]. These multiscale calculations, or so-called micro-macro calculations, are derived based on an operator splitting time integration method that decouples the macroscopic flow calculation from the microscale simulation of the molecular structures and conformations. The major challenge in the multiscale simulation is the additional degrees of freedom that are necessary to represent the microstructure information from the kinetic theory. Most developments of either microscale calculations or macroscopic computations are geared towards decoupling the large number of degrees-of-freedom into a large number of small problems, each with a small number of degrees-of-freedom. This is one of the major reasons for the success and popularity of using Brownian dynamics in a multiscale calculation such as the CONNFESSIT¹ approach proposed by Laso and and

Öttinger. This approach, in turn, could be considered as a combination of two multiscale simulation ideas introduced by Fan [69] (the use of microstructural model to calculate the stress tensor in the equation of motion), and by Petruccione and Biller [175] (the use of Brownian dynamics to simulate microstructure). The formulation of CONNFESSIT makes use of an operator splitting time integration method that decouples the flow field calculation by finite element analysis from the microstructure simulation by Brownian dynamics. For kinetic theory models with diffusion equations that are linear with respect to the distribution function, the resulting set of stochastic differential equations are independent of each other and hence is most suitable for computations in a parallel architecture. Two of the major draw-backs of this approach are convergence and particle tracking. Although increasing the number of trajectories in a single calculation improves convergence and accuracy of the calculation, it also increases the expense of particle tracking. Since the original publication, most researches on this method has focused on improving convergence by developing various variance reduction techniques based on increasing the spatial correlation of Brownian trajectories [102] and reducing the expense of particle tracking [224].

In addition to convergence and accuracy issues, there are classes of kinetic theory models that are difficult to simulate by Brownian dynamics. One example is the rigorous reptation model proposed by Doi and Edwards [59], where the functional form of the drift dynamics of the normalized link number is different for different regions of the configuration space. Furthermore, in some extreme cases, Brownian dynamics is not even a feasible simulation method for models whose diffusion equation contains “reaction” terms such as presented in a recently proposed thermodynamically admissible reptation model by Fang, et al.. [74]. Because the diffusion equation is no longer a Fokker-Planck equation, there

1. Calculation of Non-Newtonian Flows: Finite Element and Stochastic Simulation Technique

does not exist a corresponding set of stochastic differential equations; and, hence, Brownian dynamics simulation cannot be performed unless approximations are made to the treatment of the reaction term. Moreover, although the Brownian dynamics simulation method is promising in simulating molecules with a large number of degrees-of-freedom, CONNFFESSIT simulations with reasonable error are limited to simple molecular models such as elastic dumbbells, which have a small configuration space. All these reasons drive the development of direct solution methods for the diffusion equations in kinetic theory models.

The first multiscale viscoelastic flow simulation with a fully deterministic method is due to Fan [69]. He used the boundary element method to calculate the macroscopic flow variables and approximated the configuration space distribution function of a rigid-rod model with a spherical harmonics expansion. It is a general misconception that direct solution methods for the diffusion equation are limited to simulations of rigid rod models such as dilute suspensions of rod-like macromolecules and monodomain, liquid crystalline polymers. Extensions of the deterministic methods to a larger configuration space model have been developed by Warner and Fan in the simulation of FENE dumbbell model [67] and the unapproximated Bird-de Aguiar model [68]. In this chapter, the wavelet-Galerkin method presented in a Chapter 6 is extended to simulate reptation models for concentrated polymer solutions and melts.

Simulating reptation models in a complex flow environment has been a rapidly growing area in the recent years [228, 222, 224]. In addition to the practical importance of simulating polymer melt flows in complex flow geometries, advances in experimental and numerical techniques have also led to a desire to model and simulate reptation models for concentrated polymer solutions and melts in a complex flow environment. In a series of papers [228, 102, 103], van Heel and coworkers have introduced the deformation field

method for simulating the Doi-Edwards model and other integral models. This method is essentially an Eulerian numerical technique for simulating constitutive equations in integral form. Although a large number of “improved” reptation models are based on modifying the memory function of the constitutive equation [106, 147, 158], more rigorous derivations for an improved description of the reptation dynamics lead to a set of partial differential equations [168, 171, 74]; and hence the deformation field method is not applicable.

The goal of this chapter is to demonstrate the use of fully deterministic methods in performing a multiscale viscoelastic flow simulation in which the stress tensor is calculated directly from the solution of the diffusion equation. We present a coupled wavelet-Galerkin/finite-element method for calculating viscoelastic flows of reptation models for concentrated polymer solutions and melts. This method combines the strengths of the stability of the elastic-viscous stress splitting formulation of DEVSS-G, the robust and accurate representation of the orientation space distribution by a wavelet-Galerkin method reported in a previous publication, and a decoupling strategy combining the discontinuous Galerkin method and a node-by-node decomposition method to allow an efficient divide-and-conquer strategy. A semi-implicit time stepping method or a strategy of using an iterative method to calculate the steady state solution allows a decoupled calculation and is critical to our method.

The rest of this chapter is organized as follows. The governing equations and their mathematical formulations are presented in Section 8.2, where the diffusion equation and the stress tensor expressions for four different first generation reptation models are shown in a unified manner to facilitate comparison between these models. The numerical method for simulating these kinetic theory models is the focus of Section 8.3. In Section 8.4, the sample calculations of flow around an isolated cylinder for the reptation models are pre-

sented. In addition to illustrating the convergence properties and the effect of different viscous stress tensor expression, we study the characteristics of the parallel computation as well as compare the wavelet-Galerkin/finite-element method with corresponding Brownian configuration fields calculations. Finally, conclusions are offered in Section 8.5.

8.2 Mathematical formulation

The governing equations and mathematical formulations are presented in this section. Although including inertia in the equation of motion causes no extra technical difficulty, we consider calculations of isothermal, inertialness flows only. The equation of motion and the equation of continuity are written in the DEVSS-G formulation for a steady-state and inertialness flow. In terms of discretized variables, these equations are

$$\begin{aligned} \nabla \cdot [\nabla \mathbf{v}_h + \nabla \mathbf{v}_h^T] - \nabla \cdot [\boldsymbol{\tau}_{p,h} + (1 - \beta)[\mathbf{G}_h + \mathbf{G}_h^T] + p_h \boldsymbol{\delta}] &= \mathbf{0} \\ \nabla \cdot \mathbf{v}_h &= 0 \\ \mathbf{G}_h - \nabla \mathbf{v}_h &= 0 \end{aligned} \quad (8.1)$$

where the dimensionless velocity field $\mathbf{v}_h(\mathbf{r})$ is scaled with a characteristic velocity V , and the dimensionless polymer contribution to the stress tensor $\boldsymbol{\tau}_{p,h}(\mathbf{r})$ and pressure $p_h(\mathbf{r})$ are scaled with $\eta_0 V/L$ where L is a characteristic length and η_0 is a characteristic viscosity. $\beta \equiv \eta_s/\eta_0$ is the viscosity ratio between solvent viscosity η_s and η_0 . $\mathbf{G}_h$ is the discretized velocity gradient. In the limit of $h \rightarrow 0$, the DEVSS-G formulation reduces to the viscous formulation.

Traditionally, the polymer contribution to the stress tensor is written as a closed constitutive equation. In this work, the stress tensor is written in terms of moments of a distribution function, whose evolution is in turn calculated directly from a configuration space distribution function. The evolution of this configuration distribution function is governed by a diffusion equation. In this work, we considered the double reptation model proposed

by Bird, et al. [20] for simulating the rheology of concentrated polymer solutions and melts.

8.2.1 Generalized Double Reptation model

The generalized double reptation model developed by Bird, et al. [20] makes use of a diffusion equation or a Fokker-Planck equation to describe the dynamics of a reptation model under the influence of a flow field. Instead of repeating the details of the model development, the diffusion equation for the configurational distribution function $f(\mathbf{u}, \sigma, t)$, is presented as follows:

$$\frac{\partial f}{\partial t} + \text{Dev} \cdot \nabla f = -\text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u} \mathbf{u} \mathbf{u}] f + \epsilon_{\text{Br}} \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial f}{\partial \mathbf{u}} + \frac{\partial^2 f}{\partial \sigma^2} \quad (8.2)$$

Here $\mathbf{u}$ is a unit vector that denotes the orientation of a particular segment i along the polymer chain; and σ ($\sigma \in [0, 1]$) is the normalized segment number, $\sigma = i/N$, with N being the total number of segments along the polymer chain. The dimensionless time is scaled by the reptation time scale λ . De is the Deborah number defined as the ratio between the disengagement or reptation time and the characteristic flow time scale. ϵ_{Br} is the ratio between the reptation time and the segmental rotation time, which represents the partially anisotropic Brownian motion. The boundary conditions for $\mathbf{u}$ are periodic and the boundary conditions for $\sigma = 0$ and $\sigma = 1$ are,

$$f(\mathbf{u}, 0, t) = f(\mathbf{u}, 1, t) = \frac{1}{4\pi} \quad (8.3)$$

Both the Doi-Edwards and Curtiss-Bird models correspond to the diffusion equation in the pure reptation limit ($\epsilon_{\text{Br}} = 0$), where affine deformation of the tube is assumed. In this limit, Eqn. 8.2 is exactly solvable and the solution is

$$f(\mathbf{u}, \sigma, t) = \sum_{n, \text{odd}} \int_0^t \frac{n \sin(n\pi\sigma) \exp(-(n\pi)^2(t-t'))}{(1 + \gamma^{[0]} : \mathbf{u}\mathbf{u})^{3/2}} dt' \quad (8.4)$$

where $\gamma^{[0]}$ is the finite strain tensor defined in Bird, et al. [19]. Substituting this exact solution into a given stress tensor expression (c.f. Eqn 8.5) gives the constitutive equation. In the presence of the double reptation effect ($\epsilon_{\text{Br}} > 0$), however, an exact analytical solution is unavailable and the deformation fields method is not applicable because of the lack of a closed, integral form of constitutive equation. Pertubative solutions are useful but of very limited utility in complex flow calculations. Therefore, numerical methods such as the direct solution method proposed in this work or the Brownian dynamics method are the only feasible ways to explore the behavior of the model.

Calculations of the rheological properties and flow behavior of polymeric liquid require coupled simulation of the equations of change and an appropriate stress tensor expression. Starting with the generalized Kramers-Kirkwood expression and a full chain kinetic theory, Bird, et al. show that the stress tensor expression is

$$\begin{aligned} \tau_{p,h} = & -\frac{(1-\beta)}{\text{De}} \left(\int_0^1 (1 + 3\epsilon_{\text{Br}}\sigma(1-\sigma)) \langle \mathbf{u}\mathbf{u} - \frac{1}{3}\delta \rangle d\sigma \right. \\ & \left. + \epsilon_{\text{Hyd}} \text{De} \mathbf{G}^T : \int_0^1 \sigma(1-\sigma) \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle d\sigma \right) \end{aligned} \quad (8.5)$$

where ϵ_{Hyd} is the link tension coefficient that characterizes the anisotropic frictional properties of the polymer chain in a concentrated solution or melt. In the limit of $\epsilon_{\text{Br}} = \epsilon_{\text{Hyd}} = 0$, Eqn. 8.5 reduces to the original Doi-Edwards model. For $\epsilon_{\text{Br}} = 0$, Eqn. 8.5 corresponds to the Curtiss-Bird model. Although the Curtiss-Bird model fixes a number of deficiencies of the Doi-Edwards model in predicting rheological phenomena, it does not agree with the stress-optic law. Therefore, most efforts to develop new reptation models are essentially attempts to replicate the predictions of the Curtiss-Bird model

while keeping $\epsilon_{\text{Hyd}} = 0$ [59, 74]. For the double reptation model, the incorporation of the double reptation effect into the stress tensor expression was suggested to be inconsistent with a thermodynamics formulation of the time evolution equations for nonequilibrium systems developed by Jonschaap, and hence is inconsistent with thermodynamics [113]. Öttinger incorporated the effects of double reptation into the stress tensor expression through the viscous stress by introducing a new parameter ϵ_2 .

$$\tau_{p,h} = -\frac{(1-\beta)}{\text{De}} \left(\int_0^1 \langle \mathbf{u}\mathbf{u} - \frac{1}{3}\delta \rangle d\sigma + \text{De} \mathbf{G}^T : \int_0^1 (\epsilon_{\text{Hyd}} \sigma (1-\sigma) + \epsilon_2) \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle d\sigma \right) \quad (8.6)$$

However, in the light of the GENERIC structure developed by Öttinger and Germela [170], Eqn. 8.5 actually agrees with the equation formulation by replacing the osmotic pressure in Eqn. 122 of reference [170] with the elastic stress contribution (the first term in Eqn. 8.5). Hence, whether Eqn. 8.5 is consistent with thermodynamics is still arguable or debatable. However, it has been shown that the use of the stress tensor expression Equation 8.6 with a small value of ϵ_2 (and with $\epsilon_{\text{Hyd}} = 0$) gives a monotonically increasing shear stress with shear rate. This small value of ϵ_2 ensures better agreement with the stress-optical law than the Curtiss-Bird model or the general double reptation model with stress tensor given by Equation 8.5. In this work, however, both stress tensor expressions will be used in simulations to test the usefulness of each expression in the context of complex flow calculations.

8.3 Numerical method

8.3.1 Discretization of the diffusion equation

The equations of change and $\mathbf{G}$ -interpolate equations (Eqn. 8.1) are discretized by a standard mixed Galerkin finite element method, as described in detail elsewhere [200]. We will not repeat the discussion here except to note that the approximation spaces for $(\mathbf{v}_h, p_h, \mathbf{G}_h)$ are chosen to satisfy the *inf-sup* compatibility approximation for the Stokes problem. In this section, we focus on the discretization of the diffusion equation (Eqns. 8.2 and 8.3) and the stress tensor expressions.

If we assume the distribution function to be $f(\mathbf{r}, \mathbf{u}, \sigma, t) = 1/4\pi + \hat{f}(\mathbf{r}, \mathbf{u}, \sigma, t)$, then the diffusion equation for the double reptation model becomes

$$\frac{\partial \hat{f}}{\partial t} + \text{Dev} \cdot \nabla \hat{f} = 3\text{De} \mathbf{G} : \mathbf{u} \mathbf{u} - \text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u} \mathbf{u} \mathbf{u}] \hat{f} + \epsilon_{\text{Br}} \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial \hat{f}}{\partial \mathbf{u}} + \frac{\partial^2 \hat{f}}{\partial \sigma^2} \quad (8.7)$$

with the modified boundary conditions for $\hat{f}(\mathbf{r}, \mathbf{u}, \sigma, t)$ as

$$\hat{f}(\mathbf{r}, \mathbf{u}, 0, t) = \hat{f}(\mathbf{r}, \mathbf{u}, 1, t) = 0 \quad (8.8)$$

The computational domain for the diffusion equation $\Omega \subset \mathbb{R}^{2+c}$ (where c is the dimension of the configuration space) is first divided into two subdomains. The first subdomain is the projection of the computational domain onto the physical space (Ω^{2D}). A mesh discretization is defined for Ω^{2D} that consists of a set of conforming, non-overlapping subdomains which are either triangles or quadrilaterals. The discretization of the diffusion equation in Ω^{2D} is performed by the discontinuous Galerkin method where the approximation for $\hat{f}_h(\mathbf{r}, \mathbf{u}, \sigma, t)$ in Ω^{2D} is constructed by piece-wise linear polynomials that are discontinuous across boundaries. These polynomials are bilinear for quadrilateral elements ($S^h(\Omega^{2D}) \subset \mathbb{Q}_1(\Omega^{2D})$) and linear for triangular elements ($S^h(\Omega^{2D}) \subset \mathbb{P}_1(\Omega^{2D})$). The weak form in DG formulation for the diffusion equation for each element T_e is therefore written as: Find $\hat{f}_h \in S^h(\Omega^{2D})$ in all elements T_e such that for all $\Psi \in S^h(\Omega^{2D})$,

$$\begin{aligned} \left(\Psi, \frac{\partial}{\partial t} M(\hat{f}_h) \right)_{T_e} &= (\Psi, [\text{De}(\mathbf{v} \cdot \nabla M(\hat{f}_h)) - \mathcal{L}(\mathbf{G}, \hat{f}_h)])_{T_e} \\ &\quad - \left(\Psi, \mathbf{n} \cdot \mathbf{v} \text{De} M(\hat{f}_h - \hat{f}_h^-) \right)_{\partial T_e^-} \end{aligned} \quad (8.9)$$

where $\mathcal{L}(\mathbf{G}, \hat{f}_h)$ is the weak form of right hand side of the diffusion equations (Eqns 8.2 and 8.5) in the configuration space $\Omega^{\text{con}} \equiv \Omega \cap \Omega^{2D}$ and $M(\hat{f}_h)$ is the projection of $\hat{f}_h$ onto Ω^{con} . ∂T_e^- is the inflow surface of the element ($\partial T_e^- = \{\mathbf{x} \in \partial T_e^- : (\mathbf{n} \cdot \mathbf{v}) \leq 0\}$), with $\mathbf{n}$ as the outward unit normal vector on the inflow surface with respect to element, and the superscript “ $-$ ” refers to the value of the distribution function along the inflow boundary in the upstream element, whereas variables without a superscript refer to evaluations on the interior of the element.

The configuration space for the nodal value of $\hat{f}_h(\mathbf{u}, \sigma, t)$ is further divided into two subdomains, Ω^{ori} for the projection onto the orientational space for $\mathbf{u}$ and Ω^σ for the projection onto the space for σ . Ω^{ori} is discretized with a wavelet-Galerkin method, where the diffusion equation and the configuration distribution function are approximated by the use of a scaling-function expansion, as described in detail in Chapter 6. Ω^σ is discretized by a series of finite Fourier transform [53]. The specific basis functions, $\{\sin(n\pi\sigma), n \in \text{odd } \mathbb{N}^+\}$, are chosen such that the boundary conditions for $\hat{f}_h(\mathbf{u}, \sigma, t)$ are automatically satisfied. For the generalized double reptation model, Eqn. 8.2, the finite Fourier modes are decoupled, and the weak form of the right hand side of the diffusion equation for mode n is:

$$\begin{aligned} (\Psi, -\mathcal{L}(\mathbf{G}, \hat{f}_h))_{T_e} &= \left(\Psi, \left(\varphi, \frac{3\sqrt{8}\text{De}}{4n\pi^2} \mathbf{G}^T : \mathbf{u}\mathbf{u} \right)_{\Omega^{\text{ori}}} \right)_{T_e} \\ &\quad + \left(\Psi, \left(\varphi, -\text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u}\mathbf{u}\mathbf{u}] \hat{f} + \epsilon_{\text{Bf}} \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial \hat{f}}{\partial \mathbf{u}} - n^2 \hat{f} \right)_{\Omega^{\text{ori}}} \right)_{T_e} \end{aligned} \quad (8.10)$$

where φ is the scaling function and the projection of $\hat{f}_h$ in Equation 8.9, $M(\hat{f}_h)$, is defined as $M(\hat{f}_h) \equiv (\varphi, \hat{f}_h)_{\Omega^{\text{ori}}}$.

The nodal value of the stress tensor is then found by integrating the stress tensor expression (8.5 or 8.6) over the configuration space $\mathbf{u}$ and σ . The two common integrals in the stress tensor expressions, $\int \langle B \rangle d\sigma$ and $\int \langle B \rangle \sigma(1 - \sigma) d\sigma$, are evaluated as follows:

$$\int \langle B \rangle d\sigma = \langle B \rangle_{\text{iso}} + \sum_{i \in \text{odd}} \frac{2\sqrt{2}}{i\pi} \langle B \rangle_i \quad (8.11)$$

$$\int \langle B \rangle \sigma(1 - \sigma) d\sigma = \langle B \rangle_{\text{iso}} + \sum_{i \in \text{odd}} \frac{4\sqrt{2}}{(i\pi)^3} \langle B \rangle_i \quad (8.12)$$

where $\langle B \rangle_{\text{iso}}$ is the moment B of the isotropic distribution and $\langle B \rangle_i$ is the moment B of the i -th mode of the configuration space distribution. Because only the odd values of i enter into the calculation of the stress tensor, even-modes of the configuration space distribution do not need to be calculated.

8.3.2 Solution strategy for the diffusion equation

The typical dimension of the finite Fourier space ranges from one to 10 basis functions; a typical dimension of the scaling function expansion is about 16 basis functions for the θ space and 32 basis function for the ϕ direction. Depending on the shape of the element (quadrilateral or triangle), the number of DG basis functions scales as $4N_e$, where N_e is the total number of element in the mesh. Although the DG discretization allows an element-by-element decomposition strategy, the elements are coupled through the inflow boundary integrals unless the elements are ordered in a sequence that moves downstream from an inflow boundary. Hence, the typical dimension for the discrete version of the diffusion equation of a flow problem with 1000 elements is on the order of 2,000,000 unknowns for each mode for the TAR model. Solution of such problem with a direct method is infeasible, and with an iterative method would be very difficult even with an appropriate preconditioner. Therefore, we use the semi-implicit time-stepping method for

the diffusion equations where the orientation diffusion is treated *implicitly* and all other operators are treated *explicitly*.

Although this strategy allows an element-by-element decomposition, the stiffness matrix for each elemental matrix (of order 2,000 unknowns) has to be either stored or computed at each time step unless the Jacobian of the mass matrix in Ω^{2D} is a constant [161]. This greatly restricts the type of elements and problems that can be simulated with the hybrid method. By taking advantage of the tensorial product nature of the basis function used in each subspace, we construct a node-by-node decomposition strategy to further decrease the number of unknowns in each subproblem and allow the stiffness matrix for each subproblem to be the same at each node. This strategy is sketched in Chapter 4 and a summary of the strategy is described below:

Consider an entry in the mass matrix,

$$\begin{aligned} M_{\mu\nu} &\equiv \int \Phi_\mu \Phi_\nu d\Omega \\ &= \iint (\Psi_i \phi_m)_{\mu = \mu(i, m)} (\Psi_j \phi_n)_{\nu = \nu(j, n)} d\Omega^{2D} d\Omega^{\text{ori}} \end{aligned} \quad (8.13)$$

where $\mu(i, m)$ is the mapping from the i -th basis function in Ω^{2D} and m -th basis function in Ω^{ori} to the μ -th basis function in the space of $\Omega \cap (\Omega^{2D} \cup \Omega^{\text{ori}})$. By factoring out the integration over Ω^{2D} from that over Ω^{ori} , the stiffness matrix for a quadrilateral element can be represented as:

$$\begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \quad (8.14)$$

where $S_{ij} \equiv (\int \Psi_i \Psi_j d\Omega^{2D})(\int \phi_m \phi_n d\Omega^{\text{ori}})$. We first apply the inverse of the mass matrix (M^{-1}) in Ω^{2D} to Eqn 8.14 and then solve each stiffness matrix in Ω^{ori} independently. This method can be shown schematically as,

$$\begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \rightarrow \begin{bmatrix} M_{1j}^{-1} S_{j1} & 0 & 0 & 0 \\ 0 & M_{2j}^{-1} S_{j2} & 0 & 0 \\ 0 & 0 & M_{3j}^{-1} S_{j3} & 0 \\ 0 & 0 & 0 & M_{4j}^{-1} S_{j4} \end{bmatrix} \rightarrow \begin{bmatrix} I & 0 & 0 & 0 \\ 0 & I & 0 & 0 \\ 0 & 0 & I & 0 \\ 0 & 0 & 0 & I \end{bmatrix} \quad (8.15)$$

The mass matrix in Ω^{2D} is of dimension three (for triangles) and four (for quadrilaterals) and therefore can be easily stored or even computed at each time step for each element. This strategy thus allows us to use or studies a large variety of meshes and problems where the mass matrix in Ω^{2D} is different from element-to-element. Some of these include the use of quadrilateral elements and the study of axisymmetric flow geometries.

The stiffness matrix in Ω^{ori} has only 513 unknowns. Both LU decomposition solvers (DGETRF/DGETRS) in LAPACK and iterative solvers (GMRES with ILUTP preconditioner) have been tested. Depending on the complexity of the stiffness matrix, iterative solvers perform at least as fast as the LU decomposition solver.

8.3.3 Time integration algorithm

Making use of an operator splitting strategy, our time integration method decouples the calculation of the polymer stress (by solution of the diffusion equation for the double reptation model) from the temporal updating of the velocity and pressure fields (by solution of a generalized Stokes problem). The resulting system of differential-algebraic equations is of the form

$$M \cdot \begin{bmatrix} \frac{d\hat{f}_h}{dt} \\ \frac{d\lambda}{dt} \end{bmatrix} + \begin{bmatrix} \mathcal{D}(\hat{f}_h) + \lambda \mathcal{L}'(\hat{f}_h) \\ \mathcal{L}(\hat{f}_h) \end{bmatrix} = \begin{bmatrix} \mathcal{C}(\hat{f}_h, \mathbf{v}_h, \mathbf{G}_h) \\ 0 \end{bmatrix} \quad (8.16)$$

$$\mathbf{g}(\hat{f}_h, \boldsymbol{\tau}_{p,h}, \mathbf{v}_h, \mathbf{G}_h, p_h) = 0 \quad (8.17)$$

In Equation 8.16, $\mathcal{C}$ and $\mathcal{D}$ corresponds to the weak formulation for convective and diffusive operator of the diffusion equation in the discrete space, respectively. M is the mass matrix, $\mathcal{L}$ is the normalization condition in the discrete space and $\mathcal{L}'$ is the derivative of the normalization condition with respect to the discrete variable $\hat{f}_h$. $\mathbf{g}$ consists of two equations: one is the stress tensor expression in terms of the distribution function and the other is the discretization of the generalized Stokes problem for the kinematic variables $(\mathbf{v}_h, \mathbf{G}_h, p_h)$. Equation 8.17 is invertible for the kinematic variables, so that this equation can be rewritten as

$$\begin{bmatrix} \mathbf{v}_h \\ p_h \\ \mathbf{G}_h \end{bmatrix} = \tilde{\mathbf{g}}(\boldsymbol{\tau}_{p,h}(\hat{f}_h)) \quad (8.18)$$

This equation (Eqn 8.18) is then substituted into Eqn. 8.16 to give equations written solely in terms of the distribution function variables. Next, we discretize the resulting ODEs with respect to time for a specific time advancement from t_n to $t_{n+\theta}$. A single step of the resulting semi-implicit method is derived by solving the following equation, with the increment of the variable x denoted as $\delta x \equiv x(t_{n+\theta}) - x(t_n)$.

$$\begin{aligned} S(\delta \hat{f}_h, \delta \lambda) &\equiv \begin{bmatrix} M \cdot \delta \hat{f}_h + \Delta t \mathcal{D}(\delta \hat{f}_h) + \Delta t \delta \lambda \mathcal{L}'(\hat{f}_h) \\ \Delta t \mathcal{L}(\delta \hat{f}_h) \end{bmatrix} \\ &= \begin{bmatrix} -\Delta t \mathcal{D}(\hat{f}_h) + \Delta t \mathcal{C}(\hat{f}_h, \tilde{\mathbf{g}}(\boldsymbol{\tau}_{p,h}(\hat{f}_h))) \\ 0 \end{bmatrix} \equiv L(\hat{f}_h) \end{aligned} \quad (8.19)$$

and

$$\mathbf{x}(t_{n+\theta}) \equiv \begin{bmatrix} \hat{f}_h(t_{n+\theta}) \\ \lambda(t_{n+\theta}) \end{bmatrix} = \begin{bmatrix} \hat{f}_h(t_n) \\ \lambda(t_n) \end{bmatrix} + \begin{bmatrix} \delta \hat{f}_h \\ \delta \lambda \end{bmatrix} = \mathbf{x}(t_n) + \tilde{L}(\hat{f}_h) \quad (8.20)$$

where $\tilde{L} \equiv S^{-1} \cdot L$. For $\theta = 1$, the above algorithm corresponds to a first order algorithm. Higher order algorithms can be derived if $\mathcal{D} = 0$ (for example, the Doi-Edwards model). Denoting f_0 as $\hat{f}_h(t_n)$, the traditional fourth order Runge-Kutta algorithm can be written as

$$\hat{f}_h(t_{n+\theta}) = f_0 + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \quad (8.21)$$

where $k_1 = \tilde{L}(f_0)$, $k_2 = \tilde{L}(f_0 + k_1/2)$, $k_3 = \tilde{L}(f_0 + k_2/2)$, and $k_4 = \tilde{L}(f_0 + k_3)$. Other high order, explicit time integration schemes can be derived in a similar fashion. For example, the second-order, total variation diminishing (TVD-RK2) time integration scheme is developed with $k_1 = \tilde{L}(f_0 + \tilde{L}(f_0))$

$$\hat{f}_h(t_{n+\theta}) = \frac{1}{2}(f_0 + k_1) \quad (8.22)$$

Even with the first-order scheme, we notice that the time integration is stable over a range of De . At high De where the flow becomes numerically unstable, changing the time integration scheme does not increase the largest De that can be simulated. Therefore, we use the first-order time integration scheme for the rest of this chapter.

8.3.4 Brownian configuration fields method

In this work, the simulation by the wavelet-Galerkin/finite-element method is compared with a more popular CONNFESSIT calculation through the implementation of the Brownian configuration fields method [102], which is based on the coupling of a partial stochastic differential equation (for the microstructure evolution) with the finite element analysis (for the calculation of the velocity flow field). In this section, basics of the Brownian configuration fields method are reviewed briefly.

For the diffusion equation (Eqn 8.2) of the double reptation model, the mathematically equivalent set of stochastic differential equations consists of a partial stochastic differential equation that describes the evolution of the link orientation and a stochastic differential equation for the position of the link along the contour of the polymer molecule:

$$d\mathbf{u} = \text{De}[-\mathbf{v} \cdot \nabla \mathbf{u} - \mathbf{G}^T \cdot \mathbf{u}]dt + \sqrt{2\epsilon_B}d\mathbf{W}_t \quad (8.23)$$

$$d\sigma = \sqrt{2}dW_t \quad (8.24)$$

where $d\mathbf{W}_t$ is a three-dimensional Wiener processes and dW_t is an one-dimensional Wiener process. The coupling of $\mathbf{u}$ and σ occurs at $\sigma = 0$ and $\sigma = 1$ through the boundary condition, Eqn. 8.3. For both of these values of σ , the partial stochastic differential equation (Eqn. 8.23) is replaced by a random unit vector to signify that the unit vector $\mathbf{u}$ does not following the flow field at either end of the contour.

It should be noticed that $d\mathbf{W}_t$ is independent of position and hence the same three-dimensional Wiener process can be applied throughout the physical space. It is this spatial correlation of the Wiener process that leads to both dramatic variance reduction over the physical space and the significant reduction in computational demand in generating random numbers for $d\mathbf{W}_t$. It is also important to recognize that Equation 8.24 does not depend on the physical space coordinates, and hence the same Wiener process for σ can be applied throughout the physical space. The corresponding boundary condition for σ is implemented as follows: After each time step, if σ evolves out of the range $[0, 1]$, then it is reflects back to the range of $[0, 1]$ and $\mathbf{u}$ is replace by a random vector. It is possible that the stochastic variable σ evolutes outside the range of $[0, 1]$ and then back into the range within a single discrete time step. This issue is resolved by considering the conditional probability of an unobserved reflection, which is derived and implement in an simulation algorithm for homogeneous flows by Öttinger [168].

The spatial discretization of Eqn. 8.23 is performed by using the discontinuous Galerkin method with the weak form as:

$$(\Psi, \mathbf{u}_h^{n+1} - \mathbf{u}_h^n)_{T_e} = (\Psi, [\Delta t \text{De}(\mathbf{v} \cdot \nabla \mathbf{u}_h^n - \mathbf{G}^T \cdot \mathbf{u}_h^n) + \sqrt{2\epsilon_{Br}} \Delta \mathbf{W}_t])_{T_e} - (\Psi, \mathbf{n} \cdot \mathbf{v} \Delta t \text{De}(\mathbf{u}_h^n - \mathbf{u}_h^{n,-}))_{\partial T_e} \quad (8.25)$$

where the incremental three-dimensional Wiener process $\Delta \mathbf{W}_t$ has zero mean and $\Delta t \delta$ variance. The stress tensor is then evaluated at the nodal value of $\mathbf{u}$ as:

$$\boldsymbol{\tau}_{p,h}(x_i) = \frac{1}{N} \sum_i \boldsymbol{\tau}_p(\mathbf{u}_i) \quad (8.26)$$

where N is the number of configuration field used in the simulation.

8.3.5 Other computational issues

Most computations in this chapter are performed on a Dell Precision 530 workstation with Intel Xeon processor rated at 1.7 GHz, 256kb of $L2$ cache, 400 MHz system bus, and 1 Gbyte of memory. The memory requirement for both wavelet-Galerkin method and the Brownian configuration fields are dominated by the storage of the distribution function and the stochastic trajectories. Table 8.1 shows the comparison between the requirement of using the Brownian configuration fields and the wavelet-Galerkin method. For a given mesh, the memory requirement for the wavelet-Galerkin method scales linearly with the number of scaling functions and the number of the Fourier modes in a calculation.

	Memory	Speed for one time step
Wavelet-Galerkin (1 mode)	40M	18s
Wavelet-Galerkin (5 modes)	192M	85s
BCF (2000 trajectories)	212M	8s
BCF (5000 trajectories)	494M	21s

Table 8.1: Comparison of the computation requirement between the wavelet-Galerkin method and the Brownian configuration field method

Comparing the wavelet-Galerkin method and the Brownian configuration field method, the memory requirement for the wavelet-Galerkin method is milder than that of the BCF approach. This is because the number of unknowns to represent the distribution function is less than the total number of trajectories used in the BCF approach for a given accuracy.

To further reduce the memory requirement of the wavelet-Galerkin/finite element method, a topological sort is used to arrange the order for the solution of each element according to the direction of the flow. Originally, a fully explicit update of the distribution function requires the storage of the distribution function at the previous time step. Otherwise, the exterior nodes of the distribution function (in the DG formulation) for some elements may already be updated. The resulting treatment will not be full explicit for a number of elements and semi-implicit for the other elements. This introduces numerical instability even in a planar channel flow calculation. By solving the solution with a sequence according to the streamline direction, it is possible to solve the substantial derivative *implicitly*; Alternatively, by updating the elements in an order that is opposed to the streamline direction, fully explicit treatment of the substantial derivative is retained without requiring storage of all the distribution functions from the previous time step. This induces a 40% in memory saving.

8.4 Sample calculation for flow around an isolated cylinder in a channel

In this section, the accuracy and robustness of the wavelet-Galerkin/finite-element method is demonstrated by simulating the behavior of the double reptation model in flow around an isolated cylinder confined in a channel. The Deborah number De is defined as the ratio of the polymer relaxation time λ to a residence time T for a fluid particle to traverse a distance of one cylinder,

$$\text{De} \equiv \frac{\lambda}{T} = \lambda \cdot \frac{1}{RH} \cdot \frac{Q}{B} \quad (8.27)$$

where Q/B is the flow rate per unit depth and H is the half-height of the channel. In this chapter, we take H to be $2R$. The viscosity ratio β is set to be 0.1.

The computational domain is defined to have upstream length and downstream length of 12 times the radius of the cylinder. A one dimensional equation set is solved along the inflow surface, and a fully developed velocity profile is assumed at the outflow surface. A symmetric boundary condition is assumed along the centerline ($y = 0$), and a no slip condition is imposed along the solid channel wall surface and the cylinder surface.

Many of the accuracy and convergence characteristics can be demonstrated through the analysis of the predictions of an engineering property. In the calculation of the flow around an isolated cylinder confined in a channel, a natural choice of this engineering property or characteristic is the drag force per unit length exerted on the cylinder surface F_d , which can be calculated by the following expression:

$$F_d = - \int_{\Gamma_e} \{ \boldsymbol{\tau} + p \boldsymbol{\delta} \} : \mathbf{n} \boldsymbol{\delta}_x ds \quad (8.28)$$

here Γ_e is the surface of the cylinder and $\boldsymbol{\delta}_x$ is the unit vector pointing along the flow (x) direction. The calculated drag force is split into two components: form drag, the pressure contribution to the total drag force on the cylinder, and skin drag.

Three different meshes (labelled as M1, M2, M3) are used in this study. Each mesh in the sequence is essentially based on a uniform refinement near the cylinder and in the wake of the coarsest mesh M1. The central part of mesh M2 is shown in Figure 8.1, and the important dimensions of each mesh are listed in Table 8.2. In this table, the results for the computed drag force on the cylinder for a Newtonian fluid and that for the Doi-Edwards model are also presented for comparing the accuracy of the calculations done on

these meshes. The difference between the drag force calculated by the three meshes for the Newtonian fluid is within 0.1%, and that for the Doi-Edwards model at $De = 1$ are less than 1 %.

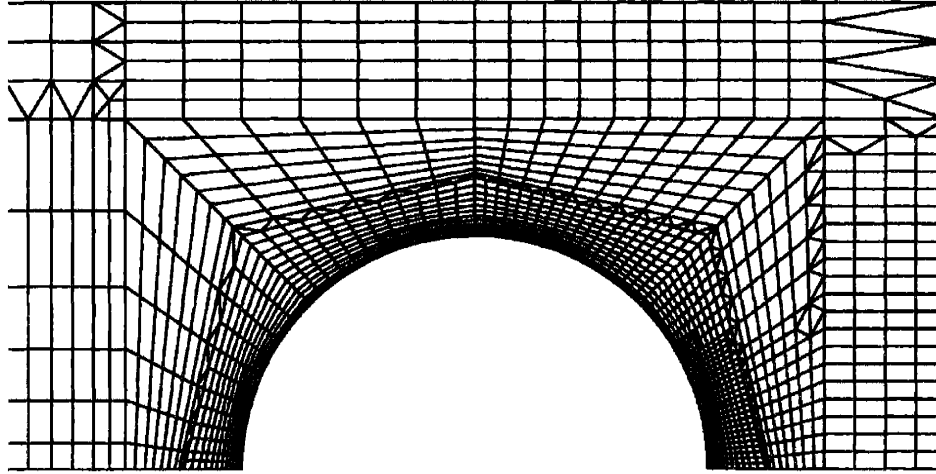


Figure 8.1: Finite element mesh M2 for calculation of the viscoelastic flow of a double reptation model past an isolated cylinder in a channel with $H = 2$.

Mesh	Δx at (0, 1)	Δy at (0, 1)	Number of elements	DOF in modified Stokes problem	Newtonian Drag Force	Drag Force calculated at $De = 1$
M1	0.0188	0.0393	1009	12273	132.412	94.216
M2	0.0094	0.0196	2213	26243	132.386	94.384
M3	0.0048	0.0100	3656	43177	132.388	94.400

Table 8.2: Mesh dimension and number of unknowns for meshes (M1, M2, M3) for the calculation of the viscoelastic flow past an isolated cylinder confined in a planar channel with $H = 2$. The drag force of viscoelastic flow at $De = 1$ is calculated by using one Fourier mode and 16×32 D6 scaling expansion for the Doi-Edwards model.

8.4.1 Convergence study

The accuracy and convergence characteristics are studied in this section. In addition to comparing the effect of the three different meshes on the field variables, we compare the simulation results based on the same mesh, but with different numbers of D6 scaling func-

tion or Fourier basis functions. As has demonstrated by Sun et al. [213] are for most viscoelastic calculations, mesh convergence characteristics are insensitive to De or We . Therefore, the convergence study is done for the Doi-Edwards model at a single Deborah number, $De = 1$.

Figure 8.3 shows the velocity profile calculated by the wavelet-Galerkin/Finite-Element method with mesh M2, a 16×32 Daubechies 6 scaling function expansion, and five Fourier modes. The near front and after symmetry of the x -component of the velocity profile shows that the memory effect is limited. Because most of the changes in the velocity field is in the gap between the cylinder surface and the wall, that is $(x = 0, y \in [1, 2])$, we focus on the velocity and microstructure fields in this gap. This study provides a general sense of the convergence of the global flow field. We also examine the dimensionless drag force acting on the cylinder surface.

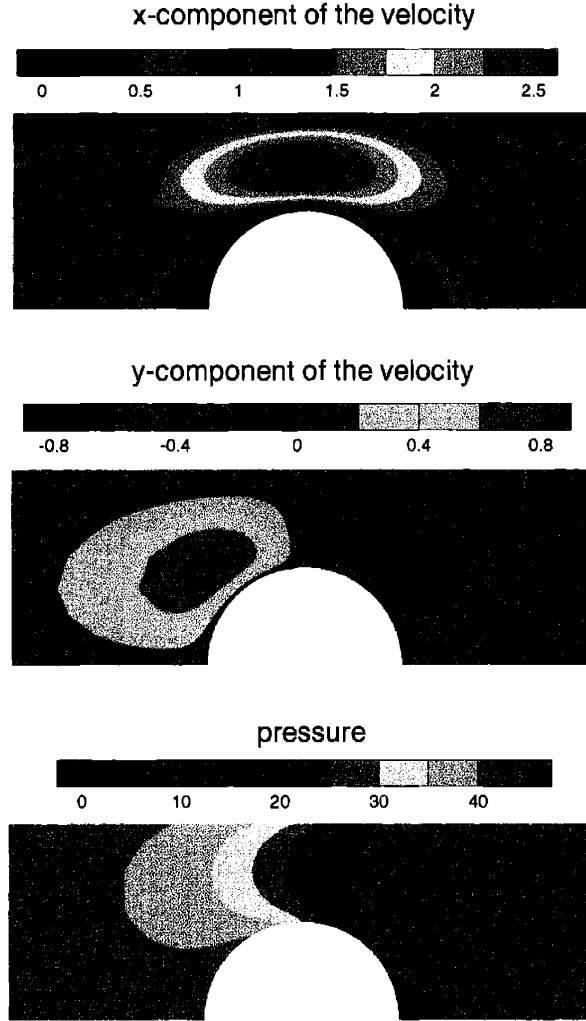


Figure 8.2: Distribution of velocity and pressure fields calculated with the wavelet-Galerkin/Finite-Element method for the Doi-Edwards model for $De = 1$.

Velocity profiles of the Doi-Edwards model and a Newtonian fluid across the gap between the cylinder and the wall are shown in Figure 8.3 to show the mesh convergence of the wavelet-Galerkin/Finite-Element method. One Fourier mode and a 16×32 Daubechies 6 scaling function expansion are used to represent the configuration space of σ and u respectively. The overlapping of the velocity profiles calculated by these three different meshes demonstrates convergence with mesh refinement. Compared with the New-

tonian velocity profile, the velocity profile of the Doi-Edwards model is anti-symmetric. This shows the viscoelastic characteristics of the Doi-Edwards model.

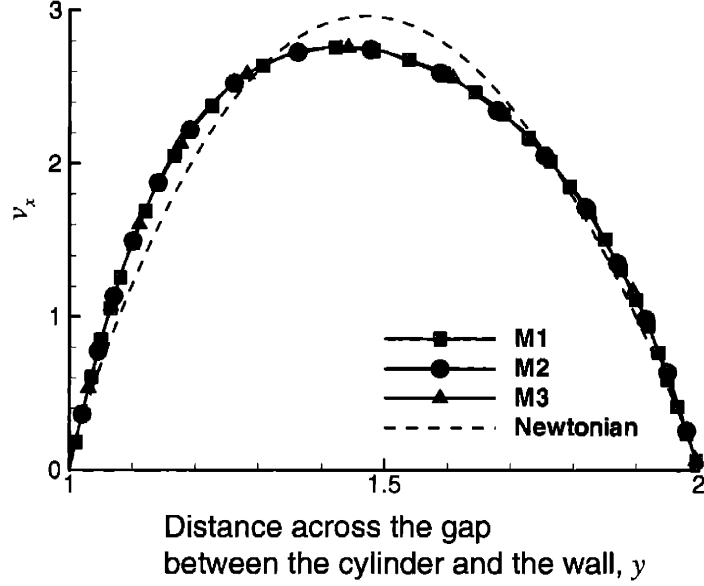


Figure 8.3: Dimensionless velocity profile in the gap between the cylinder and the wall. The three results shown for the Doi-Edwards model corresponds to the calculations with M1 (square symbol), M2 (cycle symbol), and M3 (triangle symbol). The Newtonian flow field is shown as a dashed-line for comparison.

Table 8.3 shows the calculated drag force and the wall shear rate on the cylinder for $x = 0, y = 1$ at $De = 1$ for the three meshes. Both the drag force and the wall shear rate vary by less than 2% from the coarsest to finest mesh used..

	Drag force on the cylinder	Wall shear rate, $G_{yx}(x = 0, y = 1)$
M1	94.216	18.975
M2	94.384	18.735
M3	94.400	18.707

Table 8.3: Comparison of the values of the drag force and the wall shear rate computed with the three different meshes M1, M2, and M3. 16×32 Daubechies 6 scaling functions and one Fourier mode are used to resolve the configuration space of the Doi-Edwards model.

Figure 8.4 shows the yx component of the microstructure $\langle uu - \frac{1}{3}\delta \rangle$ profile across the gap. The overlap of the results for the three meshes confirms the mesh convergence for the

wavelet-Galerkin/Finite element method for simulating microstructure of the Doi-Edwards model.

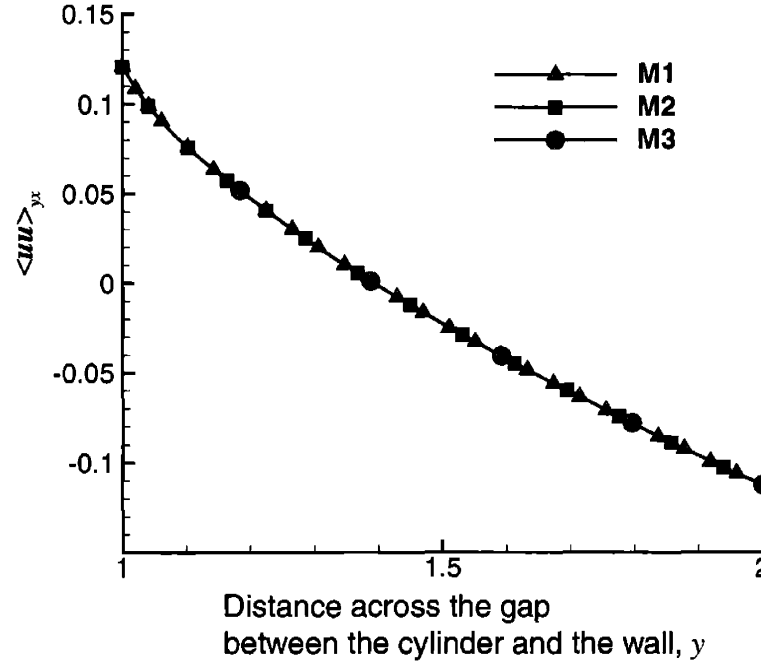


Figure 8.4: Microstructure $\langle uu \rangle_{yx}$ profile in the gap between the cylinder and the wall. The three results shown for the Doi-Edwards model correspond to calculations with by M1 (triangle symbols), M2 (square symbols), and M3 (circular symbols).

Figure 8.5 and 8.6 show the dimensionless velocity gradient and microstructure profiles across the gap for different resolutions of scaling functions. One Fourier mode is used to resolve the σ -space and mesh M2 is used to discretize the physical space. The overlapping profiles for these two computations confirms the convergence with scaling function resolutions (h -convergence in configuration space).

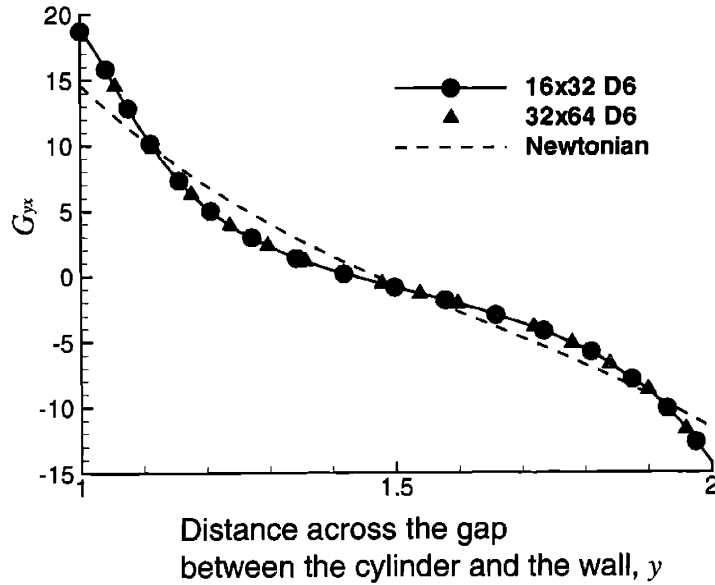


Figure 8.5: Dimensionless velocity gradient (G_{yx}) profile in the gap between the cylinder and the wall. The two results shown for the Doi-Edwards model correspond to calculations with different resolutions of the wavelet-Galerkin method: Circular symbols correspond to the calculation with a 16×32 D6 scaling function expansion; triangular symbols correspond to the calculation with a 32×64 D6 scaling function expansion. The Newtonian flow field is shown as a dashed-line for comparison.

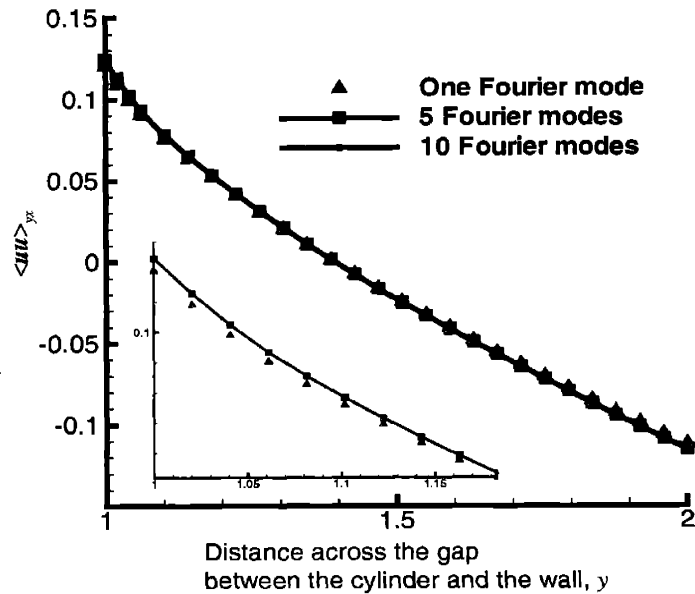


Figure 8.6: Microstructure profile in the gap between the cylinder and the wall. The two results shown for the Doi-Edwards model correspond to the calculation by different resolutions of the wavelet-Galerkin method: Circular symbols correspond to the calculation with a 16×32 D6 scaling function expansion; triangular symbols correspond to the calculation with a 32×64 D6 scaling function expansion.

Table 8.4 shows the accuracy of different resolutions of the scaling function expansion in predicting the drag force on the cylinder and the wall shear rate. The calculations by the two different resolutions of scaling function expansions agree to within one percent error.

Number of D6 scaling functions	Drag force on the cylinder	Wall shear rate, $G_{yx}(x = 0, y = 1)$
16×32	94.384	18.735
32×64	94.321	18.754

Table 8.4: Comparison between the values of the drag force and the wall shear rate with the two different Daubechies 6 scaling functions resolutions for the configuration space of $\mathbf{u}$. One Fourier mode is used for the configuration space of σ and mesh M2 is used to resolve the physical space.

Figures 8.7 and 8.8 show the dimensionless velocity and the microstructure profiles across the gap for different numbers of Fourier modes used to resolve the σ -space. The 16×32 Daubechies scaling function expansion is used to represent the configuration space $\mathbf{u}$ and mesh M2 is used to discretize the physical space. The overlapping velocity profiles suggest convergence in number of Fourier modes. However, a careful study of the structure profile near the cylinder surface (the small insert in Figure 8.8) shows that one Fourier mode is not sufficient to resolve the σ -space of the Doi-Edwards model. This result is also consistent with the calculated drag force, as shown in Table 8.5. Up to two percent difference is observed between the values of the drag force calculated by one Fourier mode and five Fourier modes.

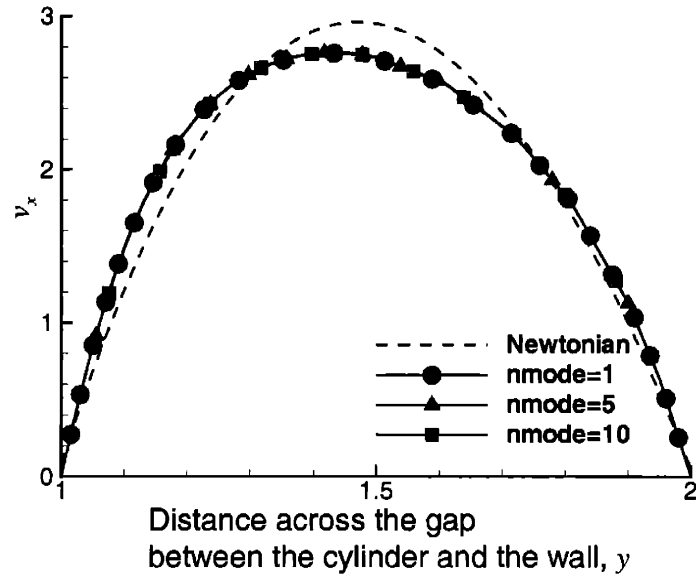


Figure 8.7: Dimensionless velocity profile in the gap between the cylinder and the wall. The three results shown for the Doi-Edwards model correspond to the calculations with different number of Fourier modes: Circular symbols correspond to one Fourier mode; triangles correspond to five Fourier modes, and squares correspond to 10 Fourier modes. The Newtonian flow field is shown as a dashed-line for comparison.

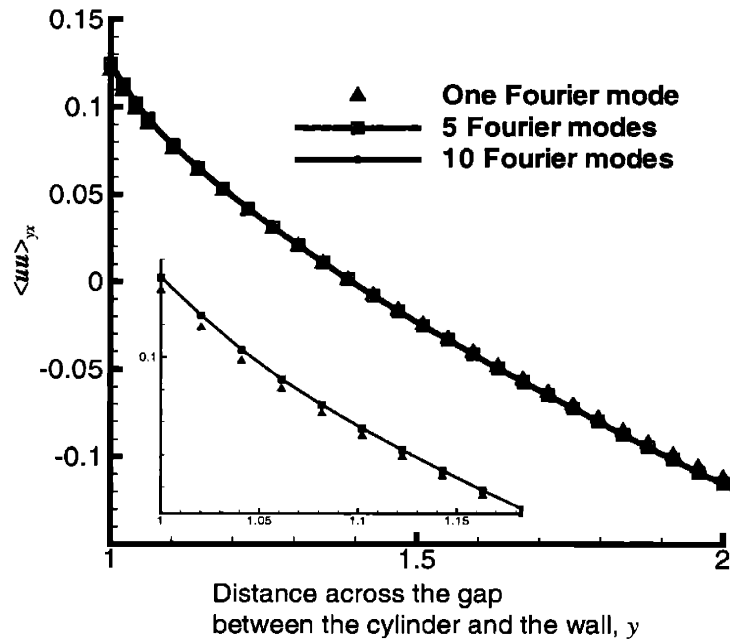


Figure 8.8: Microstructure profile in the gap between the cylinder and the wall. The three results shown for the Doi-Edwards model correspond to the calculations by with one (square symbol), five (circular symbol), and 10 (triangular symbol) Fourier modes. The small insert corresponds to same results enlarged for $y \in [1, 1.2]$.

Number of Fourier modes	Drag force on the cylinder	Wall shear rate, $G_{yx}(x = 0, y = 1)$
1	94.384	18.735
5	96.191	18.599
10	96.208	18.598

Table 8.5: Comparison between the values of the drag force and the wall shear rate with different number of Fourier modes for the σ -space: 1, 5, and 10. 16×32 Daubechies 6 scaling functions are used to resolve the u -space at each node, and mesh M2 is used to resolve the physical space.

This convergence analysis demonstrates convergence with mesh, Daubechies 6 scaling functions, and Fourier modes. Whereas the meshes and different scaling function expansions show convergence for all of the resolutions proposed, at least five Fourier modes are necessary to provide an accurate calculation for the Doi-Edwards model. Therefore, for the rest of this chapter, mesh M2 are used to represent the physical space, and 16×32 D6 scaling functions with five Fourier mode are used to represent the configuration space for all the simulations.

8.4.2 Parallel efficiency of the wavelet-Galerkin/Finite Element method

We test the implementation of the wavelet-Galerkin/finite-element method in a distributed computing environment. In contrast with the common practice in finite element analysis of viscoelastic flows [33], the calculation of the distribution function dominates the velocity update. Hence, we focus on the parallelization of the distribution function update and use a serial, frontal method for the $\nu - p - G$ update. The Message Passing Interface (MPI) is used to implement the parallel processing, because of its widely used software libraries, universality in hardware, its ease for implementation of numerical algorithms, and its high performance.

Domain decomposition in the physical domain for the distribution function update corresponds to a minimization of the interface between each of the partitioned computational subdomains. Sophisticated algorithms and theory for this minimization have been worked out by Kiwi, et al. [118]. In this chapter, we employ a very simple and fast method in which we divide the number of elements equally across domains; and the elements associated with each domain are sorted based on the sequence in the topological sort after the first $\nu - p - \mathbf{G}$ update. The steps in the parallel processing strategy are shown in Figure 8.9. The amount data (stress calculated at each sub-domain) for communication across each sub-domain for the $\nu - p - \mathbf{G}$ calculation scales with the number of elements. It is $O(10^3)$ bytes in a typical calculation with a mesh with order 10^3 elements and therefore is small. Most of the communication involves distribution function update data between the boundaries of the sub-domains. This is of $O(10^3)$ times the number of nodes on the boundary of each sub-domain, which is in turn of $O(10^2)$. The total amount of data to be communicated for the distribution function is therefore of $O(10^5)$ to $O(10^6)$.

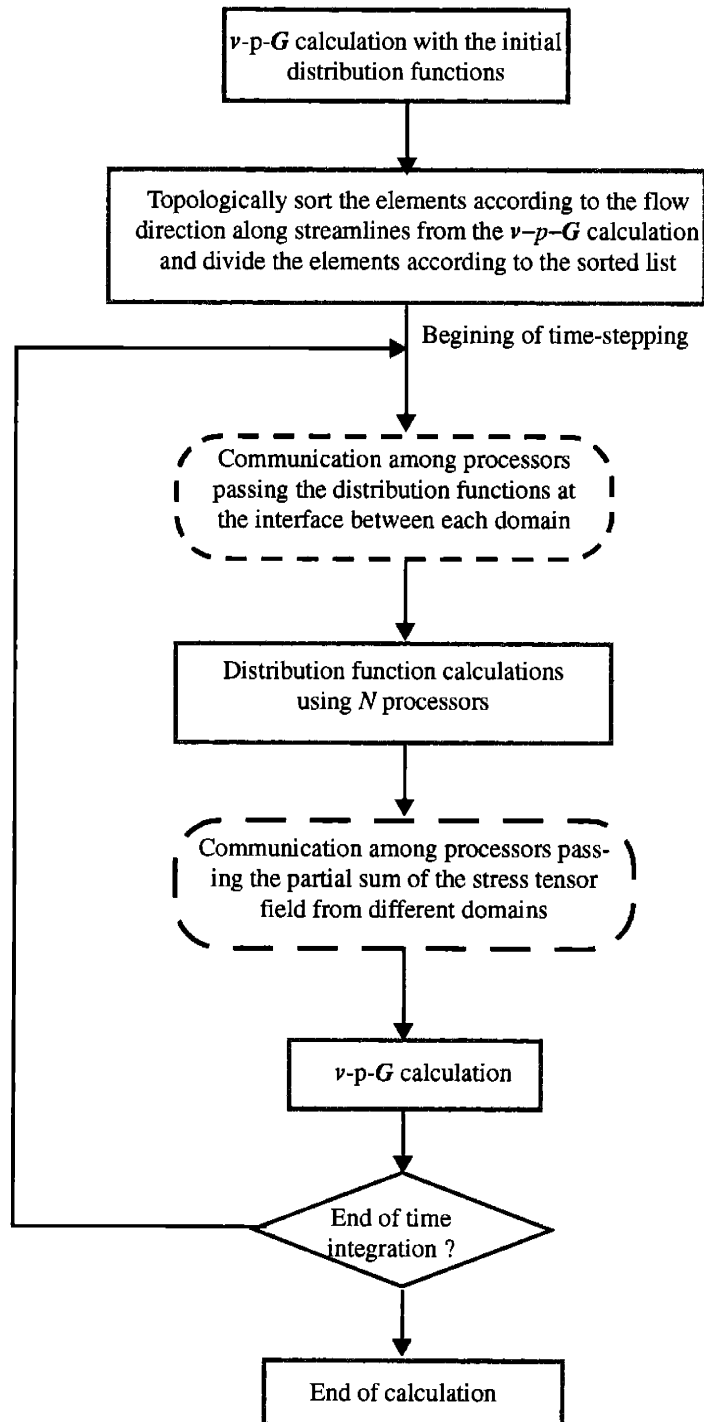


Figure 8.9: Parallel computing strategy for the multiscale simulation of viscoelastic flows with diffusion equations. Communications required at each time step for the computation are in dashed boxes.

The parallel efficiency of the wavelet-Galerkin/Finite Element method is characterized by calculating the speed-up S or efficiency E . The precise definitions for these two quantities depends on the problem studied. For a fixed problem solved by different number of processors, let T_i be the clock time required for a simulation running i processors, S and E are defined as

$$S \equiv \frac{T_1}{T_N} \quad (8.29)$$

$$E \equiv \frac{T_1}{NT_N} \quad (8.30)$$

The relationship between S and E is given by $S = N \cdot E$ where N is the number of processors. Whereas the speedup provides a measure of the speed advantage of the parallel algorithm as compared with the best possible serial algorithm, the efficiency measures the fraction of time that a typical processor is usefully employed. Ideally, for a N -processor computation, $S = N$ and $E = 1$.

In this section, we report results of a study of the parallel performance of our algorithm on a cluster of sixteen, dual-processor Dell Precision 610 workstations connected by using 1000 Mbps Gigabit Ethernet (1000BASE-SX). Details of this cluster have already been reported by Caola et al. [33] and are not repeated here. Two different problems are utilized to explore the parallel performance of our algorithm. The first one involves calculation for a fixed problem size as more processors are used in the calculation. In particular, we study the computer time required for the calculation of 100 time steps by simulating the Doi-Edwards model with mesh M2, 16×32 D6 basis functions and 4 Fourier modes. This measure represents how much faster a given problem will execute on multiple processors than on one processor. The speed-up S in this calculation is then defined as the ratio of the computer time required by one processor to that by N processors ($S = t_1/t_N$).

A second measure used to study the parallel characteristics of the wavelet-Galerkin method involves simulating the Doi-Edwards model in a planar channel flow with 16×32 D6 basis functions and 4 Fourier modes by using a series of meshes such that the computer work done by each processor is fixed. Again, we study the computer time required for a calculation of 100 time step. The series of meshes ranges from 256 to 4096 elements. The typical computer time for the $\mathbf{v} - \mathbf{p} - \mathbf{G}$ update is around 0.5 % of the total computation time. The speed-up S in this calculation is defined as the ratio of the computer time required by one processor to that by N processors times the ratio of the size of the problem for N processors to that for one processor, i.e.

$$S = \frac{t_1}{t_N} \cdot \frac{T_N}{T_1} \quad (8.31)$$

where t_i is the computer time required by an i processor run and T_i is the problem size that is being solved by i processors.

The parallel speedups based on both sets of calculations overlaps and are nearly indistinguishable. Therefore, we only present the results based on the parallel efficiency. The overall parallel efficiency for both of these problems is shown in Figure 8.10. Nearly linear scale-up is observed for both studies with calculations up to 16 processors. The relatively larger drop in the parallel efficiency for the progressively refined mesh problem is due to the increased computation time for solving the $\mathbf{v} - \mathbf{p} - \mathbf{G}$ problem, which is counted as overhead to the calculation. As the problem size increases, the computer time required to solve the $\mathbf{v} - \mathbf{p} - \mathbf{G}$ problem increases; and, hence, the overall efficiency of the parallel algorithm decreases. The fraction of computer time spent on the calculation for the $\mathbf{v} - \mathbf{p} - \mathbf{G}$ problem is around one percent of the whole calculation, which confirms our claim that in the wavelet-Galerkin/finite-element or other multiscale calculation methods, the stress update calculation dominates over the $\mathbf{v} - \mathbf{p} - \mathbf{G}$ update. However, as demon-

strated by Caola et al. [33], the computation time for solving the $\nu - p - G$ problem grows exponentially when the number of element in the problem becomes of order 10^4 or higher. In this region, however, the wavelet-Galerkin update for the stress calculation still scales linearly with the number of processors. Therefore, we expect that there will be a point (roughly at order 10^4 elements) that the $\nu - p - G$ update will be as expensive as the stress update. At that point, the incorporation of the parallel algorithm for the $\nu - p - G$ is necessary to ensure the success of the overall parallel strategy.

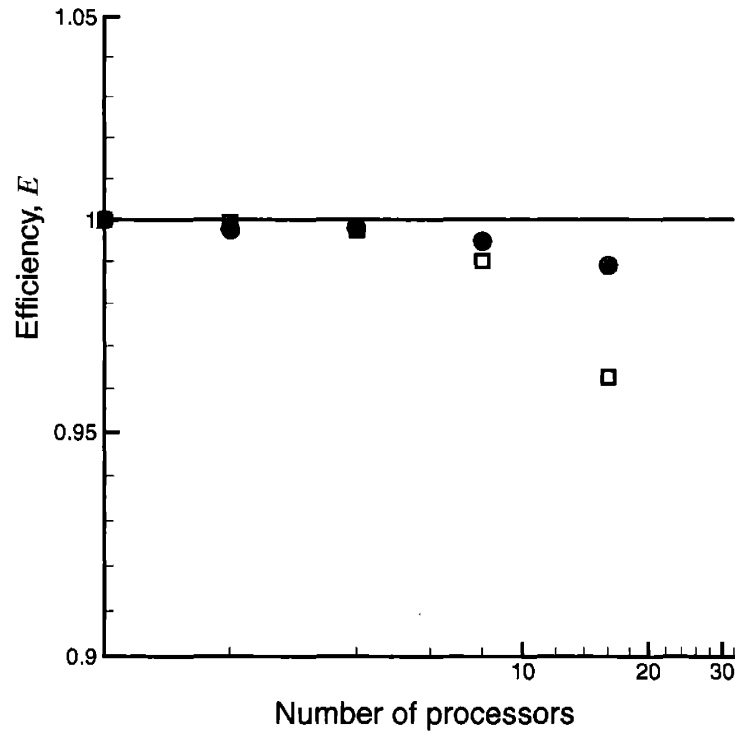


Figure 8.10: Parallel efficiency for the solution of the Fokker-Planck equation for the Doi-Edwards model by the use of wavelet-Galerkin method. The filled symbols corresponds to the speed-up for a fixed problem size using an increasing number of processors for the solution; the empty symbols correspond to speed-up evaluated for a series of progressively refined meshes (larger problems) designed so that the load per processor remains constant.

8.4.3 Comparison with Brownian configuration fields calculations

The accuracy and efficiency of the wavelet-Galerkin/finite element method is compared with a popular implementation of the CONNFESSIT algorithm through the use of

a Brownian configuration fields method. The benchmark calculation is performed on mesh M1 at $De = 1$.

All the simulations for the Brownian configuration fields calculation in this section are performed in a parallel computing environment. Domain decomposition is performed in the configuration space, i.e. at each processor, an equal number of trajectories are simulated and the partial sums of the stress tensor from each processor are then gathered to a master node for the calculation of the velocity-pressure field. The calculated velocity field is then redistributed to each node for the stress update. This domain decomposition requires a minimum amount of communication between the processors and, thus, allows a linear speed-up. Furthermore, each trajectory is stored only on the associated processor where it is simulated. Therefore, a much larger number of trajectories can be simulated. In this study, the number of trajectories simulated ranges from 4000 to 112,000 whereas most Brownian configuration fields calculations reported in the literature employ at most 5000 trajectories.

The simulation results for the drag force calculation with three different numbers of trajectories are shown in Figure 8.11. In this figure, three consecutive refinements of the number of trajectories (4000, 56,000, and 112,000) are compared with the calculation by the wavelet-Galerkin/FEM method. The black solid line in the figure corresponds to a reference calculation by the wavelet-Galerkin/finite element analysis with 16×32 D6 scaling functions and five finite Fourier modes. The drag force, calculated as the time-average of the simulation result of the Brownian configuration fields, agrees well with the simulation results of the wavelet-Galerkin/finite element method. However, the fluctuation of the Brownian configuration fields is significant especially for a small number of trajectories. This suggests that a better variance reduction technique along the time-axis is required

before the Brownian configuration fields calculation should be used for calculating the stability properties of a viscoelastic flow.

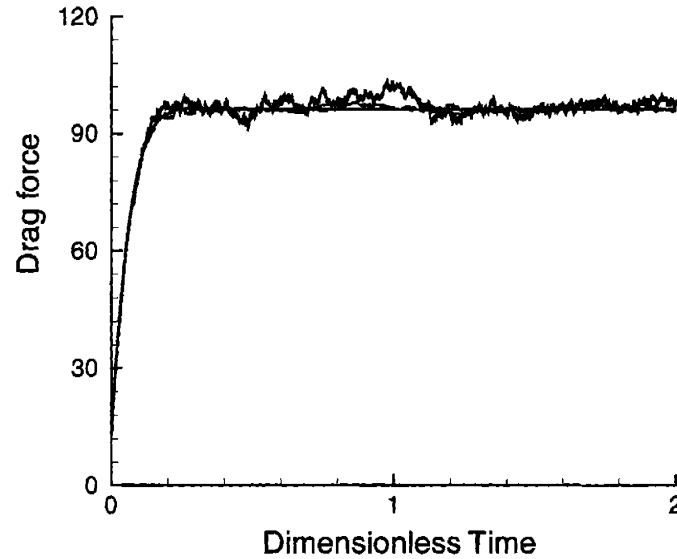


Figure 8.11: Simulation result for the drag force exerted on the cylinder for the Doi-Edwards model at $De = 1$. All calculations are performed with mesh M1. The black solid line corresponds to the wavelet-Galerkin/finite element calculation with 5 Fourier mode and 16×32 D6 scaling function expansions. The three fluctuating curves on top of the black solid line corresponds to the Brownian configuration fields calculations with different number of trajectories: blue solid line corresponds to 4,000 trajectories; the green dotted line corresponds to 64,000 trajectories, and the red dashed line corresponds to 112,000 trajectories.

A more quantitative error analysis of the Brownian configuration fields method is obtained by using two different measures based on the drag force calculation presented in Figure 8.11. First, we consider the fluctuation of the drag force around the mean drag force for a given ensemble size. Second, an error measure for the accuracy of the drag force is calculated by comparing the mean drag force calculated by the Brownian configuration fields method with the wavelet-Galerkin method with 16×32 D6 scaling function and 5 Fourier modes. The latter result is assumed to be the exact answer. Figure 8.12 shows the convergence of the Brownian configuration fields method based on these two measures. The rate of convergence based on both measures scales with $1/\sqrt{N}$, where N is the total number of trajectories used in the calculation. The close agreement of the error

scaling with the theoretical result (the law of large number, see [168]) confirms the accuracy of the Brownian configuration fields calculation.

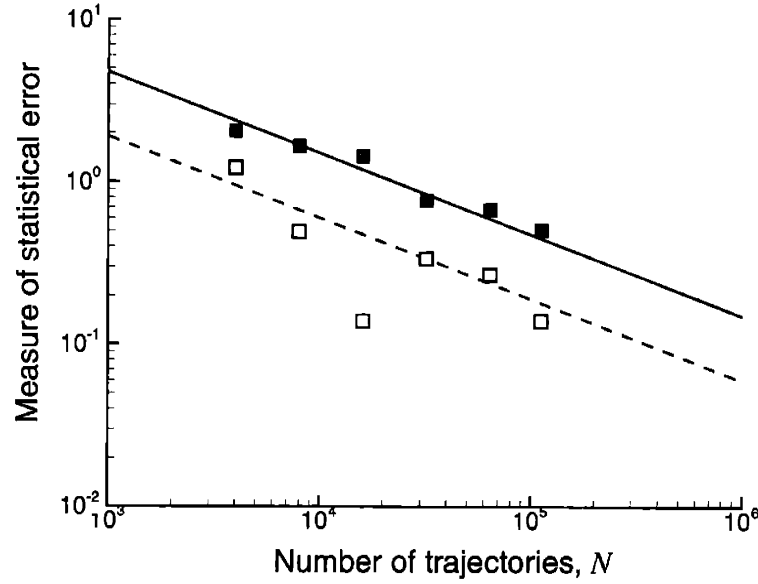


Figure 8.12: Statistical error for Brownian configuration fields calculations of the Doi-Edwards model with mesh M1. Solid symbols corresponds to the statistical error measured by the fluctuation of the drag force at steady state. The correlation equation of the solid line is $\text{error} = 150/\sqrt{N}$. Empty symbols corresponds to the error measures represented by the accuracy of the drag force calculation from a reference drag force, ($\text{error} = |\text{Calculated drag force} - \text{Reference drag force}|$). The correlation equation for the dashed line is $\text{error} = 60/\sqrt{N}$. The reference drag force is chosen to be 96.2086, which is the value computed by using the wavelet-Galerkin/Finite-Element method with 5 Fourier modes and a 16×32 Daubechies 6 scaling function expansion.

8.4.4 Effect of different viscous stress expressions on the complex flow behavior at $De = 1$

In this section, the effect of different viscous stress tensor expressions used in the double reptation model (Eqns 8.5 and 8.6) are tested for the flow around an isolated cylinder confined in a channel. From a kinetic theory or modelling point of view, both stress tensor expressions are thermodynamically consistent and provide representations for finite link tension. However, expression from Eqn. 8.6 predicts a monotonically increasing shear stress with shear rate with a much smaller value of ϵ_2 and hence agrees better with the stress-optical law, at least in the region of low shear rates. In this section, the effect of the

different stress tensor expressions will be evaluated by considering the complex flow behaviors in a flow around an isolated cylinder confined in a channel. In particular, De is fixed to be 1 and β is settled to be 0.1.

Figure 8.13 shows the xx -component of the stress tensor field evaluated from the stress tensor expressions Eqns. 8.5 and 8.6. We fix the parameter for the double reptation ϵ_{br} to be 0.3; ϵ_{hyd} for Equation 8.5 and ϵ_2 for Equation 8.6 are both taken to be 0.03. While the ranges of the stresses calculated from both expressions are the same, small difference in the spatial variation of the stresses can be observed. For example, the stresses are more intense on the cylinder surface for the Eq. 8.5 than for Eq. 8.6. Furthermore, although the length of the birefringence strand is about the same, its intensity is predicted to be higher by Eq. 8.5 than by Eq. 8.6.



Figure 8.13: Comparison between the values of xx component of the stress tensor for the double reptation model with different stress tensor expressions, Eqns 8.5 and 8.6. ϵ_{hyd} in Eqn. 8.5 = ϵ_2 in Eqn. 8.6 = 0.03. The red solid line corresponds to the calculation by Eqn. 8.5 and blue dash line corresponds to the calculation by Eqn. 8.6.

8.4.5 Effect of different De on the structure formation

The evolution of the xx -component of the stress tensor for the Doi-Edwards model along the downstream centerline for different De is shown in Figure 8.14. These results scale with the xx -component of the mean orientation $\langle uu \rangle$ and provide information on the alignment of the tube segments in the flow. Because the tube length in a reptation model is

fixed, there is no significant memory effect. Hence, τ_{xx} profile for different De are similar. The magnitude of the peak τ_{xx} scales linearly with increase in De . The location of the peak τ_{xx} is at $x = 1.42$ and is relative invariant for different De . Various types of double reptation models studied in this chapter provide a similar structure and hence is not repeated here.

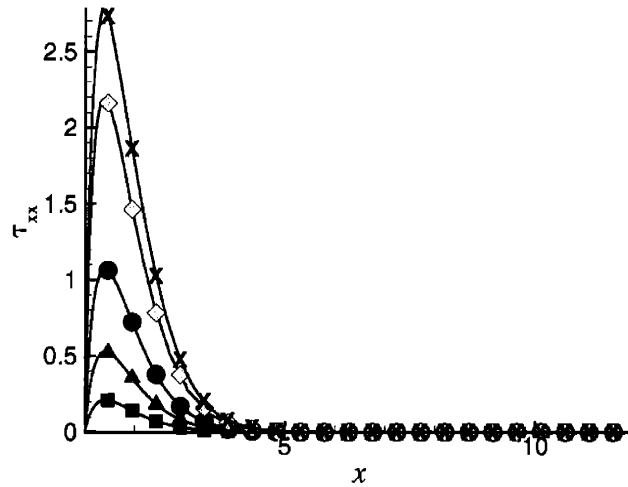


Figure 8.14: The evolution of the xx component of the stress tensor for the Doi-Edwards model along the downstream centerline. Red rectangles correspond to $De = 0.1$; green triangles correspond to $De = 0.25$; blue cycles correspond to $De = 0.5$; yellow diamonds correspond to $De = 1.0$; and “X” corresponds to $De = 1.25$.

Figure 8.15 shows the variation of the drag force acting on the cylinder surface as a function of De for a variety of reptation models including the Doi-Edwards model, Curtiss-Bird model, double reptation model given by Eqn. 8.5, and that given by Eqn. 8.6. The drag force calculated by these models decreases monotonically with increasing De except for that of the Curtiss-Bird model. The drag force of the Curtiss-Bird model increases at low De because of the large viscous stress contribution. Similar viscoelastic drag enhancement was also reported by Barakos and Mitsoulis [5], who used a four-mode KBKZ model to simulate the flow problem. For the other reptation models, we attribute the monotonically decreasing drag force to the lack of a “stretching” mechanism in the reptation model.

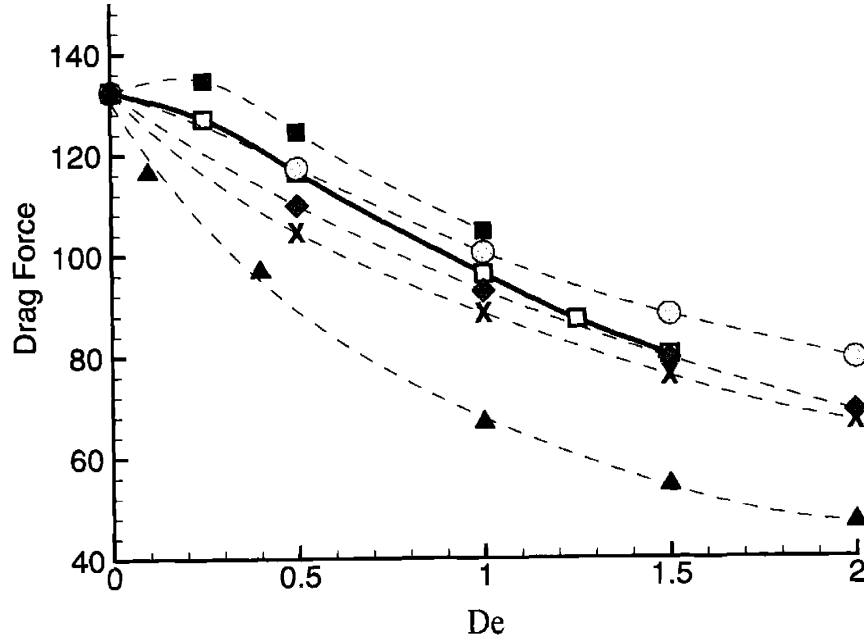


Figure 8.15: Effect of double reptation and viscous stress on the prediction of the drag force acting on the cylinder. Empty square symbols correspond to the prediction of the Doi-Edwards model; red squares correspond to the prediction of the Curtiss-Bird model with $\epsilon_{hyd} = 0.3$; yellow circles correspond to the prediction of the double reptation model without viscous stress; blue triangles correspond to the stress tensor expression evaluated with Eqn. 8.5 with $\epsilon_{hyd} = 0.03$; cyan diamonds correspond to the stress tensor expression evaluated with Eqn. 8.5 with $\epsilon_{hyd} = 0.3$; "X" corresponds to the stress tensor expression evaluated with Eqn 8.6 with $\epsilon_2 = 0.3$.

8.5 Conclusion

A wavelet-Galerkin/finite-element method is presented for computing viscoelastic flows with the constitutive description obtained directly from computing the solution of the diffusion equation with the stress tensor expressions from polymer kinetic theory. While the calculations shown in this chapter focus on the application of the Daubechies scaling function expansion and finite Fourier transform to approximate the configuration space of a double reptation model for representing the nonlinear rheology of concentrated polymer solutions and melts, our proposed numerical algorithm is general and applicable for a wide variety of basis functions ranging from the traditional spherical harmonics to various advanced wavelet functions such as spherical wavelets or other second generation wave-

lets. We computed the viscoelastic flow of the double reptation model around an isolated cylinder in a confined channel to illustrate the accuracy and robustness of the numerical method. The set of convergence studies presented here confirm that the numerical method converges with mesh refinement for the physical space, increasing resolution of different Daubechies-6 scaling functions for the orientation space ($\boldsymbol{u}$), and increasing number of Fourier modes to represent σ -space. Distributed computing has also been studied for simulating (a) a fixed problem with different numbers of processors, and (b) a series of progressively refined meshes with increasing number of processors to ensure the computational load per processor is constant. A linear scale-up is observed for both of these measures.

We have compared the calculation of the new wavelet-Galerkin method with the Brownian configuration fields method. A linear speed-up parallel strategy allows calculations of Brownian configuration fields up to $O(10^5)$ trajectories, which is two orders of magnitudes more trajectories than that are used in most previous Brownian configuration fields calculations. Because the Brownian configuration fields method provides a different representation of the underlying configuration space $(\sigma, \boldsymbol{u})$ at any given time, the configuration field and the calculated drag force fluctuates even after the macroscopic flow field achieves steady state. An error analysis for the Brownian configuration fields method shows that the simulated data agree well with the law of large numbers, that is, $\text{Error} \sim 1/\sqrt{N}$ where N is the number of trajectories used in the simulation.

We have also studied the effect of different viscous stress expressions on the dynamics of the double reptation model. The predictions for the different viscous stress expressions are qualitatively similar. Because the normal stresses are in general much smaller than the shear stress in shearing flow, limited viscoelastic effects are observed. The drag force acting on the cylinder surface is used to characterize the effect of increasing flow rate (De) on

the complex flow behavior of a variety of reptation models. Unlike traditional elastic dumbbell models, the drag force predicted by reptation models decreases monotonically with increasing De . We attribute this to the lack of a tube stretching mechanism.

The wavelet-Galerkin/finite-element method appears to be a powerful and promising approach for computing rheological dynamics and viscoelastic flows by using constitutive descriptions based directly on diffusion equations from kinetic theory. This approach is generalizable to study more advanced reptation models that involve more sophisticated relaxation mechanisms such as tube stretch and convected constraint release.

Chapter 9

Viscoelastic Flow Simulations of an Advanced Reptation Model by a Coupled Wavelet-Galerkin/Finite-Element Method

9.1 Introduction

Understanding and predicting the rheology and dynamics of entangled polymer systems such as concentrated polymer solutions and melts, is important and essential because of the predominant role of concentrated polymer solutions and melts in commercial fabrication processes such as fiber spinning or injection molding. While continuum models such as the K-BKZ model have been widely implemented in both commercial and academic software, the lack of molecular information limits the usefulness of these models aside from describing the flow field of a particular geometry. On the other hand, molecular modeling of entangled polymer systems has long been a challenge, because the dominant mechanism that leads to the rich rheological properties of entangled polymer systems is the intermolecular interaction, rather than intramolecular interaction as in dilute polymer solutions. One of the most useful physical pictures that has been used to coarse-grain the complex intermolecular interaction is the reptation motion of de Gennes [49]. Reptation assumes that the complex entangled polymer system forms an array of obstacles that limits the movement of any single polymer chain. For a given polymer chain (known as the primitive chain), motion along the direction of the backbone is much easier than lateral motion. The motion along the backbone can then be modeled as a chain moving in a “tube”. Doi and Edwards [54,55,59] first implemented this idea in a constitutive equation for describing the stress-strain relationship of polymer melts. Two different forms of the Doi-Edwards model include an integral constitutive equation and a pair of equations. This pair of equations consist of the diffusion equation that governs the evolution of a distribution

function for the orientation of the primitive chain $\mathbf{u}$ along the contour length σ and the corresponding stress tensor expression that gives the macroscopic stress in terms of the microstructure. Although the Doi-Edwards model is capable of describing a wide variety of rheological properties, it predicts excessive shear thinning in a steady shear flow, an incorrect normal stress ratio, and lack of rapid stress growth in the start-up of steady shear flow. These deficiencies of the Doi-Edwards model have led to various modifications with the goal of better describing the rheological properties of polymer melts in a molecular fashion.

Modifications of the Doi-Edwards model involve incorporating new physics such as chain-stretching, aligning-coupling¹, and constraint release in the constitutive equation. Two of the most common strategies for modifying the reptation model involve either modification of the memory function in the integral form of the constitutive equation or the modification of the diffusion equation and the corresponding stress tensor expression. Whereas incorporating the chain-stretching mechanism involves an additional variable, and hence the implementation through the constitutive equation or the diffusion equation is equivalent, the same cannot be said for including the constraint release mechanism. Two of the common constraint release mechanisms are double reptation motion and convective constraint release. Incorporation of these mechanisms in the diffusion equation involves an additional second order derivative with respect to $\mathbf{u}$, which corresponds to a modification of the “tube dynamics”. Modification of the memory function in the integral equation, however, corresponds to modifying the operators with respect to σ into the diffusion equation. This latter modification corresponds to a change in the primitive chain dynamics, which is different from the effect of modifying the diffusion equation. In seeking a precise

1. Aligning-coupling is the same as the no-independent-alignment assumption, as it is commonly known in literature.

representation of the various non-reptative mechanisms in the Doi-Edwards model, modification of the diffusion equation is preferred over modification of the memory function in the integral constitutive equation. A model that includes most of these physical ideas through modifying the diffusion equation was developed by Fang et al. [74]. They developed the model through the GENERIC structure to ensure thermodynamics consistency. We denote their model as the TAR (Thermodynamically Admissible Reptation) model.

Numerical simulations of the Doi-Edwards model or other reptation models in complex flow environments are sparse. Most simulations using various advanced reptation models focus on simple flow systems such as single/double step strain shear flow. For two dimensional, complex flow calculations, closed, integral form of constitutive equation have been used exclusively. For example, in a series of papers van den Brule and coworkers [103,174,228] developed the deformation field theory which introduces an Eulerian method for simulating various integral models such as the Doi-Edwards model, Mead-Larson-Doi model, and upper-convected Maxwell model in integral form. Wapperom and Keunings [225] have applied an integral version of Marrucci-Greco-Ianniruberto (MGI) model that includes a non-reptative relaxation mechanism of convective constraint release incorporated through modifying the memory function of the integral form of the DE model. In the simulation of a 4:1:4 contraction expansion problem, they show that flows calculated with the MGI model are qualitatively similar to the predictions of a generalized Newtonian fluid, such as the Carreau-Yasuda model. They conclude that the weak memory effect of the MGI model is due to the lack of the chain-stretching effect.

To our best knowledge, only *two* papers have appeared the report simulations of complex flows by using constitutive descriptions based on the diffusion equation (or the mathematically equivalent stochastic differential equation) of the reptation models. Hua and Schieber [99] calculated steady flow of the Doi-Edwards model in a periodic array of cyl-

inders arranged on a square grid. They employed the CONNFFESSIT approach to calculate the viscoelastic flow with stress tensor evaluated as an average over a large number of trajectories. van Heel, et al. [228] considered the flow of the Doi-Edwards model in flow around an isolated cylinder confined in a channel. Two numerical approaches, Brownian configuration fields and the deformation field method, are employed. Similar to the findings from the use of integral models for complex flow calculations [225], the lack of elastic effects lead to simulation results similar to those with simple generalized Newtonian fluid. In Chapter 8, we introduced an efficient wavelet-Galerkin/finite-element-method for simulating a general double reptation model in flow around an isolated cylinder confined in a channel. To evaluate and compare the effects of various nonreptative mechanisms in a complex flow, we extend the wavelet-Galerkin/finite element method to simulate the complex flow behavior of the TAR model. In particular, we include the effect of chain-stretching, which most papers considered as the leading order mechanism that produces strong elastic effects. For comparison with our previous calculation results in Chapter 8, we focus on the study of flow around an isolated cylinder confined in a planar channel.

The rest of this chapter is organized as follows. The governing equations and their mathematical formulation is presented in Section 9.2, where the diffusion equation and the stress tensor expressions for the thermodynamically admissible model are shown. The numerical method for simulating this model is the focus of Section 9.3. The rheological properties of the TAR model computed by using the wavelet-Galerkin method are presented in Section 9.4. To explore the accuracy of the wavelet-Galerkin method, we compare the solutions calculated by the wavelet-Galerkin method with the predictions by Brownian dynamics for the TAR model with an independent alignment assumption. In Section 9.5, sample calculations for flow around an isolated cylinder for the reptation models are presented. Finally, conclusions are offered in Section 9.6.

9.2 Governing equations

9.2.1 Mathematical formulation

The equations governing the flow around an isolated cylinder confined in a channel are scaled with the radius of the cylinder R as the characteristic length scale. The velocity scale is chosen to be the cross channel average velocity

$$V \equiv \frac{1}{2H} \int_{-H}^H u_x(-L, y) dy \quad (9.1)$$

where $-L$ is the location of the inflow surface of the truncated channel. The Deborah number is defined as $De \equiv \tau_d V/R$, where τ_d is the characteristic time for the reptation motion.

The dimensionless equation of motion for an incompressible viscoelastic fluid under inertia less, isothermal conditions is written as

$$\beta \nabla^2 \mathbf{v} - \nabla \cdot \{ \boldsymbol{\tau}_p + p \boldsymbol{\delta} \} = 0 \quad (9.2)$$

where β is the viscosity ratio of the solvent (η_s) to a total, characteristic viscosity (η_0). The variables $\boldsymbol{\tau}_p$ and p are made dimensionless with the characteristic viscous stress $\eta_0 V/R$. The incompressibility condition for the fluid is incorporated with the equation of continuity

$$\nabla \cdot \mathbf{v} = 0 \quad (9.3)$$

The spatial discretization of these governing equations is constructed by using the DEVSS-G formulation, and the dimensionless governing equations written in discretized variables are

$$\nabla \cdot [\nabla \mathbf{v}_h + \nabla \mathbf{v}_h^T] - \nabla \cdot [\boldsymbol{\tau}_{p,h} + (1 - \beta)[\mathbf{G}_h + \mathbf{G}_h^T] + p_h \boldsymbol{\delta}] = 0 \quad (9.4)$$

$$\nabla \cdot \mathbf{v}_h = 0 \quad (9.5)$$

$$\mathbf{G}_h - \nabla \mathbf{v}_h = 0 \quad (9.6)$$

where $\mathbf{G}_h$ is the discretized velocity gradient. In the limit of $h \rightarrow 0$, the DEVSS-G formulation reduces to the viscous formulation of Equation 9.2.

The polymer contribution to the stress tensor, which is traditionally written as a closed constitutive equation, is expressed in terms of moments of a distribution function, whose evolution is in turn calculated directly from a configuration space distribution function. The evolution of this configuration distribution function is governed by a diffusion equation. In this work, we considered a recently developed thermodynamically admissible reptation model proposed by Fang, et al. [74] for describing the rheology of concentrated polymer solutions and melts. For convenience, we set $\beta = 0.1$ to minimize the solvent contribution to the stress tensor and hence allow a simulation of a (nearly) undiluted polymer melt system similar to those encountered in industry.

9.2.2 Thermodynamically admissible reptation model for fast flows of entangled polymers

The reptation model used in this paper is a version of the thermodynamically admissible reptation (TAR) model developed by Fang, et al. [73,74]. Excluding the effects of “chain-length breathing” and segment connectivity, Fang, et al. [74] simulated the behavior of a simplified model that incorporates effects of constraint release (both double reptation and convective constraint release), chain stretching, and alignment coupling. The configuration space of the resulting model has three variables, $(\mathbf{u}, \sigma, \lambda)$. Whereas $\mathbf{u}$ and σ have exactly the same interpretation as in the traditional reptation model, λ is the tube length surrounding the polymer molecule normalized by the equilibrium tube length. The resulting model consists of two coupled equations, one for the chain stretch and the other for the orientation of the tube surrounding the polymer molecule. When time is made

dimensionless by the reptation time scale τ_d , the governing dimensionless equation for the chain-stretching dynamics is:

$$\frac{\partial \lambda}{\partial t} + \text{Dev} \cdot \nabla \lambda = (\dot{\lambda}_{\text{convect}} + \dot{\lambda}_{\text{dissip}}) \cdot \lambda \quad (9.7)$$

where $\dot{\lambda}_{\text{convect}}$ and $\dot{\lambda}_{\text{dissip}}$ are the dimensionless rates of convection and dissipation, respectively, for the chain stretching process scaled by τ_d are defined as

$$\begin{aligned} \dot{\lambda}_{\text{convect}} &\equiv \text{De} \mathbf{G}^T : \int_0^1 \mathbf{u} \mathbf{u} f(\mathbf{r}, \mathbf{u}, \sigma, t) d\mathbf{u} d\sigma \\ \dot{\lambda}_{\text{dissip}} &\equiv -\left(\frac{\tau_d}{\tau_s}\right) \frac{(1 - 1/\lambda^2)}{(1 - (\lambda/\lambda_{\text{max}})^2)} \end{aligned} \quad (9.8)$$

where τ_s is the characteristic stretching time (or the Rouse time scale) and λ_{max} is the tube length of the molecule divided by the equilibrium tube length. The diffusion equation for the tube orientation is as follows:

$$\begin{aligned} \frac{\partial f}{\partial t} + \text{Dev} \cdot \nabla f &= -\text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u} \mathbf{u} \mathbf{u}] f + D \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial f}{\partial \mathbf{u}} \\ &\quad - \frac{\partial}{\partial \sigma} (\gamma_1 f) + \gamma_2 f + \frac{\partial^2 f}{\partial \sigma^2} \end{aligned} \quad (9.9)$$

with boundary conditions for f as

$$f(\mathbf{u}, 0, t) = f(\mathbf{u}, 1, t) = \frac{1}{4\pi} \quad (9.10)$$

In Eqn. 9.9, D is an orientational diffusion coefficient. To implement both the double reptation idea (c.f. the first term in Eqn. 9.11) and the convective constraint release idea (c.f. the second term in Eqn. 9.11), D takes the form as follows:

$$D = \begin{cases} \epsilon_{Br} \delta_1 & \text{for } \lambda \leq 1 \\ \epsilon_{Br} (\delta_1 - \delta_2 \dot{\lambda}_{\text{dissip}}) & \text{for } \lambda > 1 \end{cases} \quad (9.11)$$

where δ_1 and δ_2 are characteristic functions for the transfer rates from the constraint release to the relaxation rate of chain orientation. ϵ_{Br} corresponds to the relative strength between the constraint release mechanism and the pure reptation motion. It can also be used a parameter for incorporating the polydispersity of the polymer [73]. In this chapter, both of these functions are set to $1/\lambda$ for consistency with Fang, et al.

The alignment-coupling assumption (also known as the “no independent alignment approximation”) is incorporated through the inclusion of convection and a “*homogeneous* reaction” term in σ . The reaction term is necessary to guarantee the normalization of the distribution function. Here, γ_1 and γ_2 account for the relative importance of the two terms. Traditional implementation of γ_1 and γ_2 involves integral expressions [171]. For example,

$$\gamma_1 = \nabla \mathbf{v} : \hat{\boldsymbol{\tau}}(\sigma) \quad (9.12)$$

$$\gamma_2 = \nabla \mathbf{v} : \mathbf{u} \mathbf{u} \quad (9.13)$$

where for $\sigma \leq 1/2$, $\hat{\boldsymbol{\tau}}(\sigma)$ is defined as:

$$\hat{\boldsymbol{\tau}}(\sigma) = \int_{1/2}^{\sigma} \int \mathbf{u} \mathbf{u} f(\mathbf{u}, s, t) d\mathbf{u} ds \quad (9.14)$$

and $\hat{\boldsymbol{\tau}}(\sigma) = -\hat{\boldsymbol{\tau}}(1 - \sigma)$ for $\sigma \geq 1/2$. A simplified set of expressions for γ_1 and γ_2 have been proposed by Fang [73]:

$$\gamma_1 = -\left(\sigma - \frac{1}{2}\right) \dot{\lambda}_{\text{dissip}} \quad (9.15)$$

$$\gamma_2 = -\dot{\lambda}_{\text{dissip}} \quad (9.16)$$

The presence of the reaction term (second term on the second line of Eqn. 9.9) in the diffusion equation means it is not a Fokker-Planck equation, and therefore there does not exist an equivalent set of stochastic differential equations. As a result, direct solution of the Fokker-Planck equation is the only way to solve such an equation. The simulation results provided by Fang, et al. [74] have attempted to replicate the effects of the reaction contribution through a trajectory removal/generation strategy based on the estimation of the flux of σ across the boundaries 0 and 1.

To evaluate the usefulness of the wavelet-Galerkin method in simulating the advanced reptation model, we compare the numerical approximations by the wavelet-Galerkin method and Brownian dynamics methods by enforcing a mathematically equivalent reptation model in the two approaches. This is done by setting $\gamma_1 = \gamma_2 = 0$, which is equivalent to assuming independent alignment. The resulting reptation model still captures a number of interesting physical features such as chain stretching, double reptation, and convective constraint release mechanisms; and the corresponding diffusion equation is

$$\frac{\partial f}{\partial t} + \text{Dev} \cdot \nabla f = -\text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u} \mathbf{u} \mathbf{u}] f + D \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial f}{\partial \mathbf{u}} + \frac{1}{\pi^2} \frac{\partial^2 f}{\partial \sigma^2} \quad (9.17)$$

with the corresponding stochastic differential equations based on *Ito's* calculus as

$$d\mathbf{r}_c = \text{Dev}(\mathbf{r}_c) dt \quad (9.18)$$

$$d\mathbf{u} = \text{De}(\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u} \mathbf{u} \mathbf{u}) dt + \sqrt{2D} d\mathbf{W} \quad (9.19)$$

$$d\sigma = \frac{\sqrt{2}}{\pi} dW \quad (9.20)$$

where the diffusion coefficient D is given by Eqn 9.11. For homogeneous flows or complex flows with straight streamlines, Equation 9.18 can be ignored.

The stress tensor proposed by Fang, et al. [74] consists of an original Doi-Edwards contribution (c.f. Eqn. 9.22) and a contribution due to the chain stretching (c.f. Eqn. 9.23). In dimensionless form with characteristic stress defined as $\tau_c \equiv \eta_{p,0} \dot{\gamma}_c$, this stress tensor expression is

$$\tau_{p,h} = -\frac{(1-\beta)}{\text{De}} \{ \tau_p^1 + \tau_p^2 \} \quad (9.21)$$

where

$$\tau_p^1 = \int_0^1 \int \mathbf{u} \mathbf{u} f(\mathbf{u}, \sigma, t) d\mathbf{u} d\sigma \quad (9.22)$$

$$\tau_p^2 = -\frac{(1-\lambda^2)}{(1-(\lambda/\lambda_{\max})^2)} \int_0^1 \int \mathbf{u} \mathbf{u} f(\mathbf{u}, \sigma, t) d\mathbf{u} d\sigma \quad (9.23)$$

Notice that this definition of the stress tensor (Eqn. 9.22) leads to finite stress at equilibrium. To ensure a zero stress at equilibrium, we propose to use the structure tensor instead of the second moment for τ_p^1 .

$$\begin{aligned} \tau_p^1 &= \int_0^1 \int \mathbf{u} \mathbf{u} (f(\mathbf{u}, \sigma, t) - f_{\text{iso}}) d\mathbf{u} d\sigma \\ &= \int_0^1 \int \left[\mathbf{u} \mathbf{u} - \frac{1}{3} \delta \right] f(\mathbf{u}, \sigma, t) d\mathbf{u} d\sigma \end{aligned} \quad (9.24)$$

The choices of various constitutive expressions in the diffusion equation and the chain-stretching dynamics equation result in only three adjustable parameters in the simulation. They are τ_d/τ_s , $\lambda_{\max}$, and ϵ_{Br} . τ_d/τ_s is the parameter that controls when the stretching mechanism will be important, $\lambda_{\max}$ controls the nonlinear effect of the chain-stretching mechanism, and ϵ_{Br} controls the relative magnitude of “tube” relaxation and primitive chain relaxation.

9.3 Numerical method

9.3.1 Spatial discretization

The equations of change (Eq. 9.6) are discretized by constructing a mixed finite element approximations for the variables $(\mathbf{v}_h, p_h, \boldsymbol{\tau}_{p,h}, \mathbf{G}_h)$ with expansions in low-order, Lagrangian finite element basis functions defined by dividing the physical domain Ω^{2D} into a set of triangular or quadrilateral elements T_e that are conforming and non-overlapping, that is, $\bigcup T_e = \Omega^{2D}$ and $\bigcap T_e = \emptyset$. We define $V_h(\Omega^{2D})$ and $S_h(\Omega^{2D})$ as the functional spaces spanned by biquadratic Lagrangian polynomials and bilinear Lagrangian polynomials, respectively. For quadrilateral elements, $S_h = \mathbb{Q}_1(\Omega^{2D})$ and $V_h = \mathbb{Q}_2(\Omega^{2D})$, where $\mathbb{Q}_1(\Omega^{2D})$ and $\mathbb{Q}_2(\Omega^{2D})$ are the spaces of bilinear and biquadratic polynomials. For triangular elements, $S_h = \mathbb{P}_1(\Omega^{2D})$ and $V_h = \mathbb{P}_2(\Omega^{2D})$ with the linear and quadratic Lagrangian polynomial approximations for triangles defined as $\mathbb{P}_1(\Omega^{2D})$ and $\mathbb{P}_2(\Omega^{2D})$.

The equations of change and $\mathbf{G}$ -interpolate equations (Eqn. 9.7) are discretized by a standard mixed Galerkin finite element method, as described in detail elsewhere [139]. For the discretized problem, $\mathbf{u}_h \in V_h(\Omega^{2D})$ and $\boldsymbol{\tau}_{p,h}, \mathbf{G}_h, p_h \in S_h(\Omega^{2D})$. The approximation spaces for $(\mathbf{v}_h, p_h, \boldsymbol{\tau}_{p,h}, \mathbf{G}_h)$ are chosen to satisfy the *inf-sup* compatibility condition for the Stokes problem. In this section, we focus on the discretization of the diffusion equation (Eqn 9.9), the stretch equation for the TAR model (Eqn. 9.8), and the stress tensor expressions.

The computational domain for the diffusion equation $\Omega \subset \mathbb{R}^{2+c}$ (where c is the dimension of the configuration space) is divided into three subdomains: the physical space, the configuration space for the tube orientation $\mathbf{u}$, and the space for σ . The physical

space for the diffusion equation Ω^{2D} is discretized by the discontinuous Galerkin method, where the approximation for $f_h(\mathbf{r}, \mathbf{u}, \sigma, t)$ in Ω^{2D} is constructed by piecewise linear polynomials that are discontinuous across boundaries, that is $S^h(T_e)$. The discretized form of the DG formulation for the diffusion equation for each element T_e is therefore written as:

$$\begin{aligned} \left(\Psi_{DG}, \frac{\partial}{\partial t} \mathcal{M}(f_h) \right)_{T_e} &= (\Psi_{DG}, [\text{De}(\mathbf{v} \cdot \nabla \mathcal{M}(f_h)) - \mathcal{A}(\mathbf{G}, f_h, \lambda_h)])_{T_e} \\ &\quad - (\Psi_{DG}, \mathbf{n} \cdot \mathbf{v} \text{De} \mathcal{M}(f_h - \bar{f}_h))_{\partial T_e^-} \end{aligned} \quad (9.25)$$

where $\mathcal{A}(\mathbf{G}, f_h)$ is the weak form of right hand side of the diffusion equations in the configuration space

$$\begin{aligned} \mathcal{A}(\mathbf{G}, f_h, \lambda_h) &= \iint \Psi_u \Psi_\sigma \left(\text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u} \mathbf{u} \mathbf{u}] f_h + D \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial f_h}{\partial \mathbf{u}} \right. \\ &\quad \left. - \frac{\partial}{\partial \sigma} (\gamma_1 f_h) + \gamma_2 f_h + \frac{\partial^2 f_h}{\partial \sigma^2} \right) d\mathbf{u} d\sigma \end{aligned} \quad (9.26)$$

and $\mathcal{M}(f_h)$ is the projection of f_h onto the configuration space

$$\mathcal{M}(f_h) = \iint \Psi_u \Psi_\sigma f_h(\mathbf{r}, \mathbf{u}, \sigma, t) d\mathbf{u} d\sigma \quad (9.27)$$

In the weak form of the physical space discretization (Eqn. 9.25), ∂T_e^- is the inflow surface of the element, with $\mathbf{n}$ denoting the outward unit normal vector on the inflow surface of the element. The superscript “-” refers to the value of the distribution function along the inflow boundary in the upstream element, whereas variables without a superscript refer to evaluations on the interior of the element.

The nodal value of the configuration space distribution function for the reptation models is divided into equilibrium (or isotropic) and nonequilibrium components, that is,

$$f_h(\mathbf{u}, \sigma, t) = 1/4\pi + \hat{f}_h(\mathbf{u}, \sigma, t) \quad (9.28)$$

This separation leads to a modified boundary condition for $\hat{f}_h(\mathbf{u}, \sigma, t)$

$$\hat{f}_h(\mathbf{u}, 0, t) = \hat{f}_h(\mathbf{u}, 1, t) = 0 \quad (9.29)$$

Directly substituting the expression (Eqn. 9.28) into Equation 9.26 yields

$$\begin{aligned} \mathcal{A}(\mathbf{G}, \hat{f}_h, \lambda_h) = & \int \int \psi_u \psi_\sigma \left(-\frac{3\text{De}}{4\pi} \mathbf{G}^T : \mathbf{u}\mathbf{u} + \text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u}\mathbf{u}\mathbf{u}] \hat{f}_h \right. \\ & \left. + D \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial \hat{f}_h}{\partial \mathbf{u}} - \frac{\partial}{\partial \sigma} \left(\gamma_1 \left[\frac{1}{4\pi} + \hat{f}_h \right] \right) + \gamma_2 \left[\frac{1}{4\pi} + \hat{f}_h \right] + \frac{\partial^2 \hat{f}_h}{\partial \sigma^2} \right) d\mathbf{u} d\sigma \end{aligned} \quad (9.30)$$

The configuration space for the orientation $\mathbf{u}$ is discretized with a wavelet-Galerkin method, where the diffusion equation and the configuration distribution function are approximated by the use of scaling-function expansions. The discretization is done by a mixed Galerkin-collocation procedure. The spatially varying (in configuration space) coefficients (such as $\mathbf{G} : \mathbf{u}\mathbf{u}$ in the hydrodynamic term) are evaluated and formed by a collocation method, and they are then projected on to the scaling function space. The fundamentals on wavelets and scaling functions, as well as the implementation details have been described in Chapters 3 and 6 and are not repeated here.

The configuration space for σ , Ω^σ , is discretized by a series of finite Fourier transform. The specific basis functions $\{\sqrt{2} \sin(n\pi\sigma), n \in \mathbb{N}^+\}$ are chosen such that the boundary conditions for $\hat{f}_h(\mathbf{u}, \sigma, t)$ are automatically satisfied. For the TAR model, the final weak form of the right side of the diffusion equation in the physical and orientation space for a specific mode n is:

$$\begin{aligned} (\Psi_{DG}, -\mathcal{A}(\mathbf{G}, \hat{f}_h, \lambda_h))_{T_e} = & \left(\Psi_{DG}, \left(\varphi, \frac{3\sqrt{2}\text{De}}{2n\pi^2} \mathbf{G}^T : \mathbf{u}\mathbf{u} \right)_{\Omega^{\text{or}}} \right)_{T_e} \\ & + \left(\Psi_{DG}, \left(\varphi, -\text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u}\mathbf{u}\mathbf{u}] \hat{f}_n + \epsilon_{\text{Br}} \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial \hat{f}_n}{\partial \mathbf{u}} n^2 \hat{f}_n + \sum_n c_{mn} \hat{f}_n \right)_{\Omega^{\text{or}}} \right)_{T_e} \end{aligned} \quad (9.31)$$

where φ is the scaling function for the $\mathbf{u}$ -orientation space discretization and for the projection of f_h . The c_{mn} are the coupling coefficients between different modes n associated with alignment coupling:

$$c_{mn} = \int_0^1 \sin(m\pi\sigma) \left(-\frac{\partial}{\partial\sigma} \left(\gamma_1 \left[\frac{1}{4\pi} + \sin(n\pi\sigma) \right] \right) + \gamma_2 \left[\frac{1}{4\pi} + \sin(n\pi\sigma) \right] \right) d\sigma \quad (9.32)$$

For γ_1 and γ_2 given by Equations 9.15 and 9.16, the c_{mn} vanishes if m is odd and n is even, or vice versa. For odd values of m and n , the c_{mn} have the relatively simple form

$$c_{mn} = \begin{cases} -0.5 & m = n \\ -2mn/(m^2 - n^2) & m \neq n \end{cases} \quad (9.33)$$

The stress tensor $\boldsymbol{\tau}_{p,h}$ is found by a least square estimate of the stress over each element with the integration over σ space performed analytically. The resulting stress tensor expression is

$$(\Psi_{DG}, \boldsymbol{\tau}_{p,h}) = \sum_{n \text{ is odd}} \left(\Psi_{DG}, -\frac{\sqrt{8}\pi}{n} \frac{(\lambda_{\max}^2 - 1)}{(\lambda_{\max}^2 - \lambda_h^2)} \lambda_h^2 \int \mathbf{u}\mathbf{u} \left(\hat{f}_h(\mathbf{u}, t) + \frac{1}{4\pi} \right) d\mathbf{u} + \frac{\sqrt{8}\pi}{3n} \boldsymbol{\delta} \right) \quad (9.34)$$

Because the stress tensor expression only involves odd values of finite Fourier basis functions and the diffusion equations for odd mode values do not interact with even mode values, only simulation of the diffusion equation over the odd values of modes is necessary. This significantly increases the number of modes that can be simulated in a single calculation.

The discretization of the chain-stretching equation in the TAR model is treated with the SUPG method and Eqn. 9.7 is then written such that for all $\Psi \in S^h$,

$$\left(\tilde{\Psi}, \frac{\partial \lambda}{\partial t} \right)_{\Omega} = \quad (9.35)$$

$$\left(\tilde{\Psi}, -\text{Dev} \cdot \nabla \lambda + \lambda \text{De} \mathbf{G}^T : \int_0^1 \mathbf{u} \mathbf{u} f(\mathbf{r}, \mathbf{u}, \sigma, t) d\mathbf{u} d\sigma + \left(\frac{\tau_d}{\tau_s} \right) \frac{\lambda_{\max}^2 (1 - \lambda^2)}{\lambda (\lambda_{\max}^2 - \lambda^2)} \right)_{\Omega}$$

In Eqn. 9.34, $\tilde{\Psi}$ is defined as

$$\tilde{\Psi} = \Psi + h \frac{\mathbf{v}_h}{|\mathbf{v}_h|} \cdot \nabla \Psi \quad (9.36)$$

for all $\Psi \in S^h$, and h defined as a characteristic element size along the flow direction. We use continuous linear approximations for λ , so that $S^h(\Omega) \subset \mathbb{Q}_1(\Omega)$ for quadrilateral elements and $S^h(\Omega) \subset \mathbb{P}_1(\Omega)$ for triangular elements.

9.3.2 Time integration algorithm

An operator splitting strategy leads to a time integration method that decouples the calculation of the polymer stress (by solution of the diffusion equation for the double reptation model) from the temporal update of the velocity and pressure fields (by solution of a generalized Stokes problem). The resulting system of differential-algebraic equations is of the form

$$\mathbf{M} \cdot \begin{bmatrix} \frac{d\hat{f}_h}{dt} \\ \frac{d\lambda_h}{dt} \\ \frac{d\gamma}{dt} \end{bmatrix} + \begin{bmatrix} \mathcal{D}_f(\hat{f}_h, \lambda_h) + \gamma \mathcal{L}'(\hat{f}_h) \\ \mathcal{R}_\lambda(\mathbf{v}_h, \mathbf{G}_h, \hat{f}_h, \lambda_h) \\ \mathcal{L}(\hat{f}_h) \end{bmatrix} = \begin{bmatrix} \mathcal{C}_f(\hat{f}_h, \mathbf{v}_h, \mathbf{G}_h) \\ 0 \\ 0 \end{bmatrix} \quad (9.37)$$

$$\mathbf{g}(\hat{f}_h, \lambda_h, \tau_{p,h}, \mathbf{v}_h, \mathbf{G}_h, p_h) = 0 \quad (9.38)$$

In Equation 9.37, $\mathcal{C}_f$ and $\mathcal{D}_f$ correspond to the weak formulations for the convective and diffusive operators of the diffusion equation in the discrete space, respectively:

$$\begin{aligned} \mathcal{C}_f(\hat{f}_h, \mathbf{v}_h, \mathbf{G}_h) \equiv & (\Psi_{DG}, [\text{De}(\mathbf{v} \cdot \nabla \mathcal{M}(f_h)) - \mathcal{C}(\mathbf{G}, f_h)])_{T_e} \\ & - (\Psi_{DG}, \mathbf{n} \cdot \mathbf{v} \text{De} \mathcal{M}(f_h - \bar{f}_h))_{\partial T_e} \end{aligned} \quad (9.39)$$

$$\mathcal{D}_f(\hat{f}_h, \lambda_h) \equiv \left(\Psi_{DG}, \iint \psi_u \psi_\sigma \left(D(\lambda_h) \frac{\partial}{\partial \mathbf{u}} \cdot \frac{\partial}{\partial \mathbf{u}} \hat{f}_h \right) d\mathbf{u} d\sigma \right)_{T_e} \quad (9.40)$$

The operator $\mathcal{C}$ is defined as

$$\begin{aligned} \mathcal{C}(\mathbf{G}, \hat{f}_h, \lambda_h) \equiv & \iint \psi_u \psi_\sigma \left(-\frac{3 \text{De}}{4\pi} \mathbf{G}^T : \mathbf{u} \mathbf{u} + \text{De} \frac{\partial}{\partial \mathbf{u}} \cdot [\mathbf{G}^T \cdot \mathbf{u} - \mathbf{G}^T : \mathbf{u} \mathbf{u} \mathbf{u}] \hat{f}_h \right. \\ & \left. - \frac{\partial}{\partial \sigma} \left(\gamma_1 \left[\frac{1}{4\pi} + \hat{f}_h \right] \right) + \gamma_2 \left[\frac{1}{4\pi} + \hat{f}_h \right] + \frac{\partial \hat{f}_h}{\partial \sigma^2} \right) d\mathbf{u} d\sigma \end{aligned} \quad (9.41)$$

$\mathbf{M}$ is the mass matrix over the physical space and configuration space. The orthogonal properties of the finite Fourier series lead to a block diagonal structure and hence each mode can be updated independently. Furthermore, by using the dual stage element-by-element decomposition developed in Chapters 4 and 8, the mass matrix resulting from the physical space and the orientation space $\mathbf{u}$ can then be updated in a node-by-node fashion. $\mathcal{L}$ is the normalization condition in the discrete space, and $\mathcal{L}'$ is the derivative of the normalization condition with respect to the discrete variable $\hat{f}_h$. $\mathcal{R}_\lambda$ is the weak form for the operator corresponding to the chain-stretching equation (Eqn. 9.7). We write λ_h as an expansion of the finite element basis functions and formulate $\mathcal{R}_\lambda$ as $\mathcal{R}_\lambda(\mathbf{v}_h, \mathbf{G}_h, \hat{f}_h, \lambda_h) = \sum \mathcal{R}_{\lambda,i} \lambda_{h,i} \equiv \mathcal{R}'_\lambda(\mathbf{v}_h, \mathbf{G}_h, \hat{f}_h, \lambda_h) \cdot \lambda_h$. This allows a semi-implicit strategy for updating λ_h where the variables in $\mathcal{R}'_\lambda$ are updated explicitly by using the information from the previous time step. The function $\mathbf{g}$ consists of two contributions: (1) the stress tensor expression that involves the moments of the distribution function together with λ that contributes to the stress tensor, and (2) the discretizations of the kinematic variables $(\mathbf{v}_h, \mathbf{G}_h, p_h)$ from the generalized Stokes problem. Equation 9.38 is invertible for the kinematic variables, so that this equation can be rewritten as

$$\begin{bmatrix} v_h \\ p_h \\ G_h \end{bmatrix} = \tilde{g}(\tau_{p,h}(\hat{f}_h, \lambda_h)) \quad (9.42)$$

Equation 9.42 is then substituted into Eqn. 9.37 to give equations written solely in terms of the distribution function variables.

We then discretize the resulting ODEs with respect to time for a specific time advancement from t_n to $t_{n+\theta}$. A single step of the resulting semi-implicit method is derived by solving the follow equation.

$$\begin{aligned} S(\delta\hat{f}_h, \delta\lambda_h, \gamma) &\equiv \begin{bmatrix} M_f \cdot \delta\hat{f}_h + \Delta t \mathcal{D}_f(\delta\hat{f}_h, \lambda_h) + \Delta t \gamma \mathcal{L}'(\hat{f}_h) \\ M_\lambda \cdot \delta\lambda_h + \Delta t \mathcal{R}'_\lambda(\hat{f}_h, \lambda_h, \tilde{g}(\tau_{p,h}(\hat{f}_h, \lambda_h))) \cdot \delta\lambda_h \\ \Delta t \mathcal{L}(\delta\hat{f}_h) \end{bmatrix} \\ &= \begin{bmatrix} -\Delta t \mathcal{D}(\hat{f}_h) + \Delta t \mathcal{C}_f(\hat{f}_h, \lambda_h, \tilde{g}(\tau_{p,h}(\hat{f}_h, \lambda_h))) \\ 0 \\ 0 \end{bmatrix} \equiv L(\hat{f}_h, \lambda_h) \end{aligned} \quad (9.43)$$

and

$$\mathbf{x}(t_{n+\theta}) \equiv \begin{bmatrix} \hat{f}_h(t_{n+\theta}) \\ \lambda(t_{n+\theta}) \\ \gamma \end{bmatrix} = \begin{bmatrix} \hat{f}_h(t_n) \\ \lambda(t_n) \\ 0 \end{bmatrix} + \begin{bmatrix} \delta\hat{f}_h \\ \delta\lambda \\ \gamma \end{bmatrix} = \mathbf{x}(t_n) + \tilde{L}(\hat{f}_h, \gamma) \quad (9.44)$$

where $\tilde{L} \equiv S^{-1} \cdot L$. For $\theta = 1$, the above algorithm corresponds to a first order algorithm. For an one-stage time integration algorithm, we evaluate the variables in $\mathcal{R}'_\lambda$ by using the variables from the previous time step. This allows us to solve the equation for $\delta\lambda_h$ independent of the distribution function and its associated constraint equation. Although higher order algorithms may be derived, we use the first order time integration scheme for the rest of this chapter because there is no obvious advantage of using the higher order time integration schemes, as has been seen in Chapter 8.

9.3.3 Solution strategy

A typical dimension of the finite Fourier space ranges from one to 10 basis functions; a typical dimension of the scaling function expansion is about 16 basis functions for the θ space and 32 basis function for the ϕ direction. Depending on the shape of the element (quadrilateral or triangle), the number of DG basis functions scales as $4N_e$ or $3N_e$, where N_e is the total number of element in the mesh. Although the DG discretization allows an element-by-element decomposition strategy, the elements are coupled through the inflow boundary integrals unless the elements are ordered in a sequence that moves downstream from an inflow boundary. Hence, the typical dimension for the discrete version of the diffusion equation for a flow problem with 1000 elements is on the order of 2,000,000 unknowns for each mode for the TAR model. Solution of such problem with a direct method is infeasible, and with an iterative method would be very difficult even with an appropriate preconditioner. Therefore, we use a semi-implicit time-stepping method for the diffusion equations, which treats the orientation diffusion *implicitly* and all other operators *explicitly*.

Although this strategy allows an element-by-element decomposition, the stiffness matrix for each elemental matrix (of order 2,000 unknowns) has to be either stored or computed at each time step unless the Jacobian of the mass matrix in Ω^{2D} is a constant [161]. This greatly restricts the type of elements and problems that can be simulated with the hybrid method. By taking advantage of the tensorial product nature of the basis functions used in each subspace, we construct a node-by-node decomposition strategy to decrease further the number of unknowns in each subproblem and allow the stiffness matrix for each subproblem to be the same at each node. This strategy was sketched in Chapter 8 and is summarized below:

Consider an entry in the mass matrix,

$$\begin{aligned}
M_{\mu\nu} &\equiv \int \Phi_\mu \Phi_\nu d\Omega \\
&= \int \int (\Psi_i \phi_m)_{\mu = \mu(i, m)} (\Psi_j \phi_n)_{\nu = \nu(j, n)} d\Omega^{2D} d\Omega^{\text{ori}}
\end{aligned} \tag{9.45}$$

where $\mu(i, m)$ is the mapping from the i -th basis function in Ω^{2D} and m -th basis function in Ω^{ori} to the μ -th basis function in the space of $\Omega \cap (\Omega^{2D} \cup \Omega^{\text{ori}})$. By factoring out the integration over Ω^{2D} from that over Ω^{ori} , the stiffness matrix for a quadrilateral element can be represented as:

$$\begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \tag{9.46}$$

where $S_{ij} \equiv (\int \Psi_i \Psi_j d\Omega^{2D}) (\int \phi_m \phi_n d\Omega^{\text{ori}})$. We first apply the inverse of the mass matrix (M^{-1}) in Ω^{2D} to Eqn 9.46 and then solve each stiffness matrix in Ω^{ori} independently. This method can be shown schematically as,

$$\begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \rightarrow \begin{bmatrix} M_{1j}^{-1} S_{j1} & 0 & 0 & 0 \\ 0 & M_{2j}^{-1} S_{j2} & 0 & 0 \\ 0 & 0 & M_{3j}^{-1} S_{j3} & 0 \\ 0 & 0 & 0 & M_{4j}^{-1} S_{j4} \end{bmatrix} \rightarrow \begin{bmatrix} I & 0 & 0 & 0 \\ 0 & I & 0 & 0 \\ 0 & 0 & I & 0 \\ 0 & 0 & 0 & I \end{bmatrix} \tag{9.47}$$

The mass matrix in Ω^{2D} is of dimension three (for triangles) and four (for quadrilaterals) and therefore can be easily stored or even computed at each time step for each element. This strategy thus allows us to use or study a large variety of meshes and problems where the mass matrix in Ω^{2D} is different from element-to-element. For example, we can use quadrilateral elements and study axisymmetric flow problems.

The stiffness matrix in Ω^{ori} has only 513 unknowns. Both LU decomposition solvers (DGETRF/DGETRS in LAPACK) and iterative solvers (GMRES with ILUTP precondi-

tioner) have been tested. Depending on the complexity of the stiffness matrix, iterative solvers perform at least as fast as the LU decomposition solver.

9.4 Review of numerical results for simple, homogeneous flows

In this section, we review and explore the rheology of the TAR model in simple, homogeneous flows. Much of the rheology and material functions for the TAR model have already been reported by Fang [74] based on Brownian dynamics simulations. The intent of repeating some of the calculations in this section is to show the robustness of the mixed wavelet-Galerkin/finite-Fourier method in simulating the complex rheology of the TAR model. In addition, we want to demonstrate the accuracy and convergence properties of the mixed wavelet-Galerkin/finite-Fourier method in approximating the underlying distribution function of the TAR model by comparing its predictions with Brownian dynamics simulation for simple shear flow. For the Brownian dynamics simulation, we consider a modification of the TAR model, which assumes independent alignment. This assumption, which is valid for single-step flows with no flow direction reversal, removes the “reaction” term in the diffusion equation and hence no approximation is needed to derive the corresponding stochastic differential equation. The three parameters in the TAR are taken to be $\epsilon_{Br} = 0.2$, $\tau_d/\tau_s = 10$, and $\lambda_{max} = 10$. The choices of these parameters are typical for polymer melt systems [74].

The two rheological experiments considered in this section are homogeneous shear flow and planar elongation flow. In the benchmark complex flow problem of a flow around an isolated cylinder in a confined channel, shear flow dominates flow in the channel and in the gap between the wall and the cylinder surface and planar elongational flow is important near the front and rear stagnation points of the cylinder, close to the center-

line. Therefore, understanding the fluid response in these two standard rheological experiments will be useful.

9.4.1 Simple shear flow

For steady state shear flow of the form $v_x = \dot{\gamma}y$, $v_y = v_z = 0$, three material functions (viscosity η , first normal stress coefficient Ψ_1 , and second normal stress coefficient Ψ_2) are defined according to Bird et al. [19] as

$$\tau_{yx} = -\eta\dot{\gamma} \quad (9.48)$$

$$\tau_{xx} - \tau_{yy} = -\Psi_1\dot{\gamma}^2 \quad (9.49)$$

$$\tau_{yy} - \tau_{zz} = -\Psi_2\dot{\gamma}^2 \quad (9.50)$$

The predictions of these material properties by the TAR model are shown in Figure 9.1 as functions of the dimensionless shear rate or Deborah number ($De \equiv \tau_d\dot{\gamma}$). The predictions of the Doi-Edwards model are also included for comparison. Apart from very low shear rates ($De < 0.1$), the predictions of the wavelet-Galerkin and Brownian dynamics methods are essentially the same. The discrepancy between two is due to the large statistical error for the Brownian dynamics simulations at low De . The agreement between the Brownian dynamics and the wavelet-Galerkin methods at high De confirms the usefulness of the wavelet-Galerkin method for high deformation rate flow calculations. Figure 9.1a shows the shear stress $-\tau_{yx}$ predicted by TAR model compared with the Doi-Edwards (DE) model. At low De ($De < 10$), both the DE and the TAR models predicts essentially the same dynamics within a constant factor. This suggests that reptation is the dominant dynamics for an entangled polymer system at low De . At intermediate shear rates ($1 < De < 100$), the shear stress varies slowly with De . This corresponds to the power law region in the viscosity (Figure 9.1b). If one defines a power law index n such that

$\eta = mDe^n$, then $n = -0.75$ in this region for the TAR model, which is a significant improvement from that of the Doi-Edwards model ($n = -1.5$). After a plateau at De between 10 to 100, the shear stress for the DE model drops with a power law behavior. The TAR model, on the other hand, predicts an upturn of the shear stress at high De ($De > 100$). This stress upturn at high De corresponds to a shear thickening in the viscosity (Figure 9.1b). This shear thickening effect is due to the fast stretching at high De , which is evident by considering the steady state stretch function shown in Figure 9.1e. For $De > 100$, λ grows rapidly to $\lambda_{\max}$. Because the stress tensor scales quadratically with λ , the fast growth of λ dominates the stress tensor. This leads to a shear-thickening of the viscosity, as well as of the normal stress coefficients (Figure 9.1c and d).

Simulation of the stretching function close to maximum extension is very difficult for two reasons. First, the value of the dissipation function close to the maximum extension is very large and nearly singular. Hence simulation of the chain-stretching equation requires a very small time step to ensure numerical stability of the chain-stretching equation. Second, a large value of chain extension activates the convective constraint release mechanism. Similar to the chain-stretching equation, the diffusion equation for the tube dynamics will have very fast dynamics due to the large value of the diffusion coefficient for the constraint release. The resulting stiff diffusion equation requires an even smaller time step size to preserve numerical stability of the diffusion equation. For both of these reasons our simulation are limited only up to or close to the plateau value of the chain-stretching function.

One of the important results from Chapter 8 is that the lack of significant elasticity leads to a generalized Newtonian-like velocity profile for the problem of flow around an isolated cylinder confined in a channel. To estimate the significance of “elasticity” and

shear thinning in the TAR model, we consider various stress ratios. First, the recoverable shear S_R is defined as the ratio between the first normal stress difference and the shear stress

$$S_R \equiv \frac{(\tau_{xx} - \tau_{yy})}{2\tau_{yx}} \quad (9.51)$$

For $S_R \ll 1$, the prediction of the associated model are expected to be similar to that of a Newtonian or generalized Newtonian model, unless strong elongational hardening is present in the model. Examining Figure 9.1e in the light of this criterion suggests that the TAR model may not provide a substantial amount of elasticity at low De because neither chain stretching nor constraint mechanisms are significant at low De .

Another interesting ratio is the ratio of the second to the first normal stress difference. This ratio is considered to be important in the study of the Weissenberg effect [142]. Figure 9.1f shows the variation of both of these stress ratios, S_R and $-\Psi_2/\Psi_1$, with De . At low De , $-\Psi_2/\Psi_1$ predicted by the TAR model is the same as for the DE model. At higher De , however, the rate of decrease of $-\Psi_2/\Psi_1$ for the TAR model is significantly slower than that for the DE model because of constraint release effects. This may lead to a Weissenburg effect at high De , which may be in accord with some of the experimental observations.

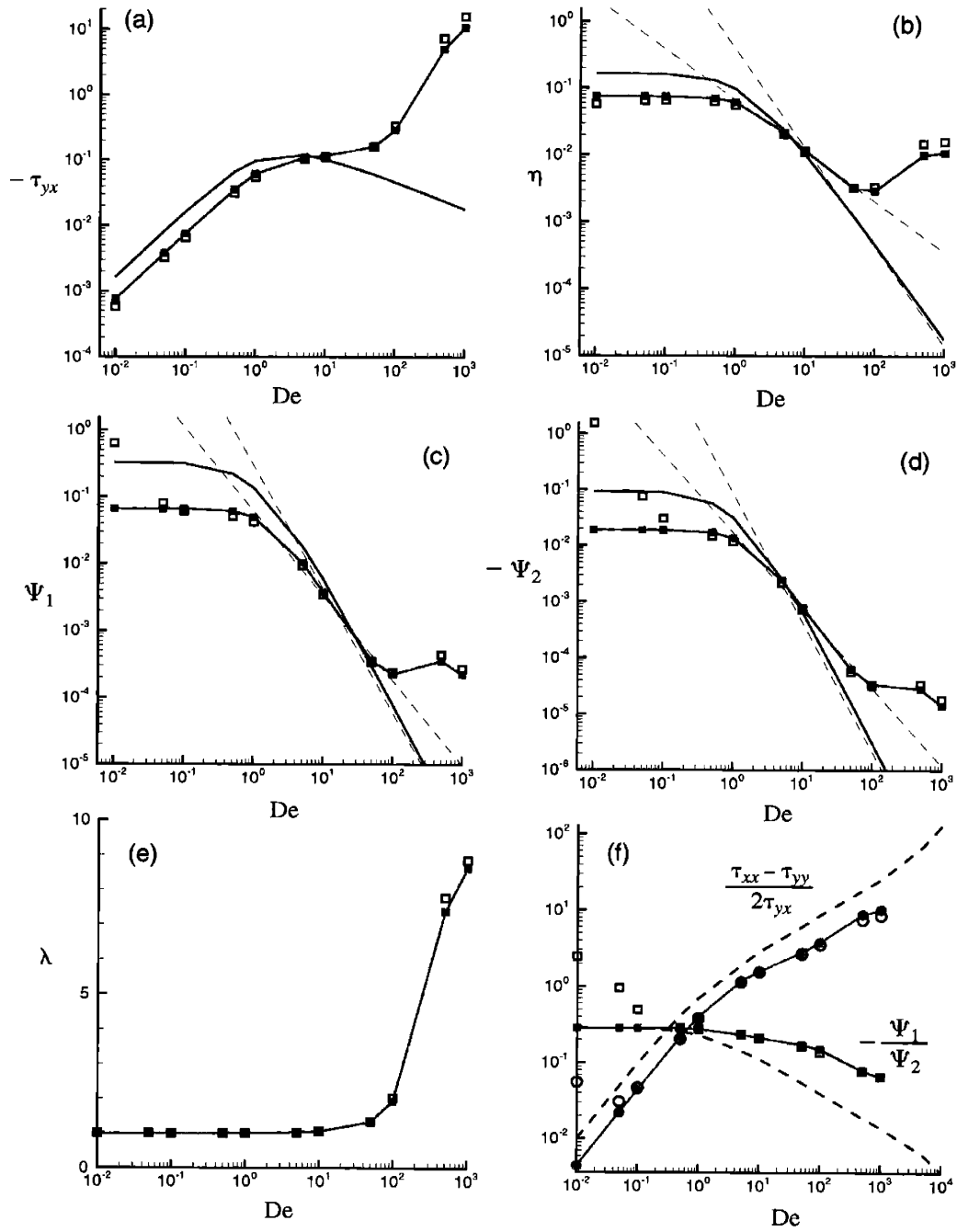


Figure 9.1: Material functions in a steady-state shear flow for the TAR model with independent alignment assumption predicted by the wavelet-Galerkin method (solid symbols) and Brownian dynamics simulation (empty symbols): (a) shear stress, (b) viscosity, (c) first normal stress coefficient, (d) second normal stress coefficient, (e) Stretch, (f) recoverable shear and ratio of normal stress coefficients. For (a) to (d) the solid blue line corresponds to predictions by the Doi-Edwards model and dashed lines to the power law fit; (f) dashed lines are the predictions of the Doi-Edwards model.

Time-dependent shear flow in which the fluid is initially at rest and then subjected to a steady-state shear flow is used to examine the stress growth behavior. The transient material functions (η^+ , Ψ_1^+ , Ψ_2^+) are defined analogously to η , Ψ_1 , Ψ_2 . These material functions and the growth of the stretch function λ are shown in Figure 9.2. Because of the large time scale for the dissipation dynamics for the chain-stretching ($\tau_d/\tau_s = 10$), λ reaches steady state much faster than the stress tensor for low to moderate De ($De < 100$). At moderate De ($De \sim 10$), stress overshoot is observed for both shear and normal stress coefficients. At high shear rates ($De > 100$), the large value of the steady state stretch function is the dominant contribution to the stress tensor, and therefore the dynamics of the transient material functions are similar to that of chain stretching.

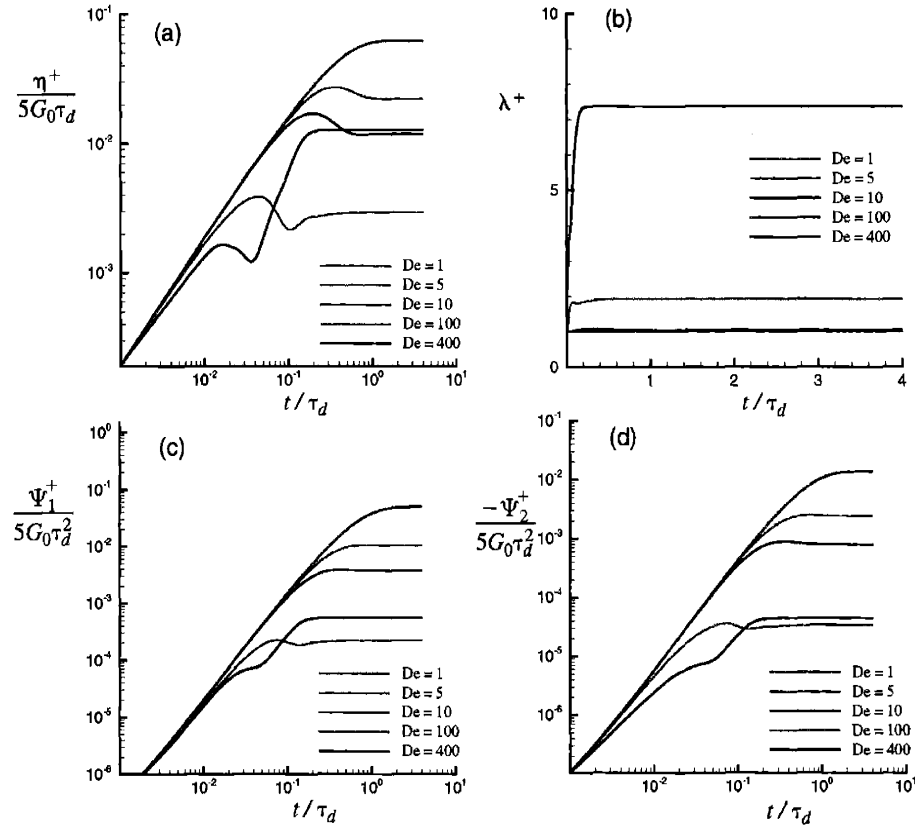


Figure 9.2: Transient material functions predicted by the TAR model during the start-up of steady simple shear flow calculated by the wavelet-Galerkin method: (a) viscosity; (b) stretch function; (c) first normal stress coefficient; (d) second normal stress coefficient

Figures 9.3 examine the sensitivity of the shear flow properties to τ_d/τ_s . Variation of $\lambda_{\max}$ leads to a faster growth of λ , as well as affecting the De at which the chain stretching mechanism is activated. All the rheological properties examined in Figure 9.3 are essentially identical up to $De \sim \tau_d/\tau_s$, after which the chain stretching mechanism is activated. For the material functions (viscosity, and first and second normal stress coefficients), the activation of the chain stretching mechanism leads to shear thickening, followed by shear-thinning after the stretching function λ reaches a plateau value.

Although the chain-stretching function is not explicitly present in the expressions for the two stress ratios, the influence of the onset of the activation of the chain-stretching mechanism is still obvious. This is shown in Figs. 9.3e and f. Similar to the material functions, the stress ratios are the same for De up to $De \sim \tau_d/\tau_s$. The growth of the recoverable shear before the activation of the chain-stretching mechanism scales linearly with increasing De for $De < 1$ and increases roughly as $De^{0.5}$ for $De > 1$. After the activation of the chain-stretching mechanism, this ratio rises rapidly owing to the activation of convective constraint release. Once the chain-stretching function reaches its plateau value, this stress ratio remains constant although this is not obvious due to the lack of numerical results for the large shear rate results.

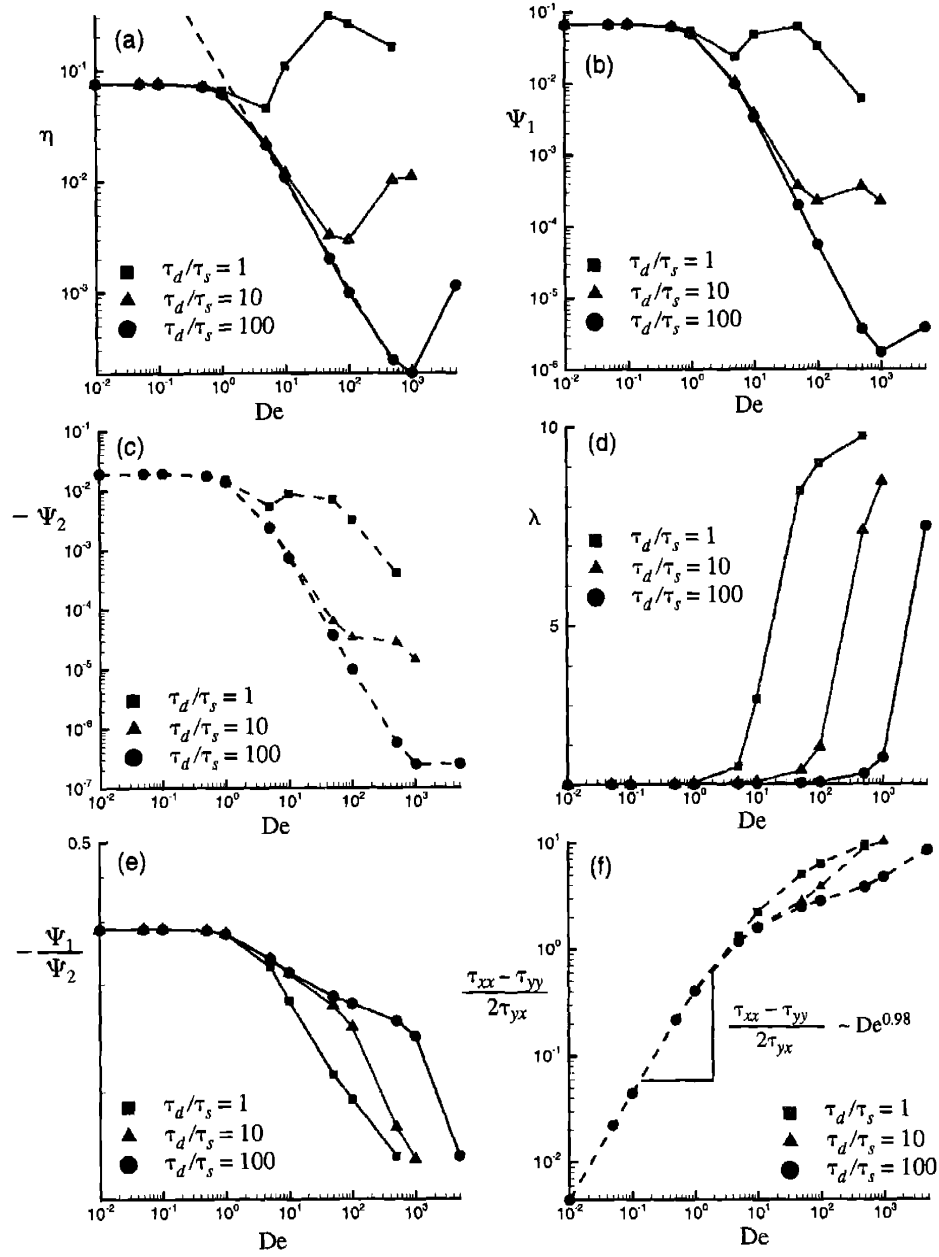


Figure 9.3: Effect of the Rouse time scale on the viscometric properties, stretch ratio, and the stress ratios for the TAR model.

9.4.2 Planar Elongational flow

The flow in the wake of a cylinder close to the symmetry plane approximates a planar extensional flow (that is $v_x = \dot{\epsilon}x$, $v_y = -\dot{\epsilon}y$, $v_z = 0$, where $\dot{\epsilon}$ is the elongational rate). Knowing and understanding the elongational rheology of the TAR model will be useful to interpreting the complex dynamics of the TAR model in the flow around an isolated cylinder confined in a channel. For a planar elongational flow, the relevant material functions are the two planar elongational viscosities defined based on the two normal stress differences as $\bar{\eta}_1 \equiv -(\tau_{xx} - \tau_{yy})/4\dot{\epsilon}$ and $\bar{\eta}_2 \equiv -(\tau_{zz} - \tau_{yy})/2\dot{\epsilon}$. The flow around an isolated cylinder confined in a channel is two dimensional and the relevant material function is $\bar{\eta}_1$. Figure 9.4 shows the steady-state values of both $\bar{\eta}_1$ and $\bar{\eta}_2$, normalized by the zero-shear-rate viscosity (calculated from steady-state shear flow) over a range of De defined as $\tau_d\dot{\epsilon}$. For $De < 1$, the elongational viscosity is a constant. Shear thinning occurs over an intermediate range of De ($1 < De < 10$) due to tube alignment. At high De, $De > 10$, the chain-stretch mechanism dominates the steady state stress; and hence the extensional viscosity increases with increasing strain rate. Although one may anticipate that elongational thickening will reach a constant plateau as λ reaches the maximum value $\lambda_{\max}$, simulation in the range of this constant plateau is extremely difficult because the large value of λ corresponds to fast dynamics due to the constraint release mechanism. In the calculation shown, the maximum De is limited to 30, which is substantially smaller than the limiting value in shear flow.

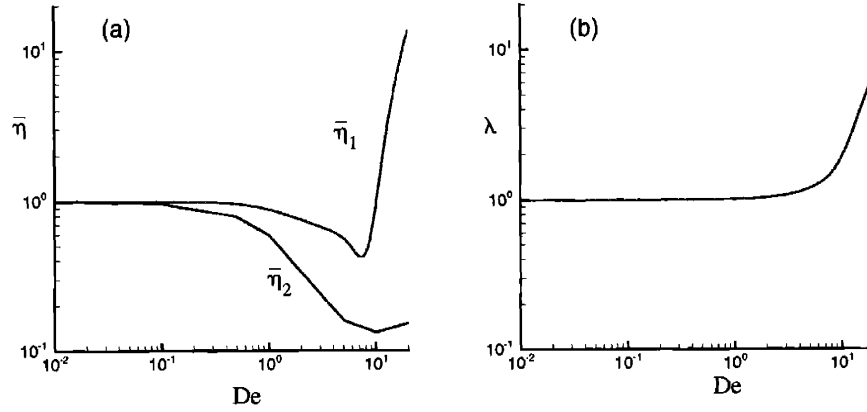


Figure 9.4: Steady state elongation viscosity ($\bar{\eta}_1$ and $\bar{\eta}_2$) and stretching function λ for the TAR model.

In the calculation of a flow around an isolated cylinder confined in a channel, the flow of a fluid particle along the downstream centerline from the rear stagnation point is essentially a transient planar elongation flow in a Lagrangian sense. The build-up of the centerline strain rate is also a time-dependent function [222]. As a result, it is the transient rheology of a molecular model that is important for the built-up of the stress. The transient behavior of the extensional viscosity predicted by the TAR model during the start-up of planar elongation flow is shown in Figure 9.5. This figure demonstrates the strong dependence of the transient rheology on the dynamics of chain-stretching. At low De where λ remains essentially at its equilibrium value, the transient rheology is independent of De . At $De = 5$, a weak chain stretching effect is observed, and the tube dynamics leads to decrease in elongational viscosity. At an even higher De , strain-hardening occurs, which will eventually saturate because of finite chain stretch ability. Similar to shear flow, we expect strain-thinning will occur after the plateau value for chain-stretching is reached. Unfortunately, this behavior is not observed in our simulation. Again, this is because of the difficulty in time resolution at high De .

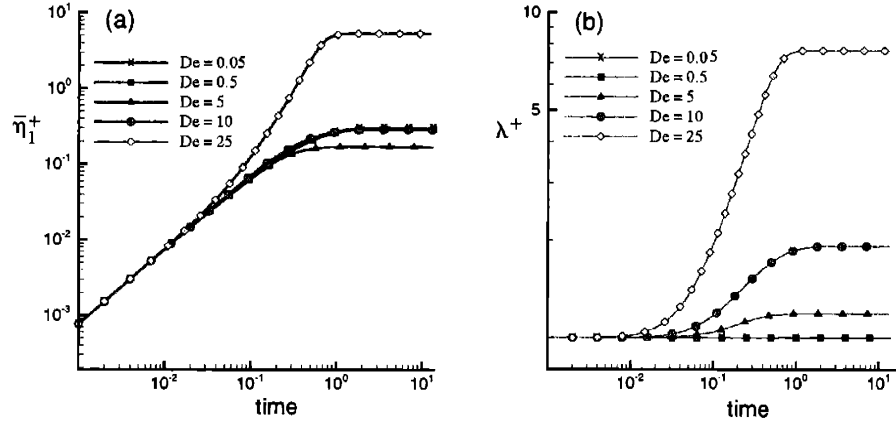


Figure 9.5: Transient elongational viscosity and the stretch function during the start up of planar elongation flow for the TAR model.

9.5 Simulation of complex flows

The effect of the rich rheological behavior of the TAR model in a complex flow simulation is explored in this section. In particular, calculations are performed to study the behavior of the TAR model in a flow around an isolated cylinder confined in a channel with a fixed ratio of the channel half width $(1/2)H$ to the cylinder radius R of two in a domain $x \in [-12, 12]$, $y \in [0, 2]$, where x is the principal flow direction. A one-dimensional equation set is solved along the inflow surface, and a fully developed velocity profile is assumed at the outflow surface. A symmetric boundary condition is assumed along the centerline ($y = 0$), and a zero velocity condition is imposed along the solid channel wall surface and on the cylinder surface.

Three meshes are used for the calculations in this chapter. Each mesh in the sequence is essentially based on a uniform refinement near the cylinder and in the wake of the coarsest mesh M1. The center part of the second mesh, M2, is shown as Figure 9.6. This mesh is the same mesh as the M2 in Chapter 8. The characteristics of the three meshes are shown in Table 9.1.

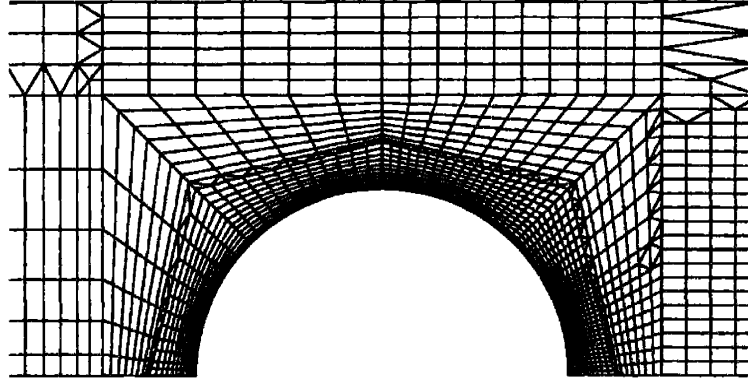


Figure 9.6: Central part of the finite element mesh for calculation of the viscoelastic flow of the TAR model past an isolated cylinder in a channel with $H = 2$

	M1	M2	M3
Number of elements	1093	2213	4400
Number of nodes	8809	17301	34717
Number of degrees of freedom for v - p - G problem	13649	26243	52623
Number of degrees of freedom for the distribution function	11,214,180	22,705,380	45,144,000

Table 9.1: Characteristic of the meshes used in the calculation for a flow around an isolated cylinder confined by a channel

Before presenting the results for the TAR model, we first examine the velocity and pressure profiles for Newtonian flow (Fig. 9.7). The expected symmetry for axial velocity v_x and the antisymmetry for v_y about the plane $x = 0$ are observed. The fluid accelerates as it approaches the cylinder. The narrow confinement of the channel wall and the cylinder surface at $x = 0$ causes intense shearing in this gap region that leads to a maximum and minimum in G_{yx} on the channel wall and the cylinder surface, respectively. The minimum and the maximum values of G_{xx} occurs at $(x = -1/\sqrt{2}, y = 1/\sqrt{2})$ and $(x = 1/\sqrt{2}, y = 1/\sqrt{2})$, respectively.

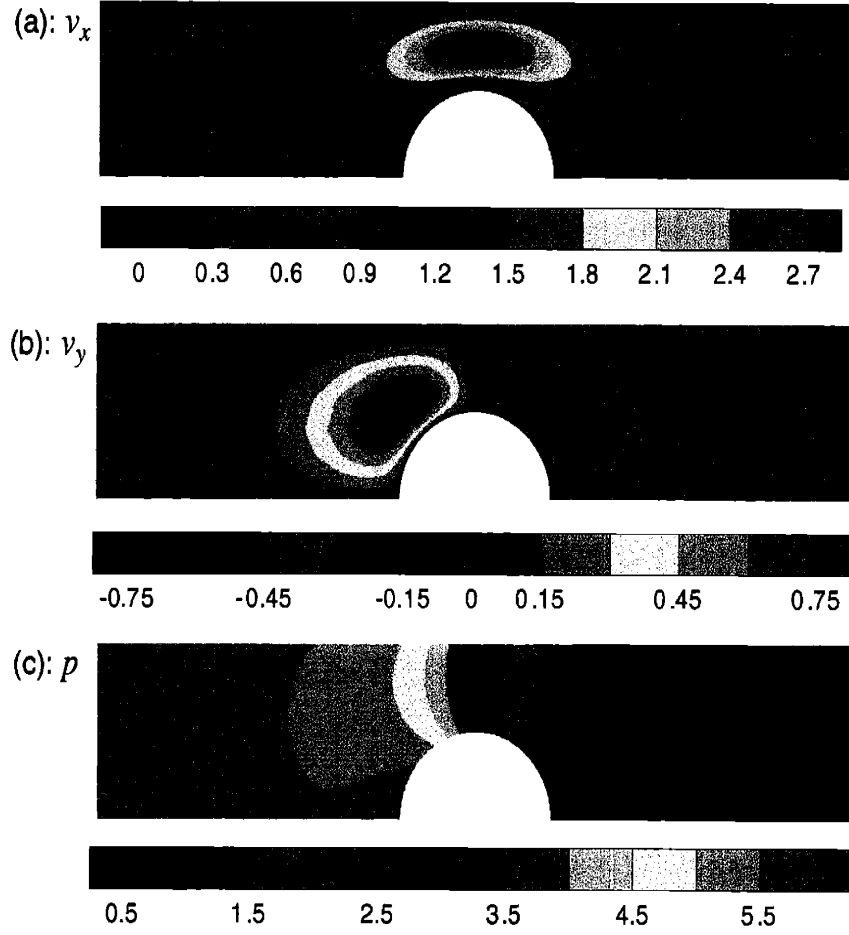


Figure 9.7: Contours for the Newtonian flow field in flow around an isolated cylinder confined in a channel. (a) v_x , (b) v_y , (c) p .

9.5.1 Mesh Convergence

Velocity profiles of the TAR model over $x \in [-4, 4]$ for different meshes are shown in Figure 9.8 to show the mesh convergence of the wavelet-Galerkin/Finite-Element method. Five Fourier mode and a 16×32 Daubechies 6 scaling function expansion are used to represent the configuration space of σ and $\mathbf{u}$ respectively. The similar velocity profiles calculated by these three different meshes demonstrates convergence with mesh refinement. Compared with the Newtonian velocity profile, the anit-symmetric velocity profile of the

TAR model around the center of the cylinder demonstrates the viscoelastic characteristics of the TAR model. A more detailed discussion is presented in the next section.

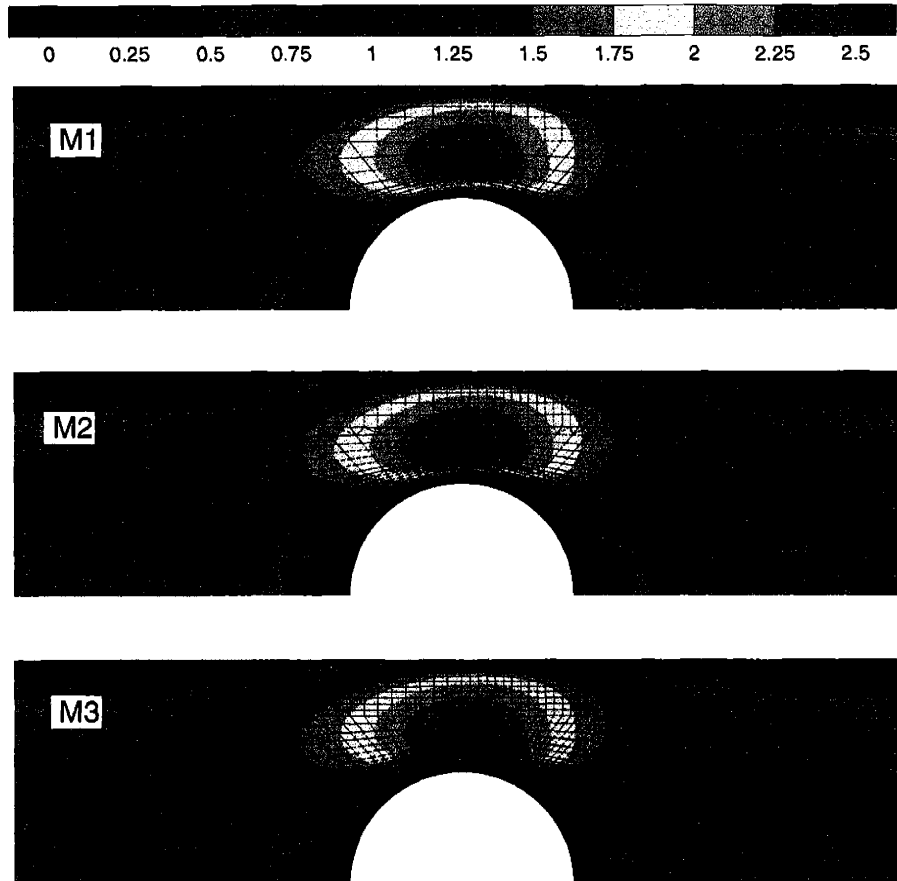


Figure 9.8: Dimensionless velocity profile in the gap between the cylinder and the wall. The three results shown for the Doi-Edwards model corresponds to the calculations with M1 (square symbol), M2 (cycle symbol), and M3 (triangle symbol). The Newtonian flow field is shown as a dashed-line for comparison.

Table 9.2 shows the calculated drag force and the wall shear rate on the cylinder for $x = 0, y = 1$ at $De = 1$ for the three meshes. Both the drag force and the wall shear rate vary by less than 2% from the coarsest to finest mesh used.

	Drag force on the cylinder	Wall shear rate, $G_{yx}(x = 0, y = 1)$
M1	50.246	16.279
M2	50.275	16.117
M3	50.272	15.810

Table 9.2: Comparison of the values of the drag force and the wall shear rate computed with the three different meshes M1, M2, and M3. 16×32 Daubechies 6 scaling functions and one Fourier mode are used to resolve the configuration space of the Doi-Edwards model.

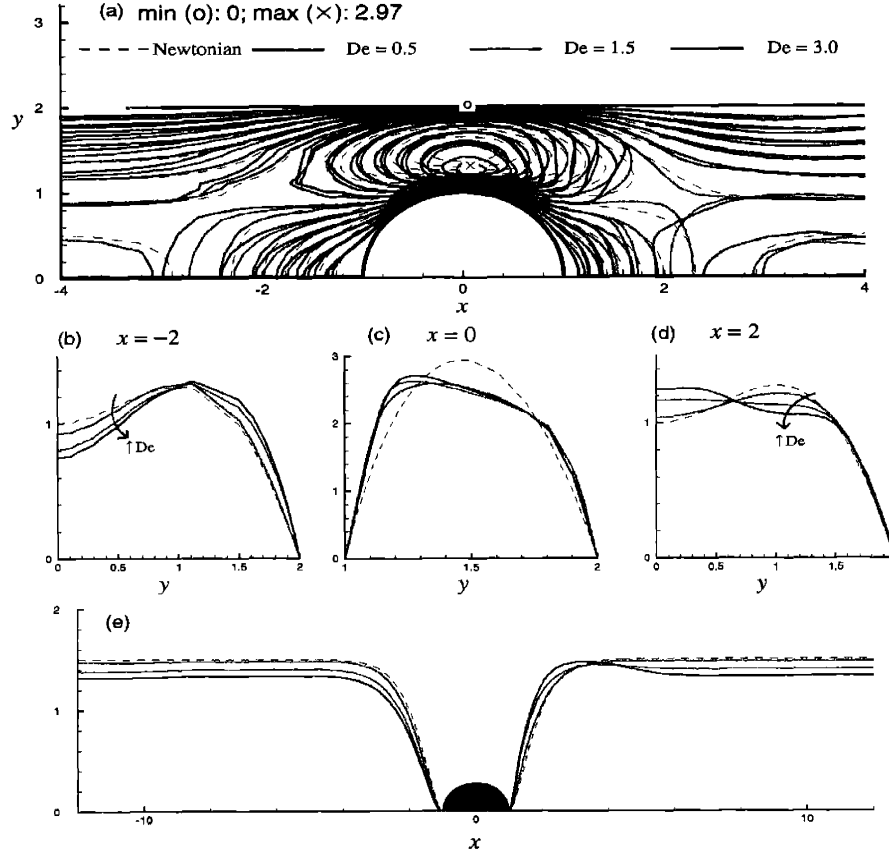
9.5.2 Predictions of the TAR model

The effect of increasing De on the velocity field predicted by the TAR model is shown in Fig. 9.9 for the whole velocity field, as well as along the centerline and for several sections. In Fig. 9.9a, 11 equally spaced contours, each of 0.3 dimensionless velocity units, are shown. Figs 9.9b, c, and d show the cross-section velocity profile at $x = -2, 0, 2$. The variation of the axial velocity along the centerline is demonstrated in Fig. 9.9e. The rich rheological behavior of the TAR model under mixed flow kinematics leads to substantial adjustments in the velocity flow field. Near the inlet, where pressure driven planar channel flow is expected, the shear-thinning behavior of the TAR model gives a much flatter velocity profile with a smaller centerline velocity than the Newtonian fluid. This is seen from the decrease in the axial velocity at the centerline with the increasing De (Fig 9.9e).

Along the narrow gap between the cylinder surface and the confining channel surface ($x = 0$), the interaction between the viscoelastic effect and the flow field leads to a anti-symmetric velocity profile with higher velocity gradient on the cylinder surface than that on the confined wall surface. While the shift of the velocity profile predicted by the TAR model is similar Doi-Edwards model, the magnitude of the shift is much more significant for the TAR model prediction for the same De .

After the rear stagnation point ($x > 1$), the TAR model predicts an increase in the axial velocity with De up to a downstream distance at about $x = 3$. This is in contrast of the well-known downstream shift predicted by typical elastic dumbbell models such as the Giesekus model [139], where the axial velocity on the centerline is shifted downstream before the velocity reaches the peak value. At high De (For example, $De = 3$), an overshoot in v_x after the rear stagnation point is even predicted by the TAR model. An explanation of this result will be presented later in this section.

Finally, cross-sectional variation of the velocity field slowly diminishes and a fully developed pressure driven channel flow profile is established. Depending on De , the channel flow profile is established at $6 < x < 8$, with the distance required for establishing the velocity of a fully developed, pressure driven channel flow increases with De .



× min

Figure 9.9: Predictions of v_x by the TAR model for $De = 0.5, 1.5, 3$ for (a) overall velocity field in the computation domain; (b) cross-section velocity profile at $x = -2$; (c) cross-sectional velocity profile at $x = 0$; and (d) cross-sectional velocity profile at $x = 2$; (e) velocity profile along the centerline. On these figures, the dashed line corresponds to the Newtonian velocity profile.

Similar plots of the normal stress τ_{xx} and shear stress τ_{yx} are shown in Figs 9.10 and 9.11, respectively. Eleven contours, each separated by 0.05 stress units are placed on the τ_{xx} profile shown in Fig 9.10a, and 7 contours, each separated by 0.1 stress units are placed for the τ_{yx} profile. The most noticeable difference between the TAR model and the Doi-Edwards or other traditional reptation model is the presence of an extended normal stress strand down the streamline behind the rear stagnation point. This is shown clearly in

Figs. 9.10a and e. For the Doi-Edwards or other double reptation models, it has been shown in chapter 8 that the normal stress vanishes is at about $x = 5$. For the TAR model, however, the normal stress strand extends further down stream with increasing De .

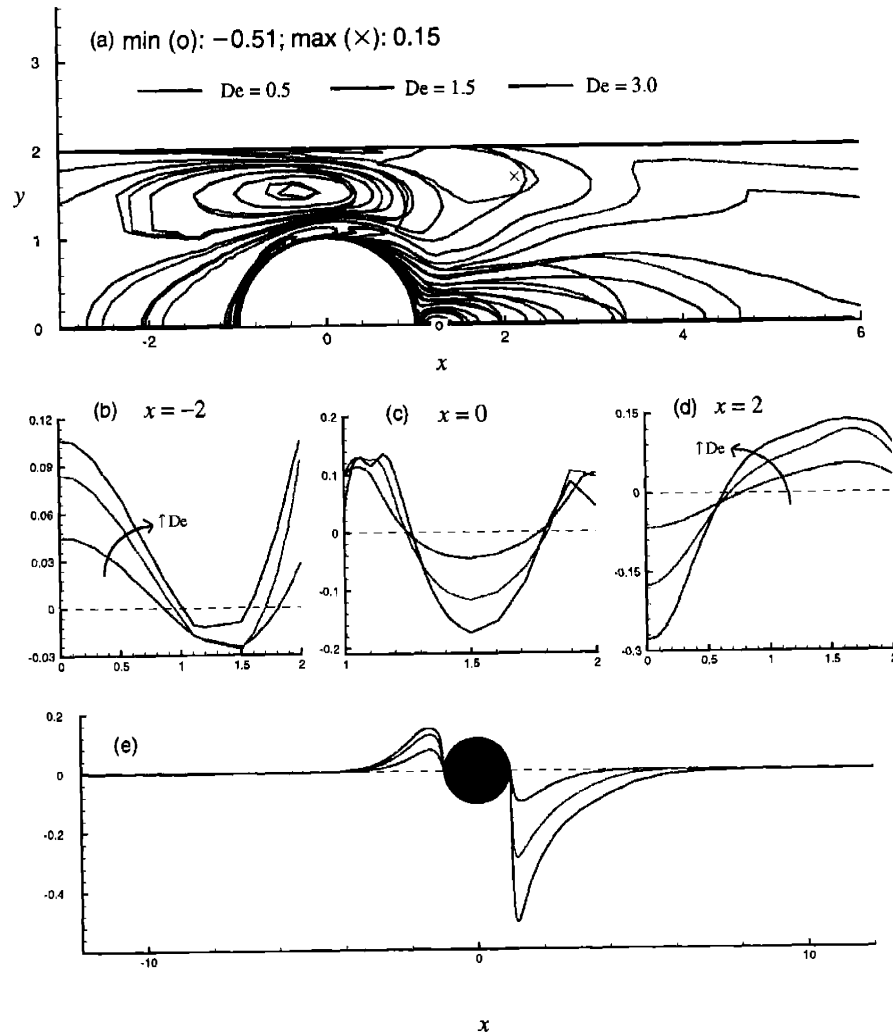


Figure 9.10: Predictions of τ_{xx} by the TAR model for $De = 0.5$, 1.5, and 3 for (a) the overall stress field in the computational domain; (b) cross-sectional profile at $x = -2$; (c) cross-sectional profile at $x = 0$; and (d) cross-sectional profile at $x = 2$; (e) and axial profile along the centerline of $y = 0$.

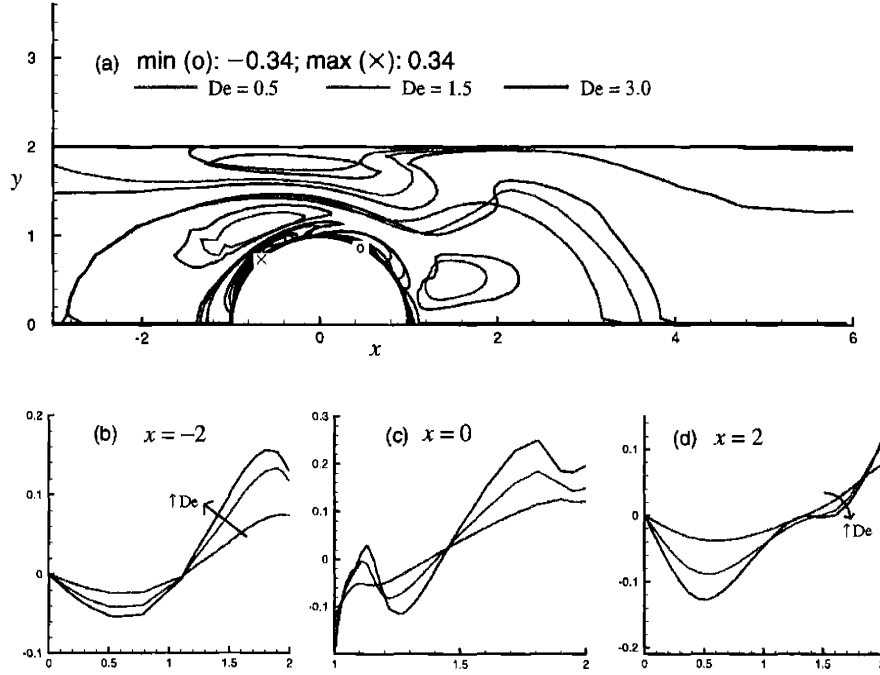


Figure 9.11: Predictions of τ_{yx} by the TAR model for $De = 0.5, 1.5$, and 3 for (a) the overall stress field in the computational domain; (b) cross-sectional profile at $x = -2$; (c) cross-sectional profile at $x = 0$; and (d) cross-sectional profile at $x = 2$.

To explain the complex interaction between the flow field and the microstructure feature of tube orientation and chain-stretching, we consider the field plots for the chain-stretching function λ . Figure 9.12 shows the λ field in the truncated domain, as well as various cross sections and along the symmetry line. Similar to the presentations of velocity and stress fields, Figure 9.12a contains the contour plot for λ , with contours placed equally with spacing of 0.03 . The cross-sectional profiles at $x = -2, 0$, and 2 are shown in Figures 9.12b, c, and d, respectively. The variation of λ along the centerline before and after the stagnation points are shown in Figure 9.12e. From all these figures, the maximum stretch for De up to 3 is only 30% of the equilibrium value.

Although one might expect that the extended tensile stress strand downstream from the rear stagnation point is due to the activation of the chain-stretching mechanism and associ-

ated large stress built-up, the mild stretch even at relatively high De suggests that the mechanism is much more involved and complicated. We attribute the complex interaction between the flow field and the microstructure to the different time constants for the relaxation of chain-stretching and tube orientation. Because the relaxation time for chain-stretching is an order of magnitude larger than that for tube orientation, the rapid growth of the chain-stretching function activates both the chain stretching and the convective constraint release mechanisms. Both of these mechanisms lead to the fast build-up of the elongational stress, which in turn causes in the upstream shift of the centerline axial velocity observed in Figure 9.9e.

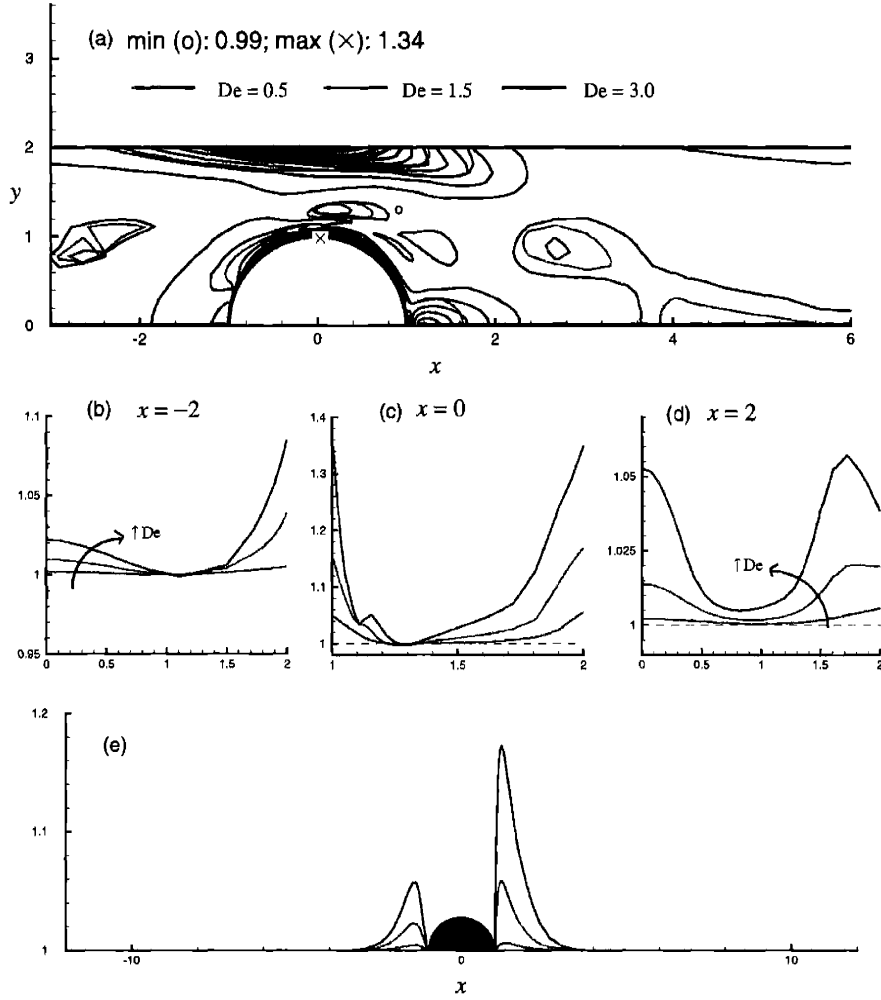


Figure 9.12: Predictions of λ by the TAR model for $De = 0.5, 1.5$, and 3 for (a) the overall stretch field in the computational domain; (b) cross-sectional profile at $x = -2$; (c) cross-sectional profile at $x = 0$; and (d) cross-sectional profile at $x = 2$; (e) and axial profile along the centerline of $y = 0$.

9.5.3 Drag force calculation

The macroscopic response of the TAR model is examined by computing the drag force on the cylinder surface by integrating the total stress over the surface of the cylinder. In dimensionless form, the drag force F_D per unit length of the cylinder surface is given by

$$F_d = - \int_{\partial\Omega_{\text{surf}}} \{ \boldsymbol{\tau} + p\boldsymbol{\delta} \} : \mathbf{n} \boldsymbol{\delta}_x ds \quad (9.52)$$

where $\partial\Omega_{\text{surf}}$ is the surface of the cylinder and δ_x is the unit vector pointing along the flow (x) direction. The calculated drag force is split into two component: form drag and skin drag where form drag is the pressure contribution to the total drag force on the cylinder.

The evolution of the drag force during the time dependent calculation is shown in Figure 9.13. The time-dependent drag force is normalized by the steady state drag force for estimation of the effect of De on the time-dependent behavior. As De increases, a clear over-shoot of the drag force is observed. Furthermore, the growth of the drag force for $De > 1$ is much faster than that for $De < 1$. This is because of the activation of the convective constraint release mechanism at large De that leads to a larger diffusion coefficient for the constraint release mechanism in the tube dynamics equation. This large diffusion coefficient corresponds to a short relaxation time and hence accelerates the transient behavior of the drag-force.

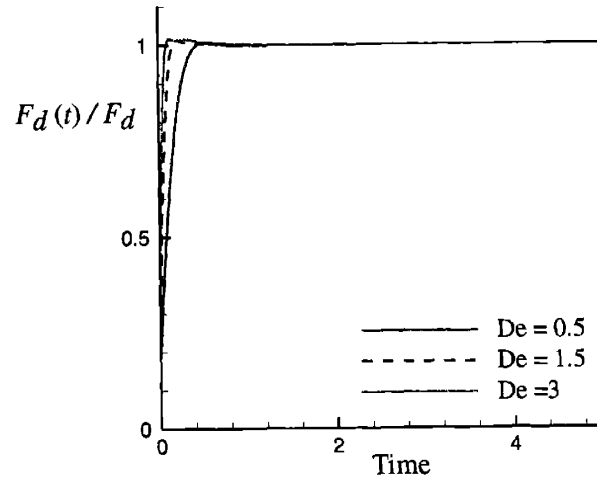


Figure 9.13: Time evolution of the drag force acting on the cylinder surface for $De = 0.5, 1.5$, and 3 for the TAR model.

Figure 9.14 shows the viscoelastic drag calculated by the TAR model. The predictions of the Doi-Edwards model and the Giesekus model are included for comparison. Despite

the rich rheological dynamics observed in the TAR model with $\tau_d/\tau_s = 10$, the predicted drag force decreases monotonically with increasing in De . This is because of the small values of the chain-stretching function around the cylinder surface. By decreasing the value of τ_d/τ_s to unity, the drag force calculated starts to increase after the initial drop at low De . This supports the argument that the small values of the chain-stretching function leads to a monotonically decreasing drag force. Although the small value of τ_d/τ_s will lead to a non-monotonic drag force, it also alters the shear flow rheology of the TAR model by, for example, inducing shear thickening in the material properties. Therefore, assuming non-monotonic drag force occurs for polymer melts in this flow, the TAR model is incapable of realistically describing this behavior and an alternative model is needed for its explanation.

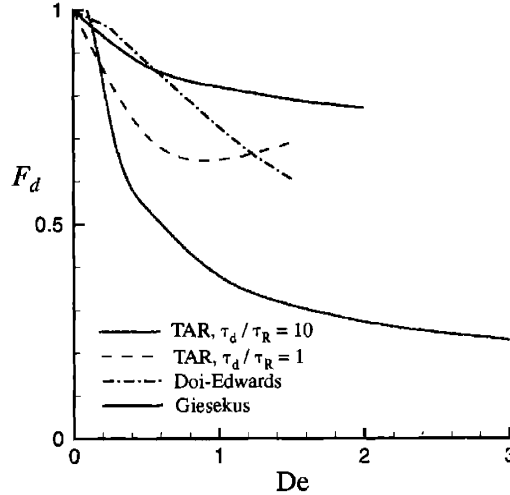


Figure 9.14: Comparison of viscoelastic drag enhancement for the TAR model with the Doi-Edwards and Giesekus models. The two different values of τ_d/τ_R for the TAR model used are 1 and 10.

9.6 Conclusion

Extension of the wavelet-Galerkin/finite-element method allows computation of viscoelastic flows in a complex geometry with advanced reptation models. The advanced reptation model simulated in this chapter is developed by Fang, et al. [74] through the use of the GENERIC approach. Because of the thermodynamical approach used in their deriva-

tion, we denote this model as TAR (Thermodynamically Admissible Reptation) model. This model consists of the conventional diffusion equation that describes the tube orientation dynamics and an additional equation that governs the chain-stretching dynamics. The resulting equation incorporates various new physics that are widely anticipated to “correct” most of the defects of the traditional reptation model due to Doi-Edwards or Curtiss-Bird.

After reviewing the rheology of the TAR model in homogeneous simple flows, the flow problem of flow around an isolated cylinder confined in a channel is revisited. The complex interaction between the flow field, reptation mechanism, and the various non-repetitive mechanisms leads to complex rheological behavior in this model. One of the most important features in these calculations is the activation of the convective constraint release mechanism. This mechanism leads to a mean, small relaxation time that leads to fast relaxation dynamics of the TAR model, which in turn enhance the dynamics for λ . Both of these mechanisms lead to the fast built-up of the elongations stress, which in turn results in the upstream shift of the centerline axial velocity, as well as in a long strand of normal stress which increases in length and strength with increasing De .

Despite the various interesting rheology properties of the TAR model, the TAR model predicts a monotonically decreasing drag force acting on the cylinder for $\tau_d/\tau_R = 10$. This is attributed to the lack of significant chain-stretching at low De in this flow. By reducing τ_d/τ_R to unity, an up-turn of the drag force is observed with increasing De . However, the early activation of the chain stretching leads to unreasonable rheological behavior such as shear thickening at small values of De . Therefore, search for alternative, new physics to be implemented into the reptation model is necessary for proper prediction of drag enhancement. Furthermore, because drag enhancement is only observed for dilute polymer system, experimental data for entangled polymer system are needed to verify the

drag force behavior with increasing De . More importantly, quantitative comparisons of the complex flow behavior of benchmark problem with entangled polymer system between experiments and the numerical prediction are necessary to verify the usefulness of the TAR model for modeling an entangled polymer system.

Even if the TAR model does not contain the proper physics for describing the rheology of an entangled polymer systems, the numerical approach used in this chapter has been shown to be useful for viscoelastic flows with this type of constitutive equation. The incorporation of the chain-stretching equation shows the feasibility of including other equations in multiscale viscoelastic flow calculations. These equations include the mapping equations for the free-surface flow calculation, equation of energy for non-isothermal flows, or other diffusion equations for various molecular models. This significantly enlarges the scope of models and flow problems that can be simulated and investigated by our numerical approach.

Chapter 10

Conclusion

The use of molecular models for calculating molecular orientation in viscoelastic flows is a very active and rapidly expanding area of research. In this thesis, we develop a numerical approach for viscoelastic flow calculation that incorporates the constitutive description directly from the diffusion equation of nonequilibrium statistical mechanics or kinetic theory. Starting with the mixed Galerkin-collocation method for the scaling function expansion developed by Nayak, we first extend the method to incorporate a range of basis functions and to solve highly complex and nonlinear diffusion equations. Then, a numerical algorithm is developed based on the synthesis of a two-stage, node-by-node decomposition strategy and an operator-splitting time integration algorithm for solving diffusion equations of the form of $\dot{f}(x_1, x_2, \dots) = A_1(f) + A_2(f) + \dots$ by a layer-by-layer approach. Here $\dot{f}$ is the time derivative of f , x_i are the vectors of configuration space variables, and $A_i(f)$ are the operators that are associated with x_i only. While the total number of unknown for the distribution function remains as $\Pi_i N_i$ (where N_i is the number of basis functions for representing the variation of the distribution function along vector x_i), the number of operation count for inverting the stiffness matrix reduces from $C(\Pi_i N_i)$ to $\sum_i C(N_i)$ (where $C(x)$ is the operation count for inverting a matrix of dimension x).

A number of examples are used to illustrate this strategy. First, the spatial variation of the distribution of a dilute suspension of rod-like polymer represented by a rigid dumbbell model in a pressure-driven, planar channel flow is computed. x_1 is taken to be the vector for the spatial variables that are represented by a finite element method that can be solved by an element-by-element condensation strategy, and x_2 is the vector for orientation space that is represented by a scaling function expansion. The stiffness matrix for the

diffusion equation is first inverted for the spatial variables and then for the orientation variables. The resulting algorithm is robust for finite element calculations with non-constant Jacobian of the transformation from global to local coordinates in the finite element method. Such calculations are impossible with the previous implementation by Nayak.

Other problems studied in this thesis with the numerical method developed here include the rigid rod model for rodlike polymers in concentrated solutions and melts and single segment theory models for highly entangled flexible polymer system, both of which are fundamentally challenging and practically important to the understanding of non-Newtonian fluid mechanics and polymer processing. In the simulation of kinetic theory models of liquid crystalline polymers, the wavelet-Galerkin method has been applied to study (1) the stability of different inhomogeneous mean-field potential for the spinodal decomposition problem, (2) a Doi model with a complicated, nonlinear function for both rotational diffusivity and intermolecular potential, and (3) the effect of concentration fluctuation on pressure-driven channel flow.

In the calculations of reptation models for concentrated flexible polymer solutions and melts, three independent vectors (x_1 , x_2 , and x_3) are chosen such that x_1 is the vector for the spatial variation, x_2 is the vector for the orientation variables for the tube, and x_3 is the vector for the chain segment number variable (σ). Similar to the Doi model and the rigid rod model, x_1 and x_2 variations are represented by the discontinuous Galerkin method and a scaling function expansion, respectively, and x_3 is represented by a finite Fourier expansion. In addition to the classical reptation models such as the Doi-Edwards or Curtiss-Bird models, the wavelet-Galerkin method is applied to the simulation of “advanced” reptation models that incorporate various nonreptative, constraint release mechanisms in a thermodynamically consistent manner. The so-called thermodynamically admissible reptation model is represented by a complicated, nonlinear diffusion equation

that is very difficult to simulate by using Brownian dynamics. Furthermore, for a multiscale calculation with Brownian dynamics, the presence of a reaction-like term with a configuration-dependent rate coefficient in the pair of stochastic differential equations excludes various variance reduction techniques that utilize a synchronization of trajectories by cancellation of fluctuations. Therefore, our numerical method based on a coupled wavelet-Galerkin/finite-Fourier/finite-element method is the only technique for simulating this model in a complex flow environment.

In this chapter, the essential conclusions for the two major parts of this thesis are summarized below. Furthermore, suggestions for future research are made, both on the subject of a fully deterministic, multiscale calculations of viscoelastic flow and to the subject of kinetic theory modeling of liquid crystalline polymers and concentrated flexible polymer solutions and melts.

10.1 Summary

10.1.1 General numerical approach for multiscale simulation of viscoelastic flows

In this thesis, we extend and develop the wavelet-Galerkin method for the simulation of the distribution function in a diffusion equation. The wavelet-Galerkin method has distinct advantages of compact support (which leads to a sparse stiffness matrix), exact evaluation of connection coefficients (inner products of basis functions), and easy implementation of periodic boundary conditions. Implementation of a storage scheme for sparse matrices allows fast computation of matrix-vector multiplication. This increases the limitation on the size of the problem that can be solved (due to the limitation of the largest size array that can be handled by FORTRAN), as well as enhances the speed for matrix assembly and solution of the linear algebra problem. Extension to various orders of Daubechies scaling functions allows the application of a vast array of scaling function expansions that makes the wavelet-Galerkin method an h - p spectral method.

An important use of solving a diffusion equation from kinetic theory is in coupling this problem with the equation of motion for a complex viscoelastic flow through a kinetic theory stress tensor equation. To this end, the numerical algorithm developed in this thesis uses the discontinuous Galerkin finite element method to solve the diffusion equation at every point in a complex flow geometry defined by the finite element mesh. The diffusion equation at every point of the mesh, in turn, is discretized by the wavelet-Galerkin method. The discontinuous Galerkin method has the advantage of element-by-element decomposition, in addition to being suitable for the solution of hyperbolic equations.

Beyond the discretization and solution method, a number of numerical algorithms are used to enhance the performance of the numerical method developed in this thesis. These algorithms include a node-by-node decomposition, topological sort for ordering elements according to the streamline direction, and a parallel computing strategy. The two stage, node-by-node decomposition is inspired by the tensorial nature of the basis functions to discretize the distribution function. This decomposition strategy reduces the solution of the distribution function for each element from a single calculation of the elemental stiffness matrix for each element to four (or three for triangular elements) calculations of the nodal stiffness matrix; the size of each nodal stiffness matrix is one fourth of the elemental stiffness matrix. The scaling of the operation count for the node-by-node decomposition is only one sixteenth of the original implementation for an LU decomposition or one fourth for a backward-forward substitution. The more condensed matrix structure of the nodal stiffness matrix leads to a smaller constant in the scaling expression, and hence the expense of the node-by-node decomposition is nearly one tenth of the original method. More importantly, the node-by-node decomposition allows calculations in which each entry of the mass matrix depends on location in the physical space. This applies to the mass matrix for rectangular elements, as well as axisymmetric calculations.

Topological sort has been well-studied in computer science. The utilization of this algorithm is extremely helpful for the calculation of hyperbolic equations in devising an update list according to the flow of the streamlines. If the velocity field is known, this update list allows a rigorous, fully implicit calculation of the distribution function approximation by an element-by-element condensation, thereby avoiding the solution of a large matrix problem that appears to be impossible for the distribution function. On the other hand, if the velocity field is not known, then an element-by-element condensation strategy based on the inverse direction of the flow along the streamlines can be used to reduce the memory requirement by not storing the external nodes from the previous time step in the DG formulation. Furthermore, the topological sort also provides a simple, fast, and computationally inexpensive method for a domain decomposition for the distribution function calculation in the physical space. The domain decomposition generated based on the topologically sorted list leads to a small number (though not minimum) of interfaces between different computational domains.

10.1.2 Modeling and simulation of kinetic theory models for liquid crystalline polymers

In Chapter 6, simulation of the exact Doi model with the Onsager mean-field potential and an orientation-dependent rotational diffusivity was performed to test the modified wavelet-Galerkin method and to illustrate the accuracy and robustness of the numerical method. The convergence properties of the numerical method with mesh refinement (h -convergence), order refinement (p -convergence), and time step (Δt -convergence) at high De ($De = 30$) and large U ($U = 12$) were established with a set of rigorous studies. At high De and U , our numerical method predicts a time-periodic state that is contrary to chaotic results obtained by stochastic simulations, we believe that latter results are incorrect.

The evolution behavior of the distribution function during various time-dependent states for the Doi model is also explored. At low De , the dynamics of the distribution func-

tion is determined through the interplay between the hydrodynamic force and the intermolecular force. This gives rise to a wide range of behavior such as tumbling, wagging, and log-rolling states for the Doi model. The long-time behavior also is dependent on the initial condition. At high De , the hydrodynamic force dominates the force balance, and the dynamics of the Doi model becomes independent of the initial condition.

The nonlinear dynamics of the exact Doi model in the transition or bifurcation from the time-dependent wagging state to the steady, flow aligning state is studied in detail to demonstrate the possibility of using the wavelet-Galerkin method for stability analysis. Together with a convergence analysis, we have shown that the wavelet-Galerkin method predicts no aperiodic behavior over a range of De close to the supercritical Hopf bifurcation point. We also demonstrate a power-law behavior of the locus for the supercritical Hopf bifurcation between the wagging and flow aligning states in the parameter space (U, De) . The slope of the power law reflects the anisotropy of the effective intermolecular potential. The exact Doi model is much more anisotropic than the simplest Doi model formulated with the Maier Saupe potential and constant, isotropic drag coefficient.

Chapter 7 extends the modified wavelet-Galerkin method and couples it with the finite element method to study the effect of spatial variation of concentration on the flow behavior of the Doi model in a pressure-driven channel flow. For the homogeneous Doi model, we confirm the result from Nayak that *infinitesimal* structure refinement occurs above a critical strength of intermolecular potential. The mechanism of this infinitesimal structure refinement is triggered by the inhomogeneity of the flow field which provides a spectrum of local De values across the channel. Since the period of the tumbling/wagging motion decreases with increases in De , high frequency oscillations start from the local De corresponding to the wagging-flow aligning transition and propagate as a wave towards the centerline. The differences in frequencies of the time-periodic motions leads to a texture

formation whose structure refines infinitesimally as time goes on. The code stops when the length scale of the structure is smaller than that of the finite element mesh.

Inhomogeneous effects such as distortional stresses have to be incorporated into the Doi model in order to rectify this aphysical behavior. While most researchers focus on modifying the mean-field intermolecular force, we take an alternative approach by incorporating the spatial variation of concentration in the Doi model. This is done in a manner similar to stress diffusion except that we require the normalization of the distribution function to be the total number of molecules in the system. This normalization condition couples the distribution function at each node in the computational domain and makes the problem impossible to solve. A possible way to simulate the resulting problem is to introduce a number density equation that decouples the physical constraint from the configurational constraint to the distribution function.

In addition to the normalization condition, the translational diffusion operator makes the diffusion equation an elliptic, rather than hyperbolic equation. To simulate this equation with the wavelet-Galerkin/finite-element method, we employed the local discontinuous Galerkin method, which is essentially an extension of the standard discontinuous Galerkin method. Although the total number of unknown increased by a factor of three due to the introduction of an auxiliary variable for the distribution function gradients, the overall cost of the computation only slightly increased.

With the use of the local discontinuous Galerkin method and the number density equation, we simulated the modified Doi model with spatially averaging concentration in a pressure-driven planar channel flow problem. As anticipated, the inclusion of an intrinsic length scale can rectify the aphysical problem suffered by the monodomain Doi model and a steady state solution for the field can be obtained. The resulting steady profile, however, has all the directors pointing along the same direction throughout the entire domain. This

is contrary to experimental observation and essential physics (such as distortional stresses) are clearly missing. Although postulating a diffusion equation that contains these missing physics may be possible (as demonstrated in Chapter 5), it is difficult to characterize the mathematical type and characteristics of the resulting diffusion equation. This leads to an extremely difficult system to solve. Much work is needed in this area.

10.1.3 Numerical simulation of confined flow around a cylinder in a planar channel for reptation models

A wavelet-Galerkin/finite-element method is presented for computing viscoelastic flows with constitutive description directly obtained from solving diffusion equations of molecular models from polymer kinetic theory. We computed the viscoelastic flow of the double reptation model and a thermodynamically admissible reptation model around an isolated cylinder in a confined channel to illustrate the feasibility, accuracy, and robustness of our numerical method. The computation of the reptation model requires an additional basis function space to discretize the σ -space (polymer backbone) in the reptation model. The natural choice of this additional basis function is a discrete sine transform, because of the operator type and the boundary conditions. For calculating the thermodynamically admissible reptation model, an additional variable λ that accounts for the chain stretching mechanism is included by using the (continuous) finite element method with SUPG for this hyperbolic equation. The convergence studies undertaken here confirm that our numerical method converges with mesh refinement for the physical space, resolution of different Daubechies 6 scaling functions for the orientation space ($\mathbf{u}$), and different Fourier modes for representing σ -space. Distributed computing has also been studied for simulating (a) a fixed problem with different numbers of processors and (b) a series of progressively refined meshes with increasing number of processors to ensure that the computational load on each processor remains constant. A nearly linear scale-up is observed for both of these measures of parallel efficiency up to a 16 processor calculation.

As an illustration of the versatility of our numerical approach, the Brownian configuration fields method is implemented into the algorithm. A linear speed-up parallel strategy by domain decomposition in the configuration space allows calculations of Brownian configuration fields up to $O(10^5)$ trajectories, as opposed to around 5,000 trajectories that are commonly used in most Brownian configuration fields calculations. Because even at steady state, the Brownian configuration fields method provides a different representation of the underlying configuration space $(\sigma, \mathbf{u})$ at any given time, the configuration field and the calculated drag force fluctuate even after the macroscopic flow field achieves a steady state. A detailed error analysis for the Brownian configuration fields method is also provided, showing the simulated data agree well with the law of big numbers, that is $\text{Error} \sim 1/\sqrt{N}$ where N is the number of trajectories used in the simulation.

We have also studied the effect of different viscous stress expressions on the dynamics of the double reptation model. The predictions for the different viscous stress expressions are qualitatively similar. Because the normal stress are in general much smaller than the shear stress, limited viscoelastic effects are observed. The drag force acting on the cylinder surface is used to characterize the effect of increasing flow rate (and hence De) on the rheological response of a variety of reptation models. Unlike traditional elastic dumbbell models, the drag force predicted by reptation models monotonically decrease with increasing De . We attribute this to the lack of a tube stretching mechanism.

To confirm this argument, the simulation for the TAR model is carried out in the sample complex flow geometry. The complex interaction between the flow field, reptation mechanism and the various non-reptative mechanism leads to a complex rheological behavior predicted by the TAR model. One of most important interactions is the activation of the convective constraint release mechanism. This mechanism leads to a small, mean relaxation time that leads to fast relaxation dynamics of the TAR model, which in turn

enhances the dynamics for λ . Both of these mechanisms lead to the fast built-up of the elongational stress, which in turn results in the upstream shift of the centerline axial velocity, as well as a long normal stress strand downstream of the rear stagnation point, the length of which increases with increasing De . To our best knowledge, this behavior has not been observed or reported by other constitutive equations.

Despite the various interesting rheological properties exhibited by the TAR model, the TAR model predicts a monotonically decreasing drag force acting on the surface of the cylinder for $\tau_d/\tau_R = 10$. This is attributed to the low magnitude of chain-stretching in low De flow calculations. By reducing τ_d/τ_R to unity, an up-turn of the drag force calculated is observed. However, the early activation of chain stretching leads to unreasonable rheological behavior such as shear thickening at small values De . Therefore, new physical ideas need to be implemented into the reptation model for the prediction of drag enhancement. Furthermore, because drag enhancement is only observed for dilute polymer system, experimental data for entangled polymer system are needed to verify the drag force behavior with increasing De . More importantly, quantitative comparisons of the complex flow behavior of benchmark problem with entangled polymer system between experiments and the numerical prediction are necessary to verify the usefulness of the TAR model for modeling an entangled polymer system.

10.2 Suggested future work

Although this thesis concentrates on the simulation of kinetic theory models for liquid crystalline polymers and concentrated polymer solutions and melts, the numerical approach developed in this thesis is robust and should be applicable for other systems as well. Some of these systems may have similar mathematical structures to the diffusion equation for rigid dumbbells or they may have a completely different set of governing equations for the configuration space distribution function. For example, the Fokker-

Planck equations for non-Brownian fiber suspension (with or without mass migration) [70, 71] have similar mathematical structure as the diffusion equation for rigid rod model and hence can be simulated by using our approach. Another example is simulation of the diffusion equation for a suspension of FENE dumbbell. Fan has demonstrated the possibility of simulating the FENE dumbbell model in a homogeneous flow by using a coupled spherical-harmonics/Jacobi-polynomial expansion [67,68]. Extension of his result to a complex flow simulation with our approach should be trivial. The fully deterministic multiscale simulation strategy should also be able to simulate various modifications of the FENE dumbbell model such as the adaptive length scale (ALS) model, once a complete equation set for the ALS model is derived. This complete set of equations consists of the diffusion equation and a mapping equation that accounts for the change in configuration space.

In this section, we focus on some possible ideas for future work for the two systems that have been studied in this thesis. The suggestions here address extensions of some of the work in this thesis. Very important needs are the experimental measurements and comparison with simulation results. For example, while the various reptation models show a monotonically decreasing drag force in the calculation of a flow around an isolated cylinder, there are no experimental data for an entangled polymer system that supports this prediction. Furthermore, quantitative interpretation at a molecular level for various experimental results must be continuously developed, implemented and revised. For example, experimental results for liquid crystalline polymers are interpreted based on defect strength, which in turn links to the director orientation. The concept of a director, however, is vaguely defined in the context of nonequilibrium statistical mechanics. Therefore, new interpretation of experimental results based on available molecular models (both from statistical mechanics or mean-field kinetic theory) is necessary. This would lead to more useful and applicable comparison between molecular model and experimental data.

Furthermore, new experimental methods for measuring more detailed molecular structure are also needed. Experimental resolution at multiscale is necessary to distinguish and to characterize data that corresponds to a macroscopic, mesoscopic, or molecular based scale.

Liquid crystalline polymers.

The kinetic theory model proposed in Chapter 5 should be useful as a basis for modeling the structure formation and complex dynamics of liquid crystalline polymers. Simplification strategies for the kinetic theory model, such as Taylor-series expansions of various inhomogeneous quantities, should be considered very carefully in the view of numerical feasibility and physical relevance. At the very least, the Taylor series expansion has to be truncated such that both the diffusion equation and the stress tensor expression contain the same order of contribution in the simplified model.

On the other hand, although Taylor series expansions are useful for obtaining a low-order model, the implicit assumption of smooth distribution function variations may lead to aphysical results. This is because the disclination core corresponds to a sharp gradient in the distribution function. Furthermore, the resulting equation may not be mathematically sound. It is difficult to characterize the mean-field contributions resulting from Taylor series expansion as diffusive, convective, or both. Therefore, even robust numerical methods are available for discretizing elliptic equations with discontinuous basis functions, it is impossible to apply the numerical to simulate the nonlinear diffusion equation resulting from the Taylor series expansion.

Explicit consideration of all inhomogeneous terms may be an attractive alternative to the use of Taylor-series expansions. Although the model simulated will be exact, and application of the local discontinuous Galerkin method would be indeed more straightforward, the maintenance of a neighbor list of spatial nodes that contribute to the molecular

potential and the stress tensor may, however, be a major obstacle. More importantly, the spatial resolution for which sufficient spatial nodes to represent inhomogeneities may prove to be too expensive for feasible computation.

It is also possible that both molecular and mesoscopic approaches should be abandoned. Instead we should develop a multiscale modeling approach to describe defect core and disclination formation, and the interactions between defect cores in different region of a domain to form microstructures. One possible strategy for achieving this based on a mixed reaction-engineering/kinetic-theory-based, multiscale approach is as follows: At the kinetic theory level, correlation of the orientations of rod-like polymer molecules leads to the formation or destruction of a single defect core. This defect core then diffuses (in a much longer time scale) within the physical space and interacts with other defect cores through reaction, aggregation, and combination to form a defect core with a larger diameter. The dynamics and the size distribution of the defect cores are then described by a population balance model. The type and size of defect core in turn affect the orientation of the rod-like polymer molecules through the intermolecular potential, which completes the description of the structure of liquid crystalline polymers. The rheology of this model is finally described by a stress tensor expression that contains the effects of both the molecular elasticity and the defect core distribution. Much creative research is needed in this area.

Concentrated polymer solutions and melts

In this thesis, various advanced reptation models are efficiently simulated in homogeneous and complex flow environments by using the wavelet/finite-Fourier discretization, coupled with a finite element method. While these models can qualitatively, and sometimes quantitatively describe experimental results, they are largely descriptive, rather than predictive. This makes the usefulness of reptation models similar to various continuum models such as the K-BKZ model. In particular, single-segment theories cannot describe the conforma-

tion changes of the primitive chain, and the application of relaxation time functions to describe various topological features of the primitive chain is of doubtful value. Although the full chain model derived by Hua and Schieber describes the configuration of the primitive chain explicitly, questionable assumptions make the various aspects of the model unreasonable. Therefore, a more careful application of the kinetic theory is necessary.

Calculation employing the various reptation models have revealed some of the inadequacies of our wavelet-Galerkin/finite-element method for simulating highly convective systems. For example, in the Doi-Edwards model, the diffusion equation is purely convective with respect to the tube orientation $\mathbf{u}$. The Galerkin method has proven to be unstable for approximating a hyperbolic equation and therefore, further development of wavelet-Galerkin method employed in this thesis for discretizing hyperbolic-type diffusion equations is necessary.

We illustrate advances in this area that make feasible the computation of molecular orientation for low-dimensional models in complex, two-dimensional, time-dependent flows. While wavelets are employed to discretize the configuration space, other basis functions (such as spherical harmonics, spherical wavelets, or other second generation wavelet functions) may be equally employable and even more efficient for a given diffusion equation. We expect the application and development of this method to continue to move forward rapidly, particularly with advances in the hybrid simulation methods that we highlight here. As computing power increases and more efficient algorithms are developed, we will have the ability to simulate more realistic models, including those with more degrees of freedom and more realism in the description of complex molecular architecture. A particularly important challenge is to simulate industrially important processing flows, such as fiber and film formation, with sufficient molecular fidelity to allow accurate prediction of final product properties.

Bibliography

- [1] M.P. Allen and D.J. Tildesley. *Computer simulation of liquids*, Oxford: Clarendon, 1987.
- [2] R.C. Armstrong, R. Nayak, and R.A. Brown. The use of kinetic theory and microstructural models in the analysis of complex flows and viscoelastic liquids. In A. Ait-Kadi, J.M. Dealy, D.F. James, and M.C. Williams, editors, *Proceedings of XIIth International Congress on Rheology*, 1996.
- [3] F.P.T. Baaijens. Mixed finite element methods for viscoelastic flow analysis: a review, *J. Non-Newtonian Fluid Mech.*, **79**:361-85, 1998
- [4] H.P. Babcock, D.E. Smith, J.S. Hur, E.S.G. Shaqfeh, and S. Chu. Relating the microscopic and macroscopic response of a polymeric fluid in a shearing flow. *Physical Rev. Letters*, **85**:2018-21, 2000
- [5] G. Barakos and E. Mitsoulis, Numerical simulation of viscoelastic flow around a cylinder using an integral constitutive equation, *J. Rheol.*, **39**: 1279-92, 1996
- [6] F. Bassi and S. Rebay. A high-order accurate discontinuous finite element method for the numerical solution of the compressible Navier-Stokes equations. *J. Comput. Phys.*, **131**: 267-79, 1997
- [7] F. Bassi, S. Rebay, M. Savini, G. Mariotti, and S. Pedinoti. A high-order accurate discontinuous finite element method for inviscid and viscous turbomachinery flows. *Proc. Second European Conference ASME on Turbomachinery Fluid Dynamics and Thermodynamics*, 1995.
- [8] T.L. Bell, G.H. Nyland, J.J. de Pablo, and M.D. Graham. Combined Brownian dynamics and spectral simulation of the recovery of polymeric fluids after shear flow, *Macromolecules*, **30**:1806-12, 1997.
- [9] T.L. Bell, J.J. de Pablo, M.D. Graham, and J.D. Schieber. Brownian dynamics simulation of the Doi theory for liquid crystalline polymers. *71st Annual Meeting of the Society of Rheology*, Madison, Wisconsin, 1999
- [10] T.L. Bell, *Simulating the flow of complex microstructured fluids*, PhD Thesis, University of Wisconsin, Madison, 1998.
- [11] A.N. Beris and B.J. Edwards. *Thermodynamics of Flowing Systems with Internal Microstructures*. Oxford University Press: New York, 1994.
- [12] A.N. Beris and H.C. Öttinger. Thermodynamically consistent reptation model without independent alignment. *J. Chem. Phys.*, **110**(14): 6593-7, 1999.
- [13] A.V. Bhawe, R.C. Armstrong, R.A. Brown, Kinetic theory and rheology of dilute, nonhomogeneous polymer solutions, *J. Chem. Phys.* **95**:2988-3000, 1991.
- [14] A.V. Bhawe, *Kinetic theory for dilute and concentrated polymer solutions: Study of nonhomogeneous effects*, PhD Thesis, Massachusetts Institute of Technology, 1992.
- [15] A.V. Bhawe, R.K. Menon, R.C. Armstrong, and R.A. Brown. A constitutive equation for liquid-crystalline polymer solutions. *J. Rheol.*, **37**(3):413-441, 1993.
- [16] P. Biller and F. Petruccione. The flow of dilute polymer solutions in confined geometries: a consistent numerical approach. *J. Non-Newtonian Fluid Mech.*, **25**: 347-364, 1987.

- [17] R.B. Bird, H.H. Saab, and C.F. Curtiss, A kinetic theory for polymer melts. 3. Elongational flows. *J. Phys. Chem.*, **86**(7): 1102-6, 1982.
- [18] R.B. Bird, H.H. Saab, and C. F. Curtiss. A kinetic theory for polymer melts. IV. Rheological properties for shear flows. *J. Chem. Phys.* **77**(9): 4747-57, 1982.
- [19] R.B. Bird, R.C. Armstrong, O. Hassager, *Dynamics of Polymeric Liquids, Vol. 1, Fluid Mechanics*, 2nd ed. New York: Wiley, 1987.
- [20] R.B. Bird, C.F. Curtiss, R.C. Armstrong, O. Hassager, *Dynamics of Polymeric Liquids, Vol. 2, Kinetic Theory*, 2nd ed. New York: Wiley, 1987.
- [21] R.B. Bird and Öttinger. Transport properties of polymeric liquids. *Annual Reviews of Physical Chemistry*, **43**: 371-406, 1992.
- [22] R.B. Bird and J.M. Wiest, Constitutive equations for polymeric liquids. *Annual Rev. Fluid. Mech.*, **27**: 169-193, 1995.
- [23] R.B. Bird, W.E. Stewart, and E.N. Lightfoot. *Transport Phenomena*, 2nd edition, New York: Wiley, 2001.
- [24] D.V. Boger and K. Walters. *Rheological Phenomena in Focus*, Amsterdam: Elsevier, 1993.
- [25] J. Bonvin, M. Picasso. Variance reduction methods for CONNFFESSIT-like simulations. *J. Non-Newtonian Fluid Mech.*, **84**:191-215, 1999.
- [26] J. Bossart and H.C. Öttinger, Orientation of polymer coils in dilute solutions undergoing shear flow: birefringence and light scattering. *Macromolecules*, **28**(17):5852-60, 1995.
- [27] A.N. Brooks and T.J.R. Hughes. Streamline upwind/Petrov-Galerkin formulations for convection dominated flows with particular emphasis on the incompressible Navier-Stokes equations. *Computational methods in applied mechanics and engineering*, **32**: 109-259, 1982.
- [28] R.A. Brown, M.J. Szady, P.J. Northey, R.C. Armstrong, On the numerical stability of mixed finite-element methods for viscoelastic flows governed by differential constitutive equations, *Theoret. Comput. Fluid Dynamics* **5**:77-106, 1993.
- [29] Burghardt W. and Mather P., *Rheology of liquid crystalline polymers: An experimental view of theoretical needs*, KITP Program on dynamics of complex and macromolecular fluids, 2002.
- [30] J.A. Byars, Experimental Characterization of Viscoelastic Flow Instabilities, Ph.D. dissertation, Massachusetts Institute of Technology, Cambridge, MA 1996.
- [31] J.A. Byars, A. Öztekin, R.A. Brown, G.H McKinley, Spiral instabilities in the flow of highly elastic fluids between rotating parallel disks, *J. Fluid Mech.*, **271**:173-218, 1994.
- [32] P.T. Callaghan, M.L. Kilfoil, and E.T. Samulski, Chain deformation for a polymer melt under shear. *Physical Reviews Letters*, **81**(20): 4524-7, 1998.
- [33] A.E. Caola, Y.L. Joo, R.C. Armstrong and R.A. Brown. Highly parallel time integration of viscoelastic flows. *J. Non-Newtonian Fluid Mech.*, **100**: 191-216, 2001
- [34] C.V. Chaubal, L.G. Leal, and G.H. Fredrickson. A comparison of closure approximation for the Doi theory of LCPs. *J. Rheol.*, **39**:73-103, 1995.

- [35] C.V. Chaubal and L.G. Leal. A closure approximation of liquid crystalline polymer models based on parametric density estimation. *J. Rheol.*, **42**:177-201, 1999.
- [36] B. Cockburn. An introduction to the discontinuous Galerkin method for convection dominated problems. In A. Quarteroni, editor, *Advanced Numerical Approximation of Nonlinear Hyperbolic Equations*, pp 151-268. Berlin: Springer-Verlag, 1998.
- [37] B. Cockburn and C.W. Shu. The local discontinuous Galerkin method for time dependent convection-diffusion systems. *SIAM J. Numer. Anal.*, **35**: 2440-63, 1998.
- [38] F.L. Colhoun, R.C. Armstrong and G.C. Rutledge. Orientation relaxation in sheared polystyrene melts measured by ^{13}C SMAS-DECODER NMR. *Macromolecules*, 2001.
- [39] T.H. Cormen and C.E. Leiserson. *Introduction to Algorithm*, 2nd edition, Cambridge: MIT Press, 2001.
- [40] J. Cormenzana, A. Ledda, M. Laso. Calculation of free surface flows using CONN-FFESSIT, *J. Rheology*, **45**(1): 237-57, 2001.
- [41] F.R. Cottrell, E.W. Merrill, and K.A. Smith. Conformation of polyisobutylene in dilute solution subjected to a hydrodynamic shear field. *J. Polymer Science: Part A-2*, **7**(8) 1415-34, 1969.
- [42] C.F. Curtiss and R.B. Bird. A kinetic theory for polymer melts. I. The equation for the single-link orientational distribution function *J. Chem. Phys.*, **74**(3): 2016-25, 1981.
- [43] C.F. Curtiss and R.B. Bird, A kinetic theory for polymer melts. II. The stress tensor and the rheological equation of state. *J. Chem. Phys.*, **74**(3): 2026-33, 1981.
- [44] C.F. Curtiss, R.B. Bird, Statistical mechanics of transport phenomena: polymeric liquid mixtures, *Adv. Poly Sci.* **125**:1-101, 1996.
- [45] C.F. Curtiss, R.B. Bird. Fokker-Planck equation for the one-molecule distribution function in polymer mixtures and its solution. *J. Chem. Phys.* **106**(23):9899-9921, 1997.
- [46] C.F. Curtiss and R.B. Bird. Thermal conductivity of dilute solution of chain-like polymers. *J. Chem. Phys.* **107**(13): 5254-5267, 1997.
- [47] C.F. Curtiss and R.B. Bird. Diffusion-stress relations in polymer mixtures. *J. Chem. Phys.* **111**(22): 10362-10370, 1999.
- [48] I. Daubechies. *Ten Lectures on Wavelets*. The Society of Industrial and Academic Mathematics, 1992.
- [49] P.G. de Gennes, Reptation of a polymer chain in the presence of fixed obstacles. *J. Chem. Phys.*, **55**: 572-79, 1971.
- [50] P.G. de Gennes, Coil-stretch transition of dilute flexible polymers under ultrahigh velocity gradient. *J. Chem. Phys.* **60**:5030-42, 1974.
- [51] P.G. de Gennes, *Scalings concepts in polymer physics*, Ithaca, New York: Cornell University Press, 1979.
- [52] J.J. de Pablo, H.C. Öttinger, Y. Rabin, Hydrodynamic changes of the depletion layer of dilute polymer solutions near a wall, *AIChE Journal*, **38**(2): 273-283, 1992.
- [53] W.M. Deen, *Analysis of Transport Phenomena*, New York: Oxford University Press, 1999.

- [54] M. Doi and S.F. Edwards. Dynamics of concentrated polymer systems. Part 1. Brownian motion in the equilibrium state. *J. Chem. Soc. Faraday Trans. 2*, **74**(10): 1789-801, 1978.
- [55] M. Doi and S.F. Edwards. Dynamics of concentrated polymer systems. Part 2. Molecular motion under flow. *J. Chem. Soc. Faraday Trans. 2*, **74**(10): 1802-17, 1978.
- [56] M. Doi and S.F. Edwards. Dynamics of concentrated polymer systems. Part 3. The constitutive equation. *J. Chem. Soc. Faraday Trans. 2*, **74**(10): 1818-32, 1978.
- [57] M. Doi and S.F. Edwards. Dynamics of concentrated polymer systems. Part 4. Rheological properties. *J. Chem. Soc. Faraday Trans. 2*, **75**(1): 38-54, 1979.
- [58] M. Doi. Molecular dynamics and rheological properties of concentrated solutions of rodlike polymers in isotropic and liquid crystalline phases. *J. of Polymer Science: Polymer Physics Edition*, **19**:229-243, 1981.
- [59] M. Doi and S.F. Edwards. *The Theory of Polymer Dynamics*. Oxford University Press, New York, 1986.
- [60] P.S. Doyle, E.S.G. Shaqfeh, A.P. Gast, Dynamic simulation of freely draining flexible polymers in steady linear flows. *J. Fluid Mech.*, **334**:251-291, 1997.
- [61] P.S. Doyle, A.P. Gast, and E.S.G. Shaqfeh. Rheology of "wet" polymer brushes via Brownian dynamics simulation: Steady vs oscillatory shear. *Phys. Rev. Letters*, **78**(6):1182-6, 1997.
- [62] P.S. Doyle, E.S.G. Shaqfeh, G.H. McKinley, S.H. Spiegelberg, Relaxation of dilute polymer solutions following extensional flow, *J. Non-Newtonian Fluid Mech.* **76**:79-110, 1998.
- [63] B.J. Edwards, A.N. Beris, and M. Grmela, Generalized constitutive equation for polymeric liquid crystals. I. Model formulation using Hamiltonian (Poisson bracket) formulation, *J. Non-Newtonian Fluid Mech.*, **35**: 51, 1990.
- [64] B.J. Edwards and Öttinger. Time-structure invariance criteria for closure approximations. *Phys. Rev. E*, **56**(4):4097-103, 1997.
- [65] B.J. Edwards, H.C. Öttinger, and R.J.J. Jongschaap. On the relationships between thermodynamics formalisms for complex fluids. *J. Non-Equilibrium Thermodynamics*, **22**(2), 1997.
- [66] X. Fan and R.B. Bird. A kinetic theory for polymer melts. VI. Calculation of additional material functions. *J. Non-Newtonian Fluid Mech.* **15**(3): 341-73, 1984.
- [67] X.J. Fan, Viscosity, first normal-stress coefficient, and molecular stretching in dilute polymer solutions, *J. Non-Newtonian Fluid Mech.* **17**:125-144, 1985.
- [68] X.J. Fan. Viscosity, first normal stress coefficient, and molecular stretching in concentrated solutions and melts, *J. Non-Newtonian Fluid Mech.* **17**:1251-265, 1985
- [69] X. Fan, Molecular models and flow calculation: II. Simulation of steady planar flow. *Acta Mechanica Sinica*, **5**:49-59, 1989.
- [70] X.J. Fan, N. Phan-Thien, and R. Zheng. Simulation of fiber suspension flows by the Brownian configuration fields method, *J. Non-Newtonian Fluid Mech.*, **84**:257-74, 1999.
- [71] X.J. Fan, N. Phan-Thien, and R. Zheng. Simulation of fiber suspension flow with shear-induced migration, *J. Non-Newtonian Fluid Mech.*, **90**:47-63, 2000.

- [72] Y. Fan, A comparative study of the discontinuous Galerkin and continuous SUPG finite element methods for computation of viscoelastic flows. *Computational methods in applied mechanics and engineering*, **141**: 47-65, 1997.
- [73] J. Fang. Development of thermodynamically admissible molecular-based models for entangled polymers, Ph.D. Dissertation, Swiss Federal Institute of Technology, Zurich, 2001.
- [74] J. Fang, M. Kröger, and H.C. Öttinger. A thermodynamically admissible reptation model for fast flows of entangled polymers. II. Model predictions for shear and extensional flows. *J. Rheol.*, **44**:1293-1317, 2000.
- [75] V. Faraoni, M. Grosso, S. Crescitelli and P.L. Maffettone. The rigid-rod model for nematic polymers: An analysis of the shear flow problem. *J. Rheol.*, **43**(3):829-843, 1999.
- [76] J. Feng, and L.G. Leal. Simulating complex flows of liquid crystalline polymers using the Doi theory. *J. Rheology*, **41**: 1317-35, 1997.
- [77] J. Feng, G. Sgalari, and L.G. Leal, A theory for flowing nematic polymers with orientational distortion. *J. Rheol.*, **44**(5): 1085-101, 2000.
- [78] J. Feng, J. Tao, and L.G. Leal. Roll cells and disclinations in sheared nematic polymers, *J. Fluid Mech.*, **449**: 179-200, 2001.
- [79] M. Fixman, Construction of Langevin forces in the simulation of hydrodynamic interaction. *Macromolecules*, **19**: 1204-7, 1986.
- [80] J.D. Ferry, *Viscoelastic Properties of Polymers*, New York: Wiley, 1980.
- [81] P.J. Flory, *Principles of Polymer Chemistry*, Ithaca: Cornell, 1953.
- [82] P.J. Flory, *Statistical mechanics of chain molecules*
- [83] G.G. Fuller. *Optical Rheometry of Complex Fluids*, New York: Oxford University Press, 1995.
- [84] V. Ganesan and G. H. Fredrickson, Field-Theoretic Polymer Simulations, *Europhysics Letters*, **55**:814, 2001.
- [85] C.W. Gardiner, *Handbook of Stochastic Methods for Physics, Chemistry, and the Natural Science*, 2nd edition, New York: Springer, 1985
- [86] C.W. Gear. *Numerical Initial value problems in ordinary differential equations*. Prentice-Hall, 1971.
- [87] L.H. Genieser, *Stress and velocity field evolution in viscoelastic planar contraction flow*, Ph.D. dissertation, Massachusetts Institute of Technology, Cambridge, MA, 1997.
- [88] I. Ghosh, G.H. McKinley, R.A. Brown, and R.C. Armstrong. Deficiencies of FENE dumbbell models in describing the rapid stretching of dilute polymer solutions. *J. Rheol.* **45**: 721-58, 2000.
- [89] I. Ghosh, Y.L. Joo, G.H. McKinley, R.C. Armstrong, R.A. Brown, A new model suitable for dilute polymer solutions, In preparation.
- [90] K.R. Geurts and L.E. Wedgewood. A finitely extensible network strand model with nonlinear backbone forces and entanglement kinetics. *J. Chem. Phys.*, **106**(1): 339-46, 1997.

- [91] M. Grmela and H.C. Öttinger. Dynamics and thermodynamics of complex fluids. I. Development of a GENERIC formalism. *Phys. Rev. E*, **56**, 1997.
- [92] M. Grosso, P.L. Maffettone, P. Halin, R. Keunings, and V. Legat. Flow of nematic polymers in eccentric cylinder geometry: influence of closure approximations, *J. Non-Newtonian Fluid Mech.*, **94**: 119-34, 2000.
- [93] M. Grosso, R. Keunings, S. Crescitelli, P.L. Maffettone. Prediction of chaotic dynamics in sheared liquid crystalline polymers, *Phys. Rev. Letters*, **86**(14): 3184-3187, 2001.
- [94] R. Guenette, M. Fortin, A new mixed method for computing viscoelastic flows, *J. Non-Newtonian Fluid Mech.* **60** (1995) 27-52.
- [95] Harwell Subroutine Library Release 11 is available from AEA Technology, Building 424.4 Harwell, Oxfordshire, OX11 0RA, England.
- [96] A. Hijazi and A. Khater, Simulations of distribution for rod-like macromolecules in linear flow near solid surfaces, *Computational Materials Science*, **20**: 213-227, 2001.
- [97] J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird, *Molecular Theory of Gases and Liquids*, New York: John Wiley and Sons, 1964.
- [98] C.C. Hua and J.D. Schieber. Application of kinetic theory models in spatiotemporal flows for polymer solutions, liquid crystals and polymer melts using the CONNFES-SIT approach. *Chemical Engineering Science*. **51**: 1473-1485, 1996.
- [99] C.C. Hua and J.D. Schieber. Viscoelastic flow through fibrous media using the CONNFESSIT approach. *J. Rheol.*, **42**: 477-91, 1998.
- [100] C.C. Hua and J.D. Schieber. Segment connectivity, chain-length breathing, segmental stretch, and constraint release in reptation models. I. Theory and single step strain predictions. *J. Chem. Phys.* **109**(22): 10018-27, 1998.
- [101] C.C. Hua and J.D. Schieber. Segment connectivity, chain-length breathing, segmental stretch, and constraint release in reptation models. II. Double step strain predictions. *J. Chem. Phys.* **109**(22): 10028-32, 1998.
- [102] M.A. Hulsen, A.P.G. van Heel, and B.H.A.A. van den Brule. Simulation of viscoelastic flows using Brownian configuration fieldss. *J. Non-Newtonian Fluid Mech.*, **70**:79-101, 1997.
- [103] M.A. Hulsen, E.A.J.F. Peters, and B.H.A.A. van den Brule. A new approach to the deformation fields method for solving complex flows using integral constitutive equations, *J. Non-Newtonian Fluid Mech.*, **98**: 201-21, 2001.
- [104] J.S. Hur and E.S.G. Shaqfeh. Brownian dynamics simulations of single DNA molecule in shear flow. *J. Rheology*, **44**: 713-41, 2000.
- [105] G. Ianniruberto and G. Marrucci, On compatibility of the Cox-Merz rule with the model of Doi and Edwards, *J. Non-Newtonian Fluid Mech.*, **65**: 241-46, 1996.
- [106] G. Ianniruberto and G. Marrucci, Convective orientational renewal in entangled polymers, *J. Non-Newtonian Fluid Mech.*, **95**: 363-74, 2000.
- [107] P. Ilg, I.V. Karlin, and H.C. Öttinger. Generating moment equations in the Doi model of liquid-crystalline polymers. *Phys. Rev. E*, **60**:5783-5787, 1999.
- [108] R.L. Jaffe, D.Y.Yoon, and A.D. McLean. Calculation of *ab initio* intrasegmental potential energy functions for use in modeling polymer properties. In R.J. Roe, editor, *Computer Simulation of Polymers*. Prentic Hall, Inc., 1991.

- [109] R.M. Jendrejack, M.D. Graham, and J.J. de Pablo. Hydrodynamic interaction in long chain polymers: Application of the Chebyshev polynomial approximation in stochastic simulations. *J. Chem. Phys.*, **113**: 2894-900, 2000
- [110] R.M. Jendrejack, M.D. Graham, and J.J. de Pablo. A multiscale approach to computation fluid dynamics. *J. Chem. Phys.*, **113**: 2894-900, 2000
- [111] C. Johnson and J. Pitkaranta. Finite element methods for linear hyperbolic problems. *Computational Methods in APplied Mechanics and Engineering*, **45**: 285-312, 1986.
- [112] C. Johnson, Numerical Solution of Partial Differential Equations by the Finite Element Method, Cambridge University Press, Cambridge, England, 1987.
- [113] R.J.J. Jongschaap, *Rheological Modelling: Thermodynamical and Statistical Approaches*, J. Casas-Vazquez, D. Jou (eds). Berlin: New York (1991); R.J.J. Jongschaap. *Appl. Sci. Res.* **48**:117, 1991.
- [114] D.D. Joseph, M. Renardy, J.C. Saut, Hyperbolicity and change of type in the flow of viscoelastic fluids, *Arch. Rat. Mech. Anal.* **87** (1985) 213-251.
- [115] R. Keunings. A survey of computational rheology. *Proc. 13th Int. Congr. on Rheology*, D.M. Binding et al. (Eds), British Society of Rheology, Glasgow, 1:7-14, 2000
- [116] M.L. Kilfoil and P.T. Callaghan. NMR measurement of the alignment tensor for a polymer melt under strong shear flow. *Macromolecules*, **33**(18): 6828-33, 2000.
- [117] R.C. King, M.R. Apelian, R.C. Armstrong and R.A. Brown, Numerically stable finite element techniques for viscoelastic calculations in smooth and singular geometries, *J. Non-Newtonian Fluid Mech.* **29**:147-216, 1989.
- [118] M. Kiwi, D.A. Spielman, and S.H. Teng. Min-Max-Boundary Domain Decomposition. Special issue of *Theoretical Computer Science* for COCOON'98, **261**(2): 253-66, 2001.
- [119] P.E. Kloeden, E. Platen. *Numerical solution of stochastic differential equations*, Berlin: Springer, 1992.
- [120] M. Kroger, A. Alba-Perez, M. Laso, and H.C. Öttinger. Variance reduced Brownian simulation of a bead-spring chain under steady shear flow considering hydrodynamic interaction effect. *J. Chem. Phys.* **113**: 4767-73, 2000.
- [121] M. Laso, H.C. Öttinger, and U.W. Suter. Bond-length and bond angle distributions in coarse-grained polymer chains. *J. Chem. Phys.*, **95**(3): 2178-82, 1991.
- [122] M. Laso, H.C. Öttinger. Calculating of viscoelastic flow using molecular models: the CONNFFESSIT approach. *J. Non-Newtonian Fluid Mech.*, **47**:1-20, 1993.
- [123] R.G. Larson. A method for calculating orientational distribution functions in flows of nematic polymers. In D.D. Kee and dP.N. Kaoloni, editors, *Recent Developments in structured continua*, **2**. Longman Scientific Technical, 1990.
- [124] R.G. Larson. Arrested tumbling in shearing flows of liquid crystal polymers. *Macromolecules*, **23**: 3983-3992, 1990.
- [125] R.G. Larson and H.C. Öttinger. Effect of Molecular elasticity on out-of-plane orientations in shear flows of liquid crystalline polymers. *Macromolecules*, **24**:6270-7282, 1991.
- [126] R.G. Larson and M. Doi Mesoscopic domain theory for textured liquid crystalline polymers, *J. Rheol.*, **35**: 539, 1991.

- [127] R.G. Larson and H. Hu. Brownian dynamics simulations of a DNA molecule in an extensional flow field. *J. Rheology*, **43**: 267-303, 1999.
- [128] R.G. Larson, L. Li, H. Hu, and T. Sridhar. Understanding polymer rheology, one molecule at a time. *Proc. 13th Int. Congr. on Rheology*, D.M. Binding et al. (Eds), British Society of Rheology, Glasgow, 1: 49-55, 2000.
- [129] A. Latto, H.L. Resnikoff, and E. Tannenbaum. The evaluation of connection coefficients of compactly supported wavelets. In *Proceedings of the USA-French Workshop on Wavelets and Turbulence*. Springer Verlag, 1992.
- [130] A.T. Lee, and A.J. Mchugh. Dynamics of dendrimeric molecules undergoing simple shear flow: A nonequilibrium Brownian dynamics study. *Macromolecular Theory and Simulation*. **10**: 244054, 2001.
- [131] E.C. Lee, M.J. Solomon, and S.J. Muller, Molecular orientation and deformation of polymer solutions under shear: A flow light scattering study. *Macromolecules*, **30**(23): 7313-21, 1997.
- [132] E.C. Lee and S.J. Muller, Flow light scattering studies of polymer coil conformation in solution under shear: effect of solvent quality, *Polymer*, **40**(10): 2501-10, 1999.
- [133] R.B. Lehoucq, D.C. Sorensen, C. Yang, ARPACK Users Guide: Solution of Large Scale Eigenvalue Problems by Implicitly Restarted Arnoldi Methods, <ftp://ftp.caam.rice.edu/pub/software/ARPACK>.
- [134] P. Lesaint and P.A. Raviart. On a finite element method for solving the neutron transport equation. In *Mathematical Aspects of Finite Elements in Partial Differential Equation*, Ed. C. de Borr. New York: Academic Press, 89-145, 1974.
- [135] L. Li, and R.G. Larson. Brownian dynamics simulations of dilute polystyrene solutions. *J. Rheology*. **44**: 291-322, 2000.
- [136] M.Y. Liao and G.C. Rutledge, Molecular orientation in poly(4-oxybenzoate-co-1,4-phenylene isophthalate) by slow-magic-angle-spinning DECODER NMR. *Macromolecules*, **30**(24): 7546-53, 1997.
- [137] A.W. Liu, Viscoelastic Flow of Polymer Solutions around Arrays of Cylinders: Comparison of Experiment and Theory, Ph.D. dissertation, Massachusetts Institute of Technology, Cambridge, MA 1997.
- [138] A.W. Liu, R.C. Armstrong and R.A. Brown, Instability in viscoelastic flow around a linear array of cylinders in a channel. *J. Non-Newtonian Fluid Mech.* to be submitted (1999).
- [139] A.W. Liu, D.E. Bornside, R.C. Armstrong, R.A. Brown, Viscoelastic flow of polymer solutions around a periodic, linear array of cylinders: comparisons of predictions for microstructure and flow fields, *J. Non-Newtonian Fluid Mech.* **77** (1998) 153-190.
- [140] T.W. Liu, Flexible polymer chain dynamics and rheological properties in steady flows, *J. Chem. Phys.*, **90**(10): 5826, 1989.
- [141] Y. Liu and I.T. Cameron, A new wavelet-based method for the solution of the population balance equation. *Chemical Engineering Science*, **56**: 5283-5294, 2001.
- [142] A.S. Lodge, J.D. Schieber, and R.B. Bird. The Weissenberg effect at finite rod-rotation speeds. *J. Chem. Phys.*, **88**(6): 4001-7, 1998.
- [143] L.S. Loo, R.E. Cohen, and K.K. Gleason, Chain mobility in the amorphous region of nylon 6 observed under active uniaxial deformation, *Science*, **288**:116-9, 2000.

- [144] W. Maier and A. Saupe. Eine einfache molekulare-statisticsche theory der nematischen kristallinflussigen phase. *Z. Naturforsch. A.*, 14a: 882-889, 1959.
- [145] G. Marrucci. The Doi-Edwards model withouth independent alignment, *J. Non-Newtonian Fluid Mech.*, **62**: 279-89, 1996.
- [146] G. Marrucci and N. Grizzuti, The Doi-Edwards model in slow flows. Predictions on the Weissenberg effect, *J. Non-Newtonian Fluid Mech.* **21**: 319-28, 1986.
- [147] G. Marrucci and N. Grizzuti, Fast flows of concentrated polymers: Predictions of the tube model on chain stretching. *Gazz Chim. Ital.* **118**: 179-85, 1988.
- [148] G. Marrucci and P.L. Maffettone. Description of the liquid-crystalline phase of rod-like polymers at high shear rates. *Macromolecules*, **22**:4076-4972, 1989.
- [149] G. Marrucci and P.L. Maffettone, Nematic phase of rodlike polymers. II Polydomain predictions in the tumbling regime, *J. Rheol.*, **34**: 1231, 1990.
- [150] G. Marrucci and F. Greco. The elastic constants of Maier-Saupe rodlike molecules nematics. *Mol. Cryst. Liq. Cryst.*, **206**: 17-30,1991
- [151] G. Marrucci, Dynamics of Entanglements: A nonlinear model consistent with the Cox-Merz rule, *J. Non-Newtonian Fluid Mech.*, **62**, 279-89, 1996.
- [152] G.H. McKinley, J.A. Byars, R.A. Brown, and R.C. Armstrong, Observations on the elasticity in cone-and-plate and parallel-plate flows of a polyisobutylene Boger fluid, *J. Non-Newtonian Fluid Mech.*, **40**: 201-29, 1991.
- [153] G. H. McKinley and T. Sridhar. Filament-stretching rheometry of complex fluids, *Annu. Rev. Fluid. Mech.* **34**:375-415, 2002.
- [154] G.H. McKinley and coworkers. <http://web.mit.edu/nnf>
- [155] T.C.B. McLeish, and R.G. Larson. Molecular constitutive equations for a class of branched polymers: The pom-pom polymer. *J. Rheology*, **42**: 81-110, 1998.
- [156] D.W. Mead and L.G. Leal, The reptation model with segmental stretch I. Basic equations and general properties, *Rheological Acta*, **34**:339-59, 1995.
- [157] D.W. Mead, D. Yavich, and L.G. Leal, The reptation model with segmental stretch II. Steady flow properties, *Rheological Acta*, **34**:360-83, 1995.
- [158] D.W. Mead, R.G. Larson, and M. Doi, A Molecular Theory for Fast Flows of Engtangled Polymers, *Macromolecules*, **31**: 7895-7914, 1998.
- [159] M. Melchior, H.C. Öttinger, Variance reduced simulations of polymer dynamics, *J. Chem. Phys.* **105**(8):3316-3331, 1996
- [160] A.J. Muller, J.J. Pesce, and C. Picot, Chain conformation in sheared polymer melts as revealed by SANS. *Macromolecules*, **26**(16): 4356-62, 1993.
- [161] R. Nayak. *Molecular Simulation of Liquid Crystal Polymer Flow: A Wavelet-Finite Element Analysis*. PhD thesis, Massachusetts Institute of Technology, 1998.
- [162] P.J. Northey, R.C. Armstrong, R.A. Brown, Finite amplitude time-periodic states in viscoelastic Taylor-Couette flow described by the UCM model, *J. Non-Newtonian Fluid Mech.* **42** (1992) 117-139.
- [163] J.G. Oldroyd. On the formulation of rheological equations of state. *Proc. Roy. Soc. London Ser. A.* **200**: 523-41, 1950.
- [164] L. Onsager. The effect of shape on the interactions of colloidal particles. *Annals of the New York Academy of Science*, 51:627-659, 1949.

- [165] Y. Oono and K.F. Freed. Conformation space renormalization of polymers. I. Single chain equilibrium properties using Wilson-type renormalization. *J. Chem. Phys.*, **75**(2):993-1008, 1981.
- [166] Y. Oono and K.F. Freed. Conformation space renormalization of polymers. II. Single chain dynamics based on chain diffusion equation model. *J. Chem. Phys.*, **75**(2): 1009-15, 1981.
- [167] H.C. Öttinger, A modified reptation model. *Phys. Rev. E*, 1994. **50**:4891-4895.
- [168] H.C. Öttinger, *Stochastic Processes in Polymeric Fluids*. Berlin: Springer (1996).
- [169] H.C. Öttinger and F. Petrillo, Kinetic theory and transport phenomena for a dumb-bell model under nonisothermal conditions, *J. Rheol.*, **40**: 857-74, 1996.
- [170] H.C. Öttinger and M. Gremla. Dynamics and thermodynamics of complex fluids. II. Illustrations of a general formalism. *Phys. Rev. E*, **56**:6633-55, 1997.
- [171] H.C. Öttinger and A.N. Beris. Thermodynamically consistent reptation model without independent alignment, *J. Chem. Phys.*, **110**(14): 6593-6596, 1999.
- [172] D.S. Pearson, E.A. Herbolzheimer, G. Marrucci, and N. Grizzuti. Transient behavior of entangled polymers at high shear rates, *J. Polym. Sci. Polym. Phys. Ed.* **29**: 1589-97, 1991.
- [173] T.T. Perkins, D.E. Smith, and S. Chu. Single polymer dynamics in an elongational flow. *Science*, **276**:2016-21, 1997.
- [174] E.A.J.F. Peters, A.P.G. van Heel, M.A. Hulsen, and B.H.A.A. van den Brule. Generalization of the deformation field method to simulate advanced reptation models in complex flow, *J. Rheol.* **44**: 811-829, 2000.
- [175] F. Petruccione, and P. Biller. A consistent numerical analysis of the tube flow of dilute polymer solutions. *J. Rheology*, **32**: 1-21, 1988.
- [176] S. Qian and J. Weiss. Wavelets and the numerical solution of partial differential equations. *J. of Computational Physics*, **106**: 155-175, 1993.
- [177] S.R. Quake, H. Babcock, and S. Chu. The dynamics of partially extended single molecules of DNA. *Nature*, **388**: 151-4, 1997.
- [178] L.M. Quinzani, R.C. Armstrong and R.A. Brown. Birefringence and laser-doppler velocimetry (LDV) studies of viscoelastic flow through a planar contraction. *J. Non-Newtonian Fluid Mech.* **52**: 1-36, 1994
- [179] L.M. Quinzani, R.C. Armstrong and R.A. Brown. Use of coupled birefringence and LDV studies of flow through a planar contraction to test constitutive equations for concentrated polymer solutions. *J. Rheology*, **39**:1201-28, 1995.
- [180] D. Rajagopalan, R.C. Armstrong, R.A. Brown, Finite element methods for calculation of steady, viscoelastic flow using constitutive equations with a Newtonian viscosity. *J. Non-Newtonian Fluid Mech.* **36** (1990) 159-192.
- [181] S. Ramalingam and R.C. Armstrong. Analysis of isothermal spinning of liquid crystalline polymers. *J. Rheol.*, **37**: 1141-69, 1993.
- [182] H.K. Rasmussen and O. Hassager, Simulation of transient viscoelastic flow, *J. Non-Newtonian Fluid Mech.* **46**: 289-305, 1993; Simulation of transient viscoelastic flow with second-order time integration, *J. Non-Newtonian Fluid Mech.*, **56**: 65-84, 1995; On the sedimentation velocity of spheres in a polymeric liquid, *Chem. Eng. Sci.* **51**: 1431-40, 1996.

- [183] M. Reiner, *Phys. Today*, **17**:62, 1964.
- [184] J.P. Ryckaert, G. Ciccotti, H.J.C. Berendsen, Numerical integration of the Cartesian Equations of Motion of a System with Constraints: Molecular Dynamics of n-Alkanes, *J. Comp. Phys.* **23**:327-341, 1977
- [185] H.H. Saab, R.B. Bird, and C.F. Curtiss. A kinetic theory for polymer melts. V. Experimental comparisons for shear-flow rheological properties. *J. Chem. Phys.*, **77**(9): 4758-66, 1982.
- [186] Y. Saad and M.H. Schultz. GMRES: a generalized minimal residual algorithm for solving non-symmetric linear systems, *SIAM J. Sci. Stat. Comput.*, **7**:856-869, 1986.
- [187] T. Saad, Iterative Method for Sparse Linear Systems, PWS, Boston 1996.
- [188] Y. Saad, Numerical Methods for Large Eigenvalue Problems, Manchester U. Press, Manchester, U.K. 1992.
- [189] Y. Saad, SPARSKIT: a basic tool kit for sparse matrix computations, Version 2, <ftp://ftp.cs.umn.edu/dept/sparse>
- [190] T.R. Salamon, Finite Element Simulation of Steady Viscoelastic Free-Surface Flows, Ph.D. Dissertation, Massachusetts Institute of Technology (1995).
- [191] P. Saramito, A new θ -scheme algorithm and incompressible FEM for viscoelastic fluid flows, *Math. Modelling and Numer. Anal.* **28** (1994) 1-35.
- [192] P. Saramito, J.M. Piau, Flow characteristics of viscoelastic fluids in an abrupt contraction by using numerical modeling, *J. Non-Newtonian Fluid Mech.* **52** (1994) 263-288.
- [193] J.D. Schieber, C.F. Curtiss and R.B. Bird. Kinetic theory of polymer melts. 7. Polydispersity effects, *Ind. Eng. Chem. Fundam.*, **25**(4): 471-5, 1986.
- [194] G. Sgalari, G.L. Leal and J.J. Feng, The shear flow behavior of LCPs based on a generalized Doi model with distortional elasticity. *J. Non-Newtonian Fluid Mech.* **102**: 361-82, 2002.
- [195] Shu
- [196] J.C. Simo and F. Armero. Unconditional stability and long-term behavior of transient algorithms for the incompressible Navier-Stokes and Euler equations. *Computer Methods in Applied Mechanics and Engineering*, **111**:111-154, 1994.
- [197] D.E. Smith and S. Chu, Response of flexible polymers to a sudden elongational flow. *Science*, **281**: 1335-40, 1998.
- [198] D.E. Smith, H.P. Babcock, and S. Chu, Single-polymer dynamics in steady shear flow, *Science*, **283**: 1724-7, 1999.
- [199] M.D. Smith, Simulation of nonisothermal and time-dependent viscoelastic flows, Ph.D. Dissertation, Massachusetts Institute of Technology (2000).
- [200] M.D. Smith, R.C. Armstrong, R.A. Brown, and R. Sureshkumar. Finite element analysis of stability of two dimensional viscoelastic flows to three-dimensional perturbation. *J. Non-Newtonian Fluid Mech.* **93**: 203-44, 2000.
- [201] M.D. Smith, Y.L. Joo, R.C. Armstrong, and R.A. Brown. Finite element analysis of stability of flow of an Oldroyd-B model through a linear array of cylinders. *J. Non-Newtonian Fluid Mech.*, to be submitted

- [202] M. Somasi and B. Khomami. Dynamics of polymeric fluids in complex geometries: a combined Brownian dynamics-finite element approach. *Binder*, 2: 152-4, 2000.
- [203] M. Somasi and B. Khomami. Linear stability and dynamics of viscoelastic flows using time-dependent stochastic simulation techniques. *J. Non-Newtonian Fluid Mech.* **93**: 339-62, 2000.
- [204] W.E. Stewart and J.P. Sørensen. Hydrodynamic interaction effects in rigid dumbbell suspensions, II Computations for the steady shear flow. *Transactions of the society of rheology*, **16**:1-14, 1972.
- [205] J. Stoer, R. Bulirsch, Introduction to Numerical Analysis, Second ed., Springer-Verlag, 1993.
- [206] J.P. Straley. Frank elastic constants of the hard-rod liquid crystal. *Phys. Rev. A.*, **8**(4): 2181-3, 1973.
- [207] S.R. Strand, S. Kim, and S.J. Karrila. Computation of rheological properties of suspensions of rigid rods: stress growth after inception of steady shear flow. *J. Non-Newtonian fluid Mech.*, **24**:311-330, 1987.
- [208] G. Strang and G.J. Fix. *An Analysis of the Finite Element Method*. Englewood Cliffs: Prentice Hall, Inc., 1973.
- [209] G. Strang and T. Nguyen. *Wavelets and Filter Banks*, Wellesley-Cambridge Press, 1997.
- [210] J.K.C. Suen, Y.L. Joo, and R.C. Armstrong. Molecular orientation effects in viscoelasticity. *Annual Review of Fluid Mech.*, **34**:2002.
- [211] J.K.C. Suen, R. Nayak, R.A. Brown, and R.C. Armstrong. A wavelet-Galerkin method for simulating the Doi model with orientation dependent drag coefficient. *J. Non-Newtonian Fluid Mech.* submitted, 2002.
- [212] F. Sugeng, N. Phan-Thien, R.I. Tanner, A study of non-isothermal extrudate swell by a mixed boundary element and finite element method, *J. Rheol.* **31** (1987) 37-58.
- [213] J. Sun, M.D. Smith, R.C. Armstrong, R.A. Brown, Finite element method for viscoelastic flows based on the discrete adaptive viscoelastic stress splitting and the discontinuous Galerkin method: DAVSS-G/DG, *J. Non-Newtonian Fluid Mech.* **86** (1999) 281-307.
- [214] R. Sureshkumar, M.D. Smith, R.C. Armstrong, R.A. Brown, Linear stability and dynamics of viscoelastic flows using time-dependent simulations, *J. Non-Newtonian Fluid Mech.* **82** (1999) 57-104.
- [215] W. Sweldens. The lifting scheme: A construction of second generation wavelets. *SIAM J.*
- [216] M.J. Szady, T.R. Salamon, A.W. Liu, D.E. Bornside, R.C. Armstrong, and R.A. Brown, A new mixed finite element method for viscoelastic flows governed by differential constitutive equations, *J. Non-Newtonian Fluid Mech.* **59**:215-43, 1995.
- [217] M.J. Szady, *Finite Element Methods for the Time Dependent Simulation of Viscoelastic Fluid Flows*, Ph. D. dissertation, Massachusetts Institute of Technology, Cambridge, MA, 1996.
- [218] R.I. Tanner. *Engineering Rheology*, New York: Oxford University Press, 1985.
- [219] L.N. Trefethen, D. Bau, *Numerical Linear Algebra*, Philadelphia: SIAM, 1997.

- [220] T.Tsuji and A.D. Rey. Effect of long range order on sheared liquid crystalline materials. I. Compability between tumbling behavior and fixed anchoring, *J. Non-Newtonian Fluid Mech.*, **73**: 127, 1997.
- [221] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*. Amsterdam: North-Holland, 1992.
- [222] W.M.H. Verbeeten, *Computational Polymer Melt Rheology*, Ph.D. dissertation, Eindhoven University of Technology, the Netherlands, 2001.
- [223] K. Walters, *Rheometry*, London: Chapman and Hall, 1975.
- [224] P. Wapperom, R. Keunings, and V. Legat, The backward-tracking Lagrangian particle method for transient viscoelastic flows. *J. Non-Newtonian Fluid Mech.*, **91**: p. 273-295, 2000.
- [225] P. Wapperom and R. Keunings, Simulation of linear polymer melts in transient complex flow, *J. Non-Newtonian Fluid Mech*, **95**: 67-83, 2000.
- [226] H.R. Warner, Jr. Kinetic theory and rheology of dilute suspensions of finitely extendible dumbbells. *Ind. Eng. Chem., Fundam.* **11**: 379-387, 1972.
- [227] G.C.K. Wong and S.C. Wong, A wavelet-Galerkin method for the kinematic wave model of traffic flow, *Communications in numerical methods in engineering*, **16**:121-131, 2000
- [228] A.P.G. van Heel, M.A. Hulsen, B.H.A.A. van den Brule, Simulation of the Doi-Edwards model in complex flow. *J. Rheology*, **43**(5): 1239-60.
- [229] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*. 2nd edition Amsterdam:North-Holland, 1992.
- [230] Z. Xu, J.J. de Pablo, and S. Kim. Anisotropic friction and excluded volume effects in a freely-jointed bead-rod chain. *J. Chem. Phys.*, **101**: 5293-304, 1994.