Simulation of self-assembled polymer and surfactant systems

by

Peter H. Nelson

M.Sc. Physics, Victoria University of Wellington (1990)

Submitted to the Department of Chemical Engineering
in partial fulfillment of the degree of

Doctor of Philosophy

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

In this thesis, lattice Monte Carlo computer simulation techniques are
developed to investigate equilibrium properties of self-assembled polymer and
surfactant systems. An alternate form of the general reptation algorithm for
moving polymers on close-packed lattices is introduced. The algorithm is first
used to simulate 2d athermal polymers on the triangular lattice and the
algorithm is shown to reproduce known results to better than one part in one
thousand. The dynamics of the algorithm are investigated as a function of
polymer concentration and indicate that the algorithm is ideally suited for
investigation of dense polymer systems because the algorithm becomes more
computationally efficient as lattice approaches full occupancy. The equilibrium
dimensions of the 2d polymers of various lengths are investigated as a function
of polymer density, and for the first time, an empirical scaling relationship is
found that predicts the equilibrium dimensions of polymers as a function of
concentration and length for polymers of finite length.

The general reptation algorithm is then used to investigate the
properties of (AB)$_n$ star copolymers in dilute aqueous solution. Simulation
shows that the properties of the polymer are significantly affected by which
end of the diblock arm is attached to the center of the star. In dilute aqueous solution, stars having the hydrophilic end of the diblock attached to the center of the star can undergo a dramatic conformational change in which the outer hydrophobic blocks aggregate into one or more compact hydrophobic globules. This aggregation transition is accompanied by a significant change in the size of the polymer as measured by the radius of gyration.

Equilibrium size and shape distributions of self-assembled micelles of short surfactant molecules are then investigated. The micellar size distributions are shown to include a Gaussian peak of spherical micelles, in combination with an exponential tail of cylindrical micelles as predicted by phenomenological theories that assume that the micelles can take on spherical and cylindrical shapes. This agreement is somewhat surprising given the observation that the spherical self-assembled micelles are not perfectly spherical and the cylindrical self-assembled micelles are quite flexible and can have one or more branch points.

Finally, the effect of oil on the equilibrium microstructure of a dilute micellar solution is investigated using these simulation techniques. Dramatic growth of the self-assembled micelles into elongated worms is observed as oil is solubilized within the oily tail region of the micelles. These results confirm a microscopic explanation for experimentally observed changes in the phase behavior of surfactant solutions as oil was added. In these simulations a two-box “Helmholtz Ensemble” is introduced to guarantee that the micellar system is stable with respect to emulsification failure (appearance of a bulk oil phase). Such guarantees are not possible using the traditional one-box “Canonical Ensemble”.

Thesis supervisors:
T. Alan Hatton and Gregory C. Rutledge
Dedicated to my mother

Jo Nelson

and

in loving memory of my father

Hugo Nelson
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# Table of contents

Acknowledgements ........................................................................................................ 7

Table of contents ........................................................................................................... 9

List of figures ............................................................................................................... 17

List of tables ................................................................................................................. 27

Chapter 1: Background ................................................................................................. 29
  1.1 Introduction ........................................................................................................... 29
  1.2 Simulating materials by computer experiment .................................................... 30
  1.3 Why simulate simplified systems? ........................................................................ 32
  1.4 Lattice models ..................................................................................................... 37
  1.5 Flory-Huggins model for polymers ..................................................................... 39
  1.6 Simulation algorithms ......................................................................................... 44
  1.7 Entropic self-segregation of 2d athermal polymers .......................................... 53
  1.8 Monte Carlo methods and the Metropolis sampling technique ......................... 56
  1.9 Self-association of star copolymers ................................................................... 62
  1.10 Complex fluids and self-assembly ..................................................................... 68
  1.11 Oil in water microemulsions ............................................................................. 77
  1.12 Periodic boundary conditions and finite size effects ........................................ 79
  1.13 Comparing lattice models to specific systems ................................................... 81

Chapter 2: Simulation technique and 2d athermal polymers ..................................... 85
  2.1 Introduction ......................................................................................................... 85

9
2.2 Simulation technique ................................................................. 89
  2.2.1 General reptation algorithm ................................................. 89
  2.2.2 Transition state formulation of general reptation ......................... 89
  2.2.3 Vacancy algorithm ............................................................ 91
  2.2.4 Examples of simulated motion .............................................. 93
  2.2.5 Bead algorithm ................................................................. 95
2.3 Requirements for a well behaved algorithm ...................................... 95
  2.3.1 Microscopic reversibility & detailed balance ............................... 95
  2.3.2 Ergodicity of isolated chains ............................................. 97
  2.3.3 Non-ergodicity of dense systems ......................................... 98
2.4 Simulation setup ............................................................................... 101
  2.4.1 Initial conditions ............................................................... 101
  2.4.2 Data collected .................................................................. 101
2.5 Results for dilute systems ............................................................... 103
  2.5.1 Isolated chains – SAW’s ....................................................... 103
  2.5.2 Equilibration ..................................................................... 104
  2.5.3 Equilibrium results ............................................................. 105
  2.5.4 Comparison with known static results .................................... 108
  2.5.5 Dynamic properties ............................................................ 110
  2.5.6 Comparison of simulation dynamics with polymer theory .............. 112
2.6 Results for concentrated systems ..................................................... 113
2.6.1 Solution conditions - melt ................................................................. 113
2.6.2 Equilibrium dimensions in the melt ................................................... 114
2.6.3 Simulated melt dynamics ................................................................... 115
2.6.4 Length independence of dimensionless quantity ............................... 117
2.6.5 Scaling of the diffusion constant ......................................................... 117
2.7 Results for intermediate systems ............................................................ 119
  2.7.1 Concentration dependence ............................................................... 119
  2.7.2 Comparison with other algorithms ..................................................... 121
  2.7.3 Static and dynamic properties .......................................................... 122
2.8 Empirical Scaling Relations .................................................................. 123
  2.8.1 Existing scaling predictions ............................................................... 123
  2.8.2 Reformulation of scaling predictions ................................................. 125
2.9 Conclusion ............................................................................................. 128

Chapter 3: Self-assembled star copolymers in dilute solution .................... 131
  3.1 Introduction .......................................................................................... 131
    3.1.1 Regular stars .................................................................................. 131
    3.1.2 Amphiphilic stars .......................................................................... 132
  3.2 Model and simulation technique ............................................................ 133
    3.2.1 Lattice model in 3d ....................................................................... 133
    3.2.2 Molecular architecture ................................................................. 133
    3.2.3 Initial conditions .......................................................................... 137
3.3 Results for 12-arm stars ......................................................... 137
  3.3.1 Equilibration and data collection ....................................... 137
  3.3.2 Comparison of hydrophilic- and hydrophobic-core stars .......... 140
  3.3.3 Aggregation transition .................................................. 141
  3.3.4 Scaling models ......................................................... 143
3.4 Results for stars with more arms ........................................... 144
  3.4.1 Multi-globule conformations .......................................... 144
  3.4.2 Arm length variation .................................................. 144
  3.4.3 Excluded volume globule repulsion ................................ 147
  3.4.4 Free energy considerations .......................................... 148
3.5 Non-reversible simulations of a 42-arm star .............................. 150
  3.5.1 Other possible low energy conformations ........................... 150
  3.5.2 Preparation of a one-globule 42-arm star ........................... 150
  3.5.3 Preparation of a two-globule 42-arm star .......................... 151
  3.5.4 Variation of properties with conformation .......................... 153
3.6 Potential applications ....................................................... 154
  3.6.1 Macromolecular amphiphiles ....................................... 154
  3.6.2 Non-dilute behavior ................................................. 155
3.7 Conclusion ........................................................................... 156
Chapter 4: Self-assembled micelles ............................................. 159
  4.1 Introduction ...................................................................... 159
4.2 The simulated system ................................................................. 161

4.2.1 Molecular architecture ......................................................... 161

4.2.2 Physical interpretation ....................................................... 162

4.3 Temperature dependence ......................................................... 163

4.3.1 Small system ................................................................. 163

4.3.1 Micelle formation ............................................................ 165

4.3.3 Finite size effects ............................................................ 166

4.4 Equilibration ........................................................................... 166

4.4.1 Larger system ...................................................................... 166

4.5 Correlations at equilibrium ....................................................... 168

4.5.1 Autocorrelation function .................................................... 168

4.5.2 Representative sampling time .............................................. 170

4.6 Micellar size and shape distributions ....................................... 171

4.6.1 Size distribution ............................................................... 171

4.6.2 Shape distribution ............................................................ 173

4.6.3 Theories for spheres and cylinders ..................................... 174

4.6.4 Micellar growth ............................................................... 177

4.7 Conclusion ............................................................................. 180

Chapter 5: Solubilization of oil in micelles .................................... 181

5.1 Introduction ........................................................................... 181

5.2 The simulated system ........................................................... 183
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.1</td>
<td>Two-box simulation technique</td>
<td>183</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Adding oil to the simulation</td>
<td>185</td>
</tr>
<tr>
<td>5.3</td>
<td>The Helmholtz Ensemble</td>
<td>186</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Applicability to other systems</td>
<td>187</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Comparison with grand-canonical ensemble</td>
<td>188</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Emulsification failure</td>
<td>189</td>
</tr>
<tr>
<td>5.4</td>
<td>Simulation results</td>
<td>190</td>
</tr>
<tr>
<td>5.4.1</td>
<td>Equilibrium oil solubility</td>
<td>190</td>
</tr>
<tr>
<td>5.4.2</td>
<td>Equilibration</td>
<td>192</td>
</tr>
<tr>
<td>5.4.3</td>
<td>Oil partitioning</td>
<td>194</td>
</tr>
<tr>
<td>5.4.4</td>
<td>Low oil concentrations</td>
<td>196</td>
</tr>
<tr>
<td>5.4.5</td>
<td>Dramatic micellar growth</td>
<td>199</td>
</tr>
<tr>
<td>5.4.6</td>
<td>Micellar shape distribution</td>
<td>201</td>
</tr>
<tr>
<td>5.4.7</td>
<td>Prediction of oil location in micelles</td>
<td>206</td>
</tr>
<tr>
<td>5.4.8</td>
<td>Observed location of oil in micelles</td>
<td>210</td>
</tr>
<tr>
<td>5.4.9</td>
<td>Emulsions and finite-size effects</td>
<td>211</td>
</tr>
<tr>
<td>5.4.10</td>
<td>Monomer concentrations (cmc)</td>
<td>213</td>
</tr>
<tr>
<td>5.4.11</td>
<td>Single site representation of oil</td>
<td>215</td>
</tr>
<tr>
<td>5.5</td>
<td>Conclusion</td>
<td>215</td>
</tr>
<tr>
<td>6.1</td>
<td>Summary</td>
<td>219</td>
</tr>
</tbody>
</table>

Chapter 6: Summary and recommendations ............................................... 219
List of figures

Figure 1.1 MANIAC – the computer used by Metropolis and coworkers for pioneering work in computer simulations ca. 1953.................................31

Figure 1.2 The Lennard-Jones potential function. There is no interaction at long distances \( r/\sigma > 1 \), attraction at intermediate distances \( r/\sigma \sim 1 \), and strong repulsions at short distances \( r/\sigma < 1 \) producing an excluded volume condition ........................................................................33

Figure 1.3 A self-avoiding walk polymer on the two-dimensional triangular lattice (dark beads), surrounded by a good solvent (open circles). The dimensions of this polymer are within 2% of the average values for \( R \) and \( R_g \). The excluded volume condition is applied. ...............................40

Figure 1.4 A random-walk polymer on the two-dimensional triangular lattice (dark beads), surrounded by a good solvent (open circles). The dimensions of this polymer are within 2% of the average values for \( R \) and \( R_g \). The excluded volume condition is not applied. .................................43

Figure 1.5 Generalized Verdier-Stockmayer method for moving polymer chains on a lattice. (1) an "end rotation", (2) an "L inversion", and (3) a "crankshaft motion"....................................................................46

Figure 1.6 Standard reptation method for moving polymer chains on a lattice. The polymer slithers along its own path like a snake.................................47
Figure 1.7 A frozen configuration for the Verdier-Stockmayer and reptation moves. I.e. none of the moves in Figures 1.5 and 1.6 are possible for this polymer chain. 48

Figure 1.8 The bond fluctuation method. Two separate moves are indicated by the outlines. Branch points may move and bond lengths may vary. 49

Figure 1.9 The general reptation method. Shown is a kink-kink motion. 50

Figure 1.10 A melt of 50-bead athermal polymers at equilibrium on the two-dimensional triangular lattice. The polymer segment density is 0.99. The polymers are shown as connected beads in the presence of a good solvent (open circles). The dimensions of the highlighted polymer are within 2% of the average values for $R$ and $R_g$. The excluded volume condition is applied. 54

Figure 1.11 A typical conformation of an (AB)$_n$ star copolymer. The interaction energy between the beads of different color and the solvent are weak. The axes indicate the center of the star. 66

Figure 1.12 A simple phase separated mixture of oil (dark beads) and water (open circles). The oil is a short homopolymer chain. Note that the oil droplet contains a small number of water beads. 69

Figure 1.13 A single phase, complex fluid. The surfactant has and oil
tail (large solid beads) and a water loving head (small solid beads). The surfactant aggregates into micelles surrounded by water (open circles). The arrow indicates a circular micelle with aggregation number 8.

**Figure 1.14** A single phase, complex fluid. With the same components as Figure 1.13, but at higher surfactant concentration. The surfactant has an oil tail (large solid beads) and a water loving head (small solid beads). The solvent is water (open circles).

**Figure 2.1.** Examples of general reptation moves according to the present algorithm. (a) An end-kink general reptation as proposed previously – [Reiter et al. 1990], (b) Newly proposed single bead pseudo-reptation using a transition state bond (ii) to perform an end bead rotation (iii). (c) Rotation of an interior bead by a pseudo-reptation along a transition state bond. (d) Transition from state (i) to state (iii) can be achieved by the two consecutive general reptations shown.

**Figure 2.2.** The two ways of generating a particular transition state.

**Figure 2.3.** (a) A partial configuration which would be frozen at high densities if there are no other vacancies in the lattice. Motion to state (b) is possible if there is another vacancy adjacent to either an end or a bond of the chain (at a position not shown in (a)).

**Figure 2.4.** Raw data from simulation of. (a) Approach to equilibrium of the ensemble average values for SAWs of length $N=50$. The error bar indicates the 95% confidence interval.
Figure 2.5. Determination of the relaxation time $\tau_R$ from a weighted least-squares fit to the linear portion of the plot of $\ln(C_R(t))$ versus time $t$ (MCS/B) for SAWs of length $N=50$. The error bars indicate the 95% confidence interval. ................................................................. 106

Figure 2.6. Calculation of the center of mass self diffusion coefficient, $D_{CM}$, from the slope of the mean-square displacement $\langle\Delta R_{CM}^2(t)\rangle$ as a function of time for SAWs of length $N=50$. The error bars indicate the 95% confidence interval. ................................................................. 107

Figure 2.7. Dilute solution properties: scaling of the equilibration and relaxation times. ................................................................. 111

Figure 2.8. Scaling of the dimensionless quantity with polymer length for both dilute and concentrated solution conditions. .................................................. 113

Figure 2.9. Variation of the scaled relaxation time with density for polymers of length $N=20$ and $N=50$. ................................................................. 120

Figure 2.10. Variation of the dimensionless quantity $D_{CM}\tau_R/\langle R_t^2\rangle$ with density for polymers of length $N=20$ and $N=50$. .................................................. 121

Figure 2.11. Fits of the proposed empirical scaling relation to the mean-square dimensions of the polymers as a function of both concentration and length. The solid curves are least-squares fits to the simulation data for $N=50$. The straight lines indicate the extrapolated
values of $\alpha$ for the existing scaling relation, which is only valid for large $X$.

Figure 3.1. A typical conformation of a 12-arm hydrophilic-core star at a $\chi$-value of 0.5. Each arm of the star is an AB diblock copolymer with $N_A=20$ hydrophilic beads (lighter color) and $N_B=20$ hydrophobic beads (darker color). The axes indicate the center of the star.

Figure 3.2. Configurational energy of 12-arm hydrophilic-core and hydrophobic-core stars as a function of solution conditions as characterized by $\chi$.

Figure 3.3. Weight average globule aggregation number of 12-arm hydrophilic-core and hydrophobic-core stars as a function of solution conditions as characterized by $\chi$.

Figure 3.4. Radius of gyration of 12-arm hydrophilic-core and hydrophobic-core stars as a function of solution conditions as characterized by $\chi$.

Figure 3.5. An aggregated conformation of the 12-arm hydrophilic-core star shown in Figure 3.1 at a $\chi$-value of 2.5. The axes indicate the center of the star.

Figure 3.6. Average aggregation numbers of 12-, 24-, and 42-arm stars as a function of solution conditions $\chi$. Above $\chi=2.2$ these have one-, two-, and three-globule conformations respectively.
Figure 3.7. A three-globule conformation of a 42-arm hydrophilic-core star at a $\chi$-value of 2.5. Each arm of the star is an AB diblock copolymer with $N_A=20$ hydrophilic beads (lighter color) and $N_B=20$ hydrophobic beads (darker color). The axes indicate the center of the star.

Figure 3.8. Average aggregation number from simulations of specially prepared 42-arm hydrophilic-core stars with (1)- (2)- and (3)-globule conformations.

Figure 3.9. Configurational energy of specially prepared 42-arm hydrophilic-core stars with (1)- (2)- and (3)-globule conformations.

Figure 4.1 Variation of the micellar size distribution with scaled temperature $T''$ (interaction strength) in a small 20x20x20 system with a surfactant volume fraction of 7.5%. Finite size effects are apparent in the $T''=2.0$ distribution (see text).

Figure 4.2 Approach to equilibrium for the 60x60x60 surfactant system with a volume fraction of 7.5%. The configurational energy $E(t)$ approaches its equilibrium value (horizontal line) approximately three times faster than the average aggregation number $a(t)$.

Figure 4.3 Semi-log plot of the single surfactant-aggregate autocorrelation function $p_{aa}(t)$ vs time $t$. The slope long-time linear portion for $t>30,000$ MCS/B is used to determine the characteristic time.
Figure 4.4 Micellar size and shape distributions in a larger 60x60x60 system at $T^\alpha=2.0$ with a surfactant volume fraction of 7.5%. $X_g$, $Y_g$, and $Z_g$ are the ordered components of the radius of gyration tensor for aggregates of size $n$.................................................................179

Figure 4.5 Micellar size distribution fitted to the forms expected for spherical and cylindrical micelles in the 7.5% surfactant volume fraction simulation. Inset is the size distribution in the range $n=50$ to $n=200$ on a semi-log plot to show the exponential tail of the cylindrical micelles..........177

Figure 4.6 Micellar size distribution fitted to the forms expected for spherical and cylindrical micelles in the 15% surfactant volume fraction simulation. Inset is the size distribution in the range $n=50$ to $n=500$ on a semi-log plot to show the exponential tail of the cylindrical micelles.........178

Figure 4.7 Micelles taken from a single snapshot of the 15% surfactant volume simulation. They have aggregation numbers of 42, 91, 125 and 269 (starting at the lower left and proceeding clockwise).................................179

Figure 5.1 Two-box simulation within the Helmholtz ensemble. The water box contains water (not shown) and oil (black beads). The micelle box contains oil, water and H$_2$T$_2$ surfactant (The hydrophilic head beads (H) are white and the hydrophobic tail beads (T) are gray). Oil and water molecules can exchange between the two simulation boxes with the constraint that the volume of each box does not change. .........................184

Figure 5.2 Approach to equilibrium of the micellar aggregation state of
a two-box simulation with an oil/surfactant molecular ratio of 1/10. The
dashed line indicates the equilibrium value (see text). ..........................193

**Figure 5.3** Partition coefficient of oil between a 7.5% surfactant volume
micellar solution and bulk water phase, as a function of oil
concentration in the water phase. Circles are from a larger system
(40x40x40) and squares are from a smaller system (20x20x20). Also
shown are the total oil/surfactant molecular ratios in the two-box
simulation, which can be used as a key to go between discussions where
we use the oil concentration in the water box to characterize the system
and those where we use the total oil/surfactant ratio. The vertical line
indicates the phase boundary for emulsification failure..........................195

**Figure 5.4** Changes in the micellar size distribution as small amounts
of oil are added. Numerical values indicate the oil/surfactant molecular
ratio in the two-box simulation ..........................................................197

**Figure 5.5** Changes in the micellar size distribution as larger amounts
of oil are added. Numerical values indicate the oil/surfactant molecular
ratio in the two-box simulation ..........................................................198

**Figure 5.6** Comparison of micellar size distributions in two-box
simulations with oil/surfactant molecular ratios of 1/10 and 1/1. ............200

**Figure 5.7** Micellar shape distributions in a two-box simulation with an
oil/surfactant molecular ratio of 1/1. $X_g$, $Y_g$ and $Z_g$ are the ordered
principle components of the radius of gyration tensor ..............................202
Figure 5.8 Snapshot of a micellar aggregate (n=288) taken from the final configuration of the two-box simulation with an oil/surfactant molecular ratio of 1/1. Also shown are single surfactant and oil molecules. The darkest beads are oil, the lightest are surfactant head beads, and the intermediate shade represents surfactant tail beads. ..............203

Figure 5.9 Snapshot of a branched micellar aggregate (n=429) taken from the final configuration of the two-box simulation with an oil/surfactant molecular ratio of 1/1. The colors are the same as in Figure 5.8. ...........................................................................................................204

Figure 5.10 An alternate view of the micellar aggregate shown in Figure 5.9. ...........................................................................................................205

Figure 5.11 Cloud points of 0.5 wt. % aqueous solutions of C_{12}E_6 as a function of nonane added. Data from Aveyard et al. [1990]. .........................208

Figure 5.12 Distribution of oil molecules in micellar aggregates of different sizes in the two-box simulation with an oil/surfactant molecular ratio of 1/1. The straight line is a least squares fit to the data......211

Figure 5.13 Surfactant monomer concentration of micellar systems (of constant total surfactant concentration) as a function of oil concentration in the bulk aqueous phase. Squares are from (20x20x20) systems and circles are from (40x40x40) systems. The vertical line indicates the phase boundary for emulsification failure.................................214
List of tables

Table 2.1 Conditional probabilities for each type of move in the vacancy algorithm for \( N \)-bead polymers in a lattice with \( Nv \) vacancies..............................96

Table 2.2 Assumed scaling exponents and parameters for the \( \rho=0 \) simulations c.f. equation (2.6)...............................................................109

Table 2.3 Assumed scaling exponents and parameters for the \( \rho=0.99 \) simulations c.f. equation (2.6)...............................................................116

Table 2.4 Empirical scaling parameters......................................................126
Chapter 1: Background

1.1 Introduction

In this thesis, computer simulation techniques are developed to investigate properties of self-assembled polymer and surfactant systems. Polymers are an important class of compounds that have a large number of repeat units connected together to form long flexible chains. Polymers are found in living things, plastics and composite materials. A simplified lattice simulation model is chosen to represent the polymers here, and most chemical details of the polymers are neglected because we are interested in properties unique to polymers that are caused by their long chain-like structure. A simulation algorithm is introduced that allows the polymers to be moved efficiently through the lattice even when it is almost filled with polymers, so that a large number of polymer configurations can be generated, allowing the average properties of the polymer chains to be determined with precision.

Surfactants or "surface-active-agents" are a type of molecule that people use every day to clean household items and themselves. Soaps and detergents
are surface-active because they are elongated molecules that have one end that likes water (is hydrophilic) and have another end that hates water (is hydrophobic). As the molecule has a part that likes water and a part that hates water, these molecules like to sit at the water's surface (or at an interface between water and oil) with the hydrophilic portion in the water and the hydrophobic portion out of the water (either in air or in the oil). These surfactants thereby coat oily residues with a water-loving layer making them more soluble in water. The surfactants also reduce the surface tension of oily residues allowing them to breakup more easily.

In this thesis, the lattice simulation technique discussed above (a Monte Carlo method) is modified to investigate aggregates of surfactant molecules (micelles) that spontaneously form in dilute aqueous solution. These self-assembled micelles are able to absorb oil inside themselves while remaining soluble in water. The effect of oil on the structure of these micelles is the subject of the final chapter of this thesis.

1.2 Simulating materials by computer experiment

Modern techniques for simulating materials were developed almost as soon as digital computers were invented [Metropolis et al. 1953]. At that time, computers such as MANIAC were room-sized devices made from vacuum tubes
Figure 1.1 MANIAC – the computer used by Metropolis and coworkers for pioneering work in computer simulations ca. 1953.

(or valves) - see Figure 1.1. They were extremely unreliable and required repairs almost on a daily basis. Their high cost of operation meant that use was limited to governments, large corporations and a few scientists.
Improvements in computer technology have long been governed by Moore's Law - that every 18 months the performance relative to cost doubles. Fifty years worth of development has now produced computers that are vastly different from their ancestors. Young children now play with computers that can sit in the palm of your hand and cost only a few dollars, but have many times more computing power than Metropolis and coworkers used in 1953. Computer technology has now become so pervasive that a 71-year-old grandmother communicates with her sons from halfway around the globe using the Internet.

While computer technology has undergone many generations of evolution, the physical laws governing the behavior of physical systems remain unchanged. Thus, we find that the "Metropolis sampling technique" developed half a century ago remains central to the current work.

1.3 Why simulate simplified systems?

In just a few years, Metropolis sampling was applied to systems in which the particles interact via the Lennard-Jones 6-12 potential [Wood and Parker 1957]. This model has been a favorite of simulators ever since. The
Figure 1.2 The Lennard-Jones potential function. There is no interaction at long distances \((r/\sigma>1)\), attraction at intermediate distances \((r/\sigma<1)\), and strong repulsions at short distances \((r/\sigma<1)\) producing an excluded volume condition.

Lennard-Jones potential has the form

\[
\varphi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right].
\]

\(\varphi(r)\) is the pair potential between two particles of radius \(\sigma\) separated by a distance \(r\), and \(\varepsilon\) characterizes the strength of the interaction (see Figure 1.2). This pairwise interaction is considered to be a reasonable approximation for argon [Allen and Tildesley 1987]. However, argon melts at \(-189^\circ\text{C}\) and boils at \(-186^\circ\text{C}\) and is a relatively uninteresting nearly ideal gas at room temperatures.
and pressures. Hence, direct comparison of everyday condensed materials with argon is impossible. So why then has the Lennard-Jones system been studied so extensively?

The answer is that many properties of simple materials can be reproduced \textit{qualitatively} by almost any potential having the following three features in common with the potential shown in Figure 1.2.

(1.2.1) At long distances ($r>\sigma$), the particles do not interact.

(1.2.2) At short distances ($r\sim \sigma$) the particles attract each other with energy $\varepsilon$.

(1.2.3) The particles are excluded from occupying the same space by very strong repulsions at distances less than $r\sim \sigma$.

Of the two adjustable parameters ($\sigma$ and $\varepsilon$), it is usually the strength of the interaction $\varepsilon$ that is most important to the material behavior. Scaling of energy by $\varepsilon$ and size by $\sigma$ can be used to \textit{qualitatively} compare real simple systems to the Lennard-Jones system. The scaled variables

$$
\phi' = \frac{\phi}{\varepsilon}, \quad r' = \frac{r}{\sigma} \quad \text{and} \quad T'' = \frac{k_B T}{\varepsilon}
$$
are of primary interest in this qualitative comparison ($k_B$ is the Boltzmann constant and $T$ is the temperature).

So which properties of what systems can be investigated using these simplified models? The answer is that it depends, both on the system and on the properties of the system that are of interest. Often, the simple fact that a simulation is capable of qualitatively reproducing experimental results provides invaluable information about real systems that is not obtainable in any other way. This is because the simulation can be set up exactly as one wishes. Impurities can be eliminated, and the atomic level details of structure and dynamics can observed without experimental error or uncertainty.

For example, simulations of the two-dimensional Lennard-Jones system have recently shown that instabilities and speed limitations in fracture dynamics of solids, have nothing to do with impurities or imperfections in the material, or difficulties in the experimental setup, but that they are inherent properties of the fracture dynamics itself [Abraham et al. 1994]. The two-dimensional Lennard-Jones system is not a very realistic model for any solid, but the fact that it qualitatively reproduces real behavior is extremely significant. It indicates that its behavior is in some sense fundamental and that it can be used as a base line for comparison with other simulations and experiments. Any deviation of real systems from the model must be explained,
either in terms of differences in the structure of the real system or deviations of the interaction potential from the model system.

Direct quantitative comparison between the 2-dimensional Lennard-Jones system and real materials such as bcc (body centered cubic) metals is not justified or even appropriate, especially because real metals are three-dimensional. Abraham and co-workers [1997] have extended the work to three-dimensional systems, including the fcc (face centered cubic) Lennard-Jones system, and they have been able to show that the brittle fracture instability also exists in three dimensional systems, and that there is a brittle-to-ductile transition. Once again, qualitative comparisons can be made, but much larger systems and more realistic force potentials would be needed to address the quantitative concerns of engineers and materials scientists regarding real-world materials.

Other properties of the Lennard-Jones system, such as dynamical heterogeneities in supercooled liquids [Kob et al. 1997] are also just beginning to be investigated today. Time scales of the physical systems range from less than $10^{-15}$ seconds to more than hundreds of years ($10^9$ seconds), so no matter how fast the computer is there will still be problems out of reach of the current technology. This has led to the use of simulation systems even more simplified than the Lennard–Jones system.
1.4 Lattice models

Lattice models have long been used by theorists because they can be used to formulate a problem solvable by analytical methods. These same models are also well suited to computer simulation. Comparison between theory, simulation and experiment has become a familiar paradigm in statistical physics. Perhaps the simplest and most popular example is the Ising model, which is used to investigate the basic properties of phase transitions [Gould and Tobochnik 1988].

The number of degrees of freedom in a lattice model is drastically reduced relative to an off-lattice model, because the particles are constrained to sit at one lattice site or another. Generally, interactions in lattice models are of the nearest-neighbor, pairwise-additive type, and only one particle can occupy a given lattice site at a time.

In this way, the three essential features of the continuous energy potential discussed above are retained. The length scale $\sigma$ is now the distance between nearest neighbor sites on the lattice.

(1.3.1) Particles that are not nearest neighbors are considered to be separated by a long distance, and thus do not interact.

(1.3.2) Nearest neighbors are separated by a short distance, and interact
with energy $\varepsilon$.

(1.3.3) The particles are excluded from occupying the same lattice site (by very strong repulsions).

Lattice models therefore retain the essential characteristics of the inter-particle energy function and allow for spatial rearrangement of the particles with the constraint that the particles sit at lattice sites. What is lost in this simplification is any realistic hope of modeling the continuum dynamics of the system, at least on a scale comparable to $\sigma$, because the smallest motion possible is a particle jump of one lattice spacing.

There are exceptions to this rule where the physical system being modeled also has a lattice structure. In this case it may be possible to quantitatively model the dynamics even for systems of just a few lattice sites - if the standard Monte Carlo simulation techniques are be modified to ensure that the correct dynamical behavior is reproduced [Nelson 1989, Nelson et al. 1991, Nelson and Wei 1992].

The inability of lattice models to reproduce continuum motion in disordered systems is not a disadvantage if one is interested in equilibrium thermodynamic properties. In fact, it can be turned into an advantage because radical changes in configuration can easily be made within the lattice framework. The "dynamics" of lattice simulations are thus usually many times
faster than comparable off-lattice simulations (in terms of wall-clock time for a computer simulation), allowing investigation of real-world systems whose intrinsic dynamics occur on much longer timescales.

1.5 Flory-Huggins model for polymers

The literature relating to polymers in solution is vast and we will not attempt to perform a detailed review as various texts are available [Flory 1953, 1971, Tanford 1961, de Gennes 1985, Doi and Edwards 1986, des Cloizeaux and Jannink 1989]. The aspects of polymer theory and experiments that are closely related to the present work will be discussed briefly, together with some recent advances.

The Flory-Huggins theory of polymer solutions [Flory 1971 Huggins 1942abc] is a mean field picture that has been used widely [de Gennes 1979]. The basic assumption of the model is that a polymer may be approximated by a string of beads on a lattice, with each lattice site being able to accommodate only one bead (the excluded volume condition) (see Figure 1.3). The beads are connected by bonds of one lattice spacing to their neighbors along the chain, and they can be considered to be a section of polymer long enough that the orientation of a segment is not correlated with the orientation of the previous
Figure 1.3 A self-avoiding walk polymer on the two-dimensional triangular lattice (dark beads), surrounded by a good solvent (open circles). The dimensions of this polymer are within 2% of the average values for $R$ and $R_g$. The excluded volume condition is applied.

segment. The solvent contained within a lattice site can likewise be considered to be a collection of solvent molecules with the same volume as a bead. The interactions between the beads $B$ and the solvent $S$ are limited to nearest neighbor interactions and are characterized by a $\chi$ parameter which can be defined as
\[ \chi = \frac{z(2\varepsilon_{BS} - \varepsilon_{BB} - \varepsilon_{SS})}{2k_B T} \]

where \( z \) is the coordination number of the lattice, \( \varepsilon_{BB}, \varepsilon_{SS} \) and \( \varepsilon_{BS} \) are the interaction energies (between two beads, two solvents, or a bead and a solvent particle respectively), \( k_B \) is the Boltzmann constant and \( T \) is the temperature. Thermodynamic properties, such as the Gibbs free energy of mixing, \( \Delta G \), can be determined analytically in this model

\[ \frac{\Delta G}{k_B T} = \frac{\Phi \ln \Phi}{N} + (1 - \Phi) \ln(1 - \Phi) + \chi \Phi (1 - \Phi) \]

where \( \Phi \) is the volume fraction of polymer beads and \( N \) is the number of beads in a chain.

These mean field calculations neglect correlations between beads which result from the excluded volume condition. It is thus implicitly assumed that the polymers are ideal (Gaussian) chains independent of concentration. However, it is well known that dilute solutions of polymers in a good solvent are not ideal. One property of ideal chains is that the mean-square end-to-end distance \( <R^2> \) and the mean-square radius of gyration \( <R_g^2> \) both scale with \( N \), whereas for dilute solutions in a good solvent they scale with \( N^{2\nu} \) where \( \nu \) is 3/4 for 2d systems and \( \nu \) is about 3/5 for 3d systems. This swelling of the chains obviously
becomes very significant for long chains. The chain shown in Figure 1.3 has dimensions $R$ and $R_g$ that are within 2% of the average values for polymers of this length (see chapter 2). The swelling is visually apparent, with the polymer having an overall configuration that is quite extended.

A major advantage of the Flory-Huggins theory is that analytical expressions can be obtained for thermodynamic properties. The major disadvantages are that it is unclear whether deviations from experimental behavior are due to simplifications inherent in the lattice model or whether they are due to crude mathematical approximations used in the statistical mechanical derivation of properties such as $\Delta G$, in the equation above [Sariban and Binder 1987].

According to de Gennes [1979] the lattice model is somewhat artificial, but it does not lose any essential [equilibrium thermodynamic] feature of the problem, and it provides a convenient framework to describe solutions at all concentrations. This last comment is extremely significant, as in this thesis we will investigate both dilute and concentrated solutions, and microphase separated solutions containing both dilute and concentrated microphases.

The simulations can be contrasted with the theory of Flory and Huggins, in which a mean-field formulation is used and a self-consistent potential, uniform in space, is calculated. Consequently, this theory is
Figure 1.4 A random-walk polymer on the two-dimensional triangular lattice (dark beads), surrounded by a good solvent (open circles). The dimensions of this polymer are within 2% of the average values for $R$ and $R_s$. The excluded volume condition is not applied.

intrinsically associated with ideal polymer chains (where the excluded volume condition is not obeyed). Figure 1.4 shows a representative random walk polymer of length 50, as assumed in the theory (mean dimensions within 2% of the average values). The excluded volume condition is not applied and the 50-bead polymer only occupies 29 lattice sites. The size and shape of the polymer is strikingly different from the polymer with excluded volume shown in Figure
1.3. The Flory-Huggins theory does not account for the intra-chain excluded volume effects cause this difference.

An essential feature of the lattice model simulated here is that it does satisfy the excluded volume condition (1.3.3) for polymers.

1.6 Simulation algorithms

Now that we have selected a static lattice model, there remains the question of how to generate polymer configurations on the lattice. For this we will use lattice Monte Carlo techniques, which, in principle, can provide "numerically exact" solutions to the Flory-Huggins lattice model [Sariban and Binder 1987-1989], apart from statistical uncertainties (which can be made arbitrarily small) and finite size effects that can be accounted for, or reduced to negligible size. There are no approximations in the method other than those inherent in the lattice model, so the method provides a unique opportunity to determine the consequences of the approximations made in the statistical mechanics of the Flory-Huggins theory, and to possibly adjust these theories to reduce the effects of the assumptions. In addition, the Monte Carlo method can be used to check the validity of the lattice model by direct comparison with laboratory experiments.
Numerically exact results can only be found using a Monte Carlo method that satisfies the condition of detailed balance (or microscopic reversibility) and that is ergodic [Kremer and Binder 1988]. The condition of detailed balance is required to ensure that the accessible configuration space is sampled without bias. The ergodicity requirement is needed to ensure that the full configuration space of the system can be sampled. All the methods discussed here satisfy the condition of detailed balance, however most of the methods are known to be nonergodic in some circumstances. The best methods available are known to be ergodic for isolated chain systems (dilute solution conditions) but for dense polymer systems they are either known to be nonergodic or their ergodicity is uncertain.

Investigation of lattice polymer properties by Monte Carlo techniques has a long history, dating back to the early 1950's. For a review of currently used methods see Kremer and Binder [1988], Binder [1992], and Baumgärtner [1992]. The two methods that are most commonly applied to dense polymer systems are the generalized Verdier-Stockmayer method and the reptation method.

Figure 1.5 shows typical motions provided for in the generalized Verdier-Stockmayer methods [Verdier and Stockmayer 1962]. These motions were originally used because they are thought to approximate the bond
Figure 1.5 Generalized Verdier-Stockmayer method for moving polymer chains on a lattice. (1) an "end rotation", (2) an "L inversion", and (3) a "crankshaft motion".

rotations that are responsible for the relaxation of real polymers. Move (1) is an "end rotation", move (2) is an "L inversion", and move (3) is a "crankshaft motion".

Later, a method that is conceptually similar to de Gennes' reptation theory for polymer motion was developed [Wall and Mandel 1975]. As shown in Figure 1.6, the polymer slithers along its length so that the "head" of the polymer moves to a new site and the remainder of the polymer slides along behind leaving a vacancy behind the "tail".

46
Figure 1.6 Standard reptation method for moving polymer chains on a lattice. The polymer slithers along its own path like a snake.

However, both these methods are known to be not ergodic [Madras and Sokal 1987] even for isolated chains. As shown in Figure 1.7 it is possible to construct configurations that are "frozen" for the Verdier-Stockmayer and standard reptation algorithms, as none of the motion types shown in Figure 1.5 and 1.6 is possible. In addition, for polymer volume fractions greater than about $\rho=0.8$ the dynamics of the system slow down dramatically. To improve the speed of these algorithms, it has become common for a combination of both of them to be used for dense polymer systems and micellar systems. However,
Figure 1.7 A frozen configuration for the Verdier-Stockmayer and reptation moves. I.e. none of the moves in Figures 1.5 and 1.6 are possible for this polymer chain.

This combined method still suffers from ergodicity problems for isolated chains that can be expected to become more severe for dense systems. In addition, the combined method is still quite slow.

The bond fluctuation method [Carmesin and Kremer 1988, 1990] does not suffer from ergodicity problems at densities less than about $\rho=0.8$ and has the significant advantage that it can be used for branched polymers. In the 2d implementation of the bond fluctuation method a monomer occupies four lattice sites and the bond length $l$ can vary between $4^{1/2} \leq l < 16^{1/2}$. Two typical motions are shown in Figure 1.8. At high polymer densities the method is
known to be nonergodic and it is expected to slow down dramatically as the density approaches unity. In addition, as the bond lengths between beads are not fixed, the model does not directly correspond to the simple fixed bond length lattice model of the Flory-Huggins formalism.

The computational efficiency of the general reptation method is approximately independent of density for athermal polymer systems [Reiter et
Figure 1.9 The general reptation method. Shown is a kink-kink motion.

*al. 1990, Nelson et al. 1997a*, and thus has significant advantages over the previous methods for micellar systems where the core of the micelle is expected to be dense.

A newly developed alternative form of the general reptation method has been developed for close-packed lattices in two and three dimensions [Nelson et al. 1997a]. Anywhere from 1 to $N$ beads (inclusive) can reptate along the chain in a similar manner to that used to untie knots in a rope. The motion type shown in Figure 1.9 is a kink-kink motion in which a portion of the chain slithers along its own length forming a new kink at the "head" of the portion which moves and removing a kink from the chain at the "tail" of the portion of
the chain which moves. Kink-end, end-kink and end-end motions are also possible; the last of these is the longest motion possible and corresponds to the standard reptation move. The shortest moves correspond to the end rotations and L inversions of the generalized Verdier-Stockmayer method. The allowed moves in the alternative form of the general reptation method correspond to all possible moves, wherein a portion of the chain moves so that a single bead moves into a vacancy which is a nearest neighbor to it.

This alternative form has been shown to be nonergodic in specific circumstances but the fraction of configuration space excluded by the non-ergodicity is estimated be vanishingly small for most practical applications [Nelson et al. 1997a], so that the lack of ergodicity is not expected to affect the results. In addition, it has been determined that for 2d systems on the close-packed triangular lattice, that the dimensions of polymer chains of length $N \geq 20$ are consistent with a scaling theory modified to take into account the finite length of the chains. This can be contrasted with previous general reptation results for the (loose-packed) simple cubic lattice, which were inconsistent with the scaling theory. This difference was attributed [Reiter et al. 1990] to "packing constraints", which do not appear to occur for close-packed lattices, at least in 2d.

Numerous studies of interfacial adsorption have been conducted over the last few years [Balazs et al. 1991a-d, Baljon-Haakman and Witten 1992,
Harris and Rice 1988, Zhulina and Pakula 1992]. These simulations will not be discussed in detail here as the results relate to macroscopic interfaces rather than the properties of self-assembled aggregates. Simulations of the thermodynamic properties of bulk polymer solutions are more closely related to the present work.

Sariban and Binder [1987-1989] have used lattice Monte Carlo techniques to investigate the phase behavior of symmetric polymer mixtures in the presence of solvent. The solvent volume fraction was always greater than 0.2 due to the slowness of the algorithm they used at lower solvent volume fractions. The polymer mixture comprised homopolymers of type A and homopolymers of type B where the lengths of each type of polymer \((N_A=N_B)\) were the same. The simulation was conducted in the grand canonical ensemble where the chemical potential difference \(\Delta \mu\) between the A and B monomers was held fixed rather than their concentrations (canonical ensemble). Using this approach they were able to determine the phase diagram (coexistence curves), excess specific heats and the structure factor in the long wavelength limit. They found that the critical temperature was a factor of two less than the Flory-Huggins prediction. The dimensions of the chains also had pronounced dependence on both concentration and temperature even in the concentrated regime where one might have expected the chains to become ideal.
Minchau et al. [1990] have studied the order-disorder transition of symmetric diblock copolymers using lattice Monte Carlo techniques. They found that Liebler's theory [1980] gives a reasonable approximation for the transition temperature but that the radius of gyration of the chains increases by about 10% as the transition temperature is approached.

1.7 Entropic self-segregation of 2d athermal polymers

The alternative form of the general reptation algorithm used here is new and so must be tested and verified by studying well known systems. This is necessary to ensure that the simulation behaves as expected and to determine its dynamic properties. The static properties of isolated athermal lattice polymer systems are well known, particularly in 2d [e.g. Rapaport 1985ab, Nienhuis 1982, Madras and Sokal 1988]. Consequently, in chapter 2 we will use the general reptation method to study the same systems on the triangular lattice.

Although, the properties of athermal polymers have been studied for nearly fifty years, the knowledge of their behavior is primarily limited to comparison with power law predictions for long chain lengths in either the dilute or the semidilute (concentrated) regime. Before the present work there
Figure 1.10 A melt of 50-bead athermal polymers at equilibrium on the two-dimensional triangular lattice. The polymer segment density is 0.99. The polymers are shown as connected beads in the presence of a good solvent (open circles). The dimensions of the highlighted polymer are within 2% of the average values for $R$ and $R_e$. The excluded volume condition is applied.

was no quantitative expression available for the dimensions of 2d polymers over the whole concentration range from dilute solution conditions to a concentrated melt.
Polymers in two dimensions are known to self-assemble into compact disks [Carmesin and Kremer 1990]. A polymer melt at a segment density of \( \rho = 0.99 \) is shown in Figure 1.10. Once again, this polymer is representative, in that its dimensions are within 2% of the average values. The compact nature of this chain is apparent. Close inspection of Figure 1.10 reveals that the other chains present also have a compact structure. The "tail" of the highlighted polymer was observed to be a common feature of these 2d structures. Motion of the polymers through the lattice can occur by a compact blob ser ding out an arm (or tail). The arm can then bunch up and form a well-defined blob. The polymer can then move by transferring beads from one blob to the other by generalized reptation motions.

The self-aggregation of the 2d polymers into these compact blobs is driven only by entropy. The system is athermal, so all configurations of the lattice have the same enthalpy. The combination of entropy and the excluded volume condition causes the polymer to self-assemble into these compact shapes. Within the highlighted region of Figure 1.10, the polymer is free to rearrange itself without interference from the other polymers. More extended configurations such as that shown in Figure 1.3 (in dilute solution conditions) are extremely rare in a concentrated melt – simply because the number of configurations available to the polymer, while occupying the same outline, is much smaller.
Finally we can note that the highlighted polymer configuration in Figure 1.10 has much in common with the compact configuration of Figure 1.7 that could not be moved by the generalized Verdier-Stockmayer and standard reptation methods. In particular, note that the right hand end of the polymer is completely surrounded by beads on the same chain, so that the standard reptation move is not possible. There are also very few L inversions (and only one crankshaft motion) possible – even if the other (thin line) polymer chains were removed from the lattice. Thus, it is easy to see why the generalized Verdier-Stockmayer and standard reptation methods slow down dramatically as the polymer segment density approaches unity.

1.8 Monte Carlo methods and the Metropolis sampling technique

In athermal polymer systems, all that is required for simulation is a method to move the polymers through the lattice – such as the general reptation algorithm. This is because all configurations of the system have the same energy. All that is required is that the algorithm obey the condition for detailed balance, be unbiased and ergodic (or at least largely so).

However, when configurations of different energy are possible the question arises as to how those energy differences should affect the motion of the particles. The simplest answer is that it need not. One can calculate
average thermodynamic properties from a randomly generated collection of system configurations. Thus the polymer melt configurations, such as that shown in Figure 1.10, which were generated without regard to energy, could be used to calculate properties of a system where each of the polymers is a diblock copolymer. For example, consider if the first \( N_A = 25 \) beads of the polymer are of type A, and the last \( N_B = 25 \) beads of the polymer are of type B. If \( \varepsilon_{AA} = \varepsilon_{BB} = 0 \) and \( \varepsilon_{AB} = \varepsilon \) then we have a simple model for a 2d diblock copolymer melt such as has been investigated by Sariban and Binder [1987-1989].

Suppose that we are interested in calculating the average number of polymers whose B-blocks are touching each other as a function of temperature (the aggregation number). Statistical mechanics tells us that the average within the canonical ensemble can be calculated from our random collections of configurations as

\[
\langle \alpha \rangle = \frac{\int dr^{2N} \alpha \exp(-U/k_BT)}{\int dr^{2N} \exp(-U/k_BT)},
\]

where \( \langle \alpha \rangle \) is the desired thermodynamically correct average aggregation number and \( \alpha \) is the value obtained for a particular configuration. \( U \) is the configurational energy of the system \( k_B T \) is the scaled temperature, and the integral over \( dr^{2N} \) indicates an average over all possible configurations of our
2d system with \( N \) beads. The only problem with this is that it is incredibly inefficient at low temperatures and concentrations. Most of the randomly generated configurations have the A and B blocks distributed randomly whereas in a real system at low temperature the A and B blocks segregate due to the lowered enthalpy of such configurations. This is reflected by the weighting factor \( \exp(-U/k_BT) \) being (exponentially) low for high-energy configurations.

At low temperatures (where the system will be phase separated) the ratio of the weighting factors for high and low energy configurations is so large - that for all practical purposes, the high-energy configurations never occur. See Kittel and Kroemer [1980] (problem 4 of chapter 2) and Adams [1979] (chapter 9) for a discussion of the meaning of never in this context. The rate at which highly ordered, low energy states are generated by this random procedure is similar to the problem of how long it would take 10 billion monkeys to come up with Shakespeare’s Hamlet by tapping random keys on a keyboard at a rate of ten keystrokes per second. The answer is that it will never happen. The actual probability of generating Hamlet throughout the age of the known universe (10^{18} s) is [Kittel and Kroemer 1980]

\[
\left( \frac{1}{44} \right)^{100,000} = 10^{-164.345}.
\]
Calculating thermodynamic properties from randomly generated configurations is as futile as trying to get a finite number of monkeys to type *Hamlet*.

In 1953, Metropolis and coworkers came up with a simple elegant way of getting around the problem. All you do is choose configurations with weight $\exp(-/k_BT)$ and then average them all evenly. Here is how it works for our polymer system, assuming we start from an initial configuration $C(n)$.

(a) Generate a new configuration $C(t)$ from the first using the general reptation algorithm.

(b) Calculate the change in energy for the trial configuration $C(t)$

$$\Delta U = U(t) - U(n).$$

(c) If $\Delta U \leq 0$, accept the move, so that the trial configuration $C(t)$ becomes the $(n+1)^{\text{th}}$ configuration $C(n+1)$ i.e. $C(n+1) = C(t)$.

(d) If $\Delta U \geq 0$, generate a random number $r(n+1)$ between zero and one.

(e) If $r(n+1) \leq \exp(-\Delta U / k_BT)$, accept the move. i.e.: $C(n+1) = C(t)$.

(f) If $r(n+1) > \exp(-\Delta U / k_BT)$, reject the move. i.e.: $C(n+1) = C(n)$. In this case the new configuration is the same as the old one! - This *must* be done to calculate the average correctly.

This procedure can be shown to choose configurations with the desired weighting as follows. Consider a very large ensemble of systems, $C(a)$, $C(b)$,...
Let \( k(a) \) be the number of systems in configuration \( C(a) \). What we want to show is that \( k(a) \) is proportional to \( \exp(-U/k_B T) \).

Do one step for each system in the ensemble and let:

\[ P(a \rightarrow b) = \text{probability that the trial configuration for } C(a) \text{ is } C(b). \]

\[ P(b \rightarrow a) = \text{probability that the trial configuration for } C(b) \text{ is } C(a). \]

The general reptation algorithm is microscopically reversible so \( P(a \rightarrow b) = P(b \rightarrow a) \) whenever \( C(b) \) can be reached from \( C(a) \) by one general reptation move. If this is not the case, the probabilities are zero.

If we assume that \( U(a) > U(b) \) then the number of systems actually moving from \( C(a) \rightarrow C(b) \) is

\[ k(a)P(a \rightarrow b) \]

(as all trials are allowed, step(c)).

The number of systems actually moving from \( C(b) \rightarrow C(b) \) is

\[ k(b)P(b \rightarrow a)\exp(-\Delta U/k_B T) \text{ ; where } \Delta U = U(a) - U(b), \]

as the fraction of moves accepted in step(e) is \( \exp(-\Delta U/k_B T) \).

At equilibrium, we assume that the rates of
\[ C(a) \to C(b) \]
\[ C(b) \to C(a) \]

are equal (microscopic reversibility), hence

\[ k(a)P(a \to b) = k(b)^*P(b \to a) \exp(\Delta U / k_B T) \]

so that

\[ k(a)/k(b) = \exp(-\Delta U / k_B T) = \exp(-[U(a) - U(b)]/k_B T) \]

as \( P(a \to b) = P(b \to a) \), and

\[ k(a)/k(b) = \exp(-U(a)/k_B T) / \exp(-U(b)/k_B T) \]

i.e. \( k(a) \) is proportional to \( \exp(-U(a)/k_B T) \) so that the configurations are weighted by \( \exp(-U/k_B T) \) at equilibrium as required.

In the above, we have implicitly assumed that all equilibrium configurations can be reached from the starting configuration. (This is the ergodic assumption, which will be discussed in chapter 2). Another perhaps more important question is whether we are at equilibrium. If equilibrium is not yet reached the above analysis is not valid and the properties calculated are not thermodynamically representative.

A significant point about the above procedure is that the acceptance rate
for moves with a positive $\Delta U$ is proportional to $\exp(-\Delta U/k_BT)$. This means that processes where the energy of the system increases are governed by an Arrhenius type behavior. For example, consider extracting a surfactant monomer from a micelle. This process has a positive $\Delta U$, and has a rate (in units of successful attempts per Monte Carlo step) that is dependent on temperature in the familiar Arrhenius manner.

Using this procedure we can generate a reasonable number of representative samples, if the system temperature is not too low. Therefore, according to our analogy, this might be like teaching our monkeys to spell English words and construct grammatically correct sentences. They still probably won't come up with a masterpiece like *Hamlet*, but they could come up with a good limerick, or perhaps a sit-com.

1.9 Self-association of star copolymers

Star polymers have attracted much attention in recent years owing to their unique properties. Much of the work has focused on homopolymer stars but star copolymers have an even richer range of existing and potential applications in such diverse fields as drug delivery and other biological applications, separation processes, viscosity modification and materials design.
The properties of star polymers in which all the arms are homopolymers of the same type are reasonably well understood [Grest 1994][Grest 1996]. A blob model for the arms of the star polymer, based on de Gennes scaling approach [de Gennes 1979] for linear polymers, has been developed [Daoud and Cotton 1982][Birshtein and Zhulina 1984][Birshtein et al.]. The star is considered to consist of three regions: an inner, melt-like, extended core region; an intermediate region resembling a concentrated solution; and an outer, semi-dilute region. The arms of the star are considered to be constrained to lie within a cone emanating from the core of the star. Results from molecular simulations have been shown to be consistent with scaling models for properties such as the mean-square radius of gyration, monomer density profiles, center-to-end distribution functions, and the relaxation of shape fluctuations [Grest 1994]. These results were for good, θ, and poor solvent conditions and were found to compare favorably with experiments on many-arm stars in dilute solution conducted by Burchard [1983], Roovers and coworkers [1972, 1974, 1983, 1989, 1993], Huber et al. [1984] Toporowski and Roovers [1986], Khasat et al. [1988], Bauer et al. [1989] and Zhou et al. [1992].

Amphiphilic star copolymers have been synthesized by a variety of techniques by Tsitsilianis [1993], Winnik [1992], Saunders et al. [1992], Kanaoka et al. [1992], Ishizu and Uchida [1994][1995], Floudas et al. [1996], Zhou and Smid [1993] and Chen and Smid [1996]. These fall into two main
types, heteroarm (or miktoarm) star copolymers of the form \( A_x B_y \), which have \( x \) arms of type A blocks and \( y \) arms of type B blocks and homoarm star block copolymers of the type \((AB)_n\) in which there are \( n \) arms each of which is an AB block copolymer.

Condensed phases of polystyrene-polyisoprene \((AB)_n\)-type stars with \( n=4 \) to 41 arms have been investigated recently experimentally by Ishizu and Uchida [1994][1995] and by Floudas et al. [1996] and via computer simulation [Floudas et al. 1996]. Ordered lamellar, cylindrical and bicontinuous cubic structures were found to form in the condensed phase.

Aqueous solution behavior of three and four armed stars with poly(ethylene oxide) (PEO) arms capped with hydrophobic end-groups have shown [Zhou and Smid 1993] that the arm ends tend to associate, and that above a critical star concentration the system phase separates into a dilute phase and a condensed gel phase. In the dilute phase, intramolecular association was dominant whereas in the gel phase intermolecular association was more prevalent. Three-armed stars with hydrophobic cores and PEO arms were found [Chen and Smid 1996] to form micelles in aqueous solution above a critical micelle concentration (cmc).

Solubilization of polycyclic aromatic compounds in solutions containing \((AB)_n\) poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) stars with \( n=2 \) and \( n=4 \) was investigated both experimentally and using self-consistent mean-
field lattice theory by Hurter and coworkers [1992, 1993ab]. It was found that the $n=2$ stars formed larger micellar aggregates than the $n=4$ stars of the same molecular weight. This was attributed to steric hindrance within the hydrophobic core of the low molecular weight $n=4$ micelles.

An area of amphiphilic star copolymers that has gone largely unexplored is the behavior of isolated (dilute solution) behavior of many armed stars of the form $(AB)_n$, (see Figure 1.11). Two variants of amphiphilic star block copolymers of this form are possible, in which different ends of the AB block copolymer arms are attached to the center of the star.

Hydrophobic-core $(AB)_n$ stars are a prototype for block copolymer micelles formed from $n$ (AB) copolymers. They are subject to the constraint that the micelle has a fixed aggregation number and all the arms are attached at a central point. A significant practical advantage of studying these single molecule systems is that periodic boundary conditions need not be applied as the system is of finite spatial extent. In addition, the size of the aggregate is specified in advance and one does not need to wait for the molecule to self-assemble. Thus, problems associated with aggregate growth to sizes larger than the simulation box can be avoided entirely.

Study of these single molecule polymer systems also has a precedent in the literature, where single homopolymers have been studied as a function of
Figure 1.11 A typical conformation of an (AB)_n star copolymer. The interaction energy between the beads of different color and the solvent are weak. The axes indicate the center of the star.

the self interaction strength in dilute solution [Kolinski et al. 1986, Poole et al. 1989, Meirovitch et al. 1990ab and Baumgärtner 1992]. A polymers in a good
solvent are swollen and the polymer adopts the configuration of a self-avoiding random walk (e.g. see Figure 1.3). As the solvent quality is reduced, the polymer tends to self-aggregate, as the solvent quality is reduced further the polymer (if it is flexible enough) will collapse into a compact globule that has properties similar to a liquid drop.

This self-aggregation, in (extremely) dilute solution, is caused by the reduced enthalpy of the collapsed state. Generally, entropy favors more expanded configurations of isolated polymers, and this effect is enhanced by the excluded volume condition. This trade-off between enthalpic and entropic terms is a common feature of phase separations in general and their counterpart - conformational changes in isolated molecules, and as we will see later the self-assembly of surfactants into microphase separated micelles.

The other variant of the molecule in Figure 1.11 is a hydrophilic-core (AB)_n star copolymer whose outer hydrophobic blocks tend to aggregate in solution. Behavior of this class of molecules has gone largely unexplored. We therefore have the opportunity to investigate the behavior of a new type of molecule.
1.10 Complex fluids and self-assembly

As everyone knows, oil and water do not mix. Figure 1.12 shows a simple fluid system of oil and water. The oil and water have phase-separated and there is a well-defined oil droplet in the center of the simulation box. If we were to double the linear dimensions of the box while maintaining the same ratio of oil to water the picture would remain similar with a single oil droplet surrounded by water. This doubling could be continued until a box of macroscopic size is shown, with a circular oil drop in the center of the box. There is no gravity in our simple picture, so the oil has no reason to float “on top” of the water.

Thermodynamically, the system shown in Figure 1.12 is a simple two-phase system. Each of the phases is homogeneous on length scales larger than the size of the molecules. If the size of the system is increased the ratio of interfacial surface area to system volume can be made arbitrary small. Thus, the system of Figure 1.12 is a mixture of two simple molecular fluids.

If the oil molecules are modified by covalently bonding a section hydrophilic (water loving) beads to one end, the behavior of the system is drastically changed(Figure 1.13). The grafted molecules are now surface-active agents or surfactants. The surfactants have water loving heads (small solid circles) and an oily tail (large solid circles).
Figure 1.12 A simple phase separated mixture of oil (dark beads) and water (open circles). The oil is a short homopolymer chain. Note that the oil droplet contains a small number of water beads.

The oily tail of the surfactant still wants to separate from the water, but this process is hindered by the water-loving head. Consider the aggregate of 8 surfactants indicated on the left-hand side of Figure 1.13 with an arrow. This
Figure 1.13 A single phase, complex fluid. The surfactant has an oil tail (large solid beads) and a water loving head (small solid beads). The surfactant aggregates into micelles surrounded by water (open circles). The arrow indicates a circular micelle with aggregation number 8.

surfactant aggregate, or micelle, has an oily center where the tails are touching. The water loving head beads surround the oily center and prevent any other surfactants from adsorbing to its surface. The water-loving head beads are excluded from the core of the micelles due to the high energy of
including the water-like beads in an oily region. The net result is the minimum dimension of the aggregates shown in Figure 1.13 is determined by the length of the oily tail. Specifically the radius of the circular micelle in Figure 1.13 is determined by the average end to end distance of the tails $<R_T>$.

If the size of the system shown in Figure 1.13 is doubled at constant surfactant concentration, the average size of the micellar aggregates does not increase. Thermodynamically, the system shown in Figure 1.13 is a simple one-phase system. The phase is homogeneous on length scales larger than the distance between the micelles. If the size of the system is increased the ratio of interfacial surface area (of the small oily regions) to system volume remains constant.

The scale of the microstructure of the fluid is determined by the size of the tails $<R_T>$, and the fluid is microphase separated on this length scale. The use of micro serves reminds us that the system can be thought of being phase separated on a microscopic scale, but it must be remembered that from a thermodynamic point of view, the system has only one macroscopic phase, which is homogeneous and isotropic (at least in the case of the example shown – it is possible for surfactant systems to bulk (or macro) phase separate into micellar systems with different microstructures, and to form ordered phases
Figure 1.14 A single phase, complex fluid. With the same components as Figure 1.13, but at higher surfactant concentration. The surfactant has an oil tail (large solid beads) and a water loving head (small solid beads). The solvent is water (open circles).

that are not isotropic [Larson 1989-1996]. Self-assembly into well-defined microscopic structures is the cause for the complexity of the fluid and its behavior.
Complex fluids can change their structure depending on solution conditions. Changes in temperature and concentration can drastically alter the macroscopic behavior of the system. It is well known that the micelles can become more elongated as more surfactant is added, until they interconnect with each other over macroscopic length scales. Figure 1.14 shows an example of this growth. The structure can be described as an irregular bicontinuous gel. Note that the characteristic dimension of this gel remains the length of the oily tails $<R>$, which determines the width of the dark stripes in the figure.

In this thesis, we will investigate dilute systems, like the one shown in Figure 1.13. Concentrated systems, such as the one shown in Figure 1.14, have been extensively studied by Larson [1988-1996] in three-dimensions and an extraordinarily wide variety of ordered phases were found using simulation techniques quite similar to those to be used here. Dilute systems are of particular practical interest for separations and for making hydrophobic (water hating) compounds soluble is aqueous solution. Dilute systems have been studied by numerous workers as discussed in [Nelson et al. 1997b] and in chapter 4.

Simple thermodynamic theories have been developed for micellar systems in three-dimensions [e.g. Israelachvili 1992]. These theories form the basis for more advanced theoretical treatments aimed at predicting more complicated behavior [e.g. Blankschtein et al. 1986 and Puvvada and
Blankschtein 1990]. The basic premise of these theories is that the micelles have simple shapes such as spheres or spherically capped cylinders. The theories are based on the well-established thermodynamic principle that the chemical potential of the surfactant must be the same throughout the complex fluid. Thus, the chemical potential $\mu$ of all surfactant molecules is the same independent of their state of aggregation. Surfactant molecules that are not aggregated (monomers) must have the same chemical potential as dimers, trimers and $n$-mers of arbitrary size.

$$\mu = \mu_1^0 + k_B T \log X_1 = \mu_n^0 + \frac{k_B T}{n} \log \left( \frac{X_n}{n} \right) = \text{constant, } n=1,2,3,...$$

$\mu_n^0$ is the standard part of the chemical potential, due to the mean interaction energy per molecule in an aggregate of size $n$. This is the part of the chemical potential that depends on the shape of the aggregate. The second term $(k_B T / n) \log(X_n / n)$ represents the entropy of mixing for aggregates of size $n$, assuming ideal solution behavior. $X_n$ is the concentration (or more accurately the activity) of surfactant molecules in aggregates of size $n$.

If one assumes that the micelles are cylindrical one obtains
\[ \mu_n^0 = \mu_\infty^0 + \frac{\alpha k_B T}{n} \]

where \( \mu_\infty^0 \) is the interaction energy for a molecule in the barrel part of the cylinder and the second term accounts for molecules in the spherical end caps. This form, together with the constraint that the \( X_n \)'s must add up to the bulk surfactant concentration, gives an exponential size distribution for cylindrical micelles.

For spherical micelles, it is assumed [Israelachvili 1992] that variations in energy about the most preferred size are parabolic

\[ \mu_n^0 - \mu_m^0 = \Lambda (\Delta n)^2, \]

where \( m \) is the size of the aggregate that has the lowest value. This assumption produces gives an aggregate size distribution that is very nearly Gaussian.

The consequences of these assumptions have been confirmed experimentally for a variety of micellar systems but it has not been possible to verify the exact functional form of the distributions. Experimental techniques such as dynamic light scattering do not measure form of the size distribution, but rather generate estimates for the first and second moments of the size distribution.
Previous simulations of micellar systems have produced size distributions with varying degrees of success [Nelson et al. 1997b] and none have made comparison with the forms of the size distributions expected from the simple phenomenological models discussed above. Many of the previous size distributions have suffered from signal to noise ratios of less than one, as the length of the simulation was not sufficient to representatively sample the size distribution. Others appear to suffer from problems associated with insufficient equilibration time. For example, simple arguments can be made that any symmetric surfactant should form cylindrical micelles as the surfactant concentration is increased. The immediately observable consequence in the simulation is that the micellar size distribution becomes significantly more polydisperse as the concentration is increased.

Another important question, which may be solved by direct computer simulation, is whether shape fluctuations and deviations from the idealized behavior have a significant effect on the expected shape of the size distributions. The spherical micelles are not expected to be perfect spheres, and the cylinders are not expected to be rigid. For example, branched thread-like micelles have recently been observed directly using cryo-TEM techniques [Danino et al. 1995].
1.11 Oil in water microemulsions

If oil is added to an aqueous surfactant solution, the behavior of the complex fluid becomes - well, even more complex. The phase diagram is now ternary, and the additional degree of freedom provides the system with more scope to exhibit coexisting phases.

Recently, molecular dynamics simulations have been conducted to investigate the dynamics of oil solubilization by surfactant solutions [Karaborni et al. 1993, 1994 and Esselink et al. 1994]. In these simulations, three mechanisms were identified for dissolution of an oil droplet in a surfactant solution. These simulations were far from equilibrium and the effect of the solubilized oil on equilibrium micellar structure could not be investigated.

Extensive equilibrium studies of oil-water-surfactant systems have been conducted by Larson in recent years [1988-1996] using a similar lattice model to the one used here. The rich phase behavior of (mainly) ordered condensed phases of systems with high (>20%) surfactant concentrations was successfully demonstrated using this model. However, the structure and properties of disordered systems with low oil and surfactant concentrations has gone largely unexplored. Larson [1996] found that the ternary phase diagrams of oil-water-surfactant mixtures on lattices of size (ca. 40x40x40) did not match the good
correspondence he had found for binary phase diagrams. He identified two potential reasons: the finite size of the lattice; or the single site representation of the oil molecules.

It is generally believed that good emulsifying surfactants should prefer adsorb at interfaces of low curvature [Gelbart and Ben-Shaul 1996]. Key to this statement is that surfactants have a preferred curvature. However, according to these authors it is not feasible at present to predict a priori which curvature will be preferred at the cmc (critical micellar concentration) for any given amphiphile in water. In simulations, we can do away with many of the complications surrounding real surfactant systems, and investigate a model surfactant that is structurally symmetric, and whose interactions with oil and water are also symmetric. According to Gelbart and Ben-Shaul [1996] this model surfactant should be an ideal emulsifying agent, as it will prefer to adsorb at flat planar interfaces. The symmetry of its structure and interactions mean that it has a preferred curvature of zero.

We can also investigate the proposal [Aveyard et al. 1990] that the addition of relatively small amounts of oil to a dilute surfactant system can make the micelles grow into more elongated structures. This was given as an explanation of macroscopic phase behavior of dilute micellar systems containing small amounts of oil. No direct microscopic evidence of the proposed
structural changes was provided. However, the arguments were based on a discussion of the packing factor.

The model is based on old ideas revived by Mitchell and Ninham [1981], in which effective cross-sectional areas $a_h$ and $a_t$ are assigned to the head and tail of the surfactant. A packing factor may then be defined as

$$P = \frac{a_t}{a_h}.$$

The cross-sectional areas, and the packing factor $P$, can be affected by the local environment of the head and tail groups. Hence, $P$ is not determined solely by molecular structure of the surfactant. This is exactly the type problem that simulation techniques can address in a qualitative manner.

1.12 Periodic boundary conditions and finite size effects

A key factor in the simulation of any material is that only a small number of molecules are in the simulation box, whereas we are generally interested in the behavior of systems of macroscopic size (say an Avogadro's number of molecules $\sim 10^{23}$). It is a remarkable feature of most simulations that only a small number of molecules (hundreds to thousands) are needed to
represent behavior of systems so much larger. Particularly important in this regard are periodic boundary conditions. Periodic boundary conditions are a well-established method of removing surface effects in computer simulations [Allen and Tildesley 1987]. This is done by connecting the edges of the simulation space in a manner similar to some video games: if something moves off the right hand side it arrives on the left hand side, as if the two sides were connected seamlessly together. In two-dimensional simulations, the left- and right-hand edges are connected together in this way, as are the top and bottom edges of the simulation space (see Figures 1.12 -1.14).

According to Allen and Tildesley [1987] (p. 26), the common experience in simulation work is that periodic boundary conditions have little effect on the equilibrium properties and structures of fluids away from phase transitions and where the interactions are short-ranged. However, in polymer and surfactant systems, an additional complication arises even in fluids that are far from any phase boundaries and where the interactions are short ranged. This complication is that the molecular weight of a polymer or surfactant-aggregate (defined as the combined molecular weight of all entities in the aggregate) is limited to the size of a single periodic image. This finite-size effect can easily be shown to affect the phase behavior polymers and surfactant aggregates.

The effect of low thermodynamic molecular weight on simulations can
be readily investigated by changing the system size. However, a systematic study of different simulation box sizes is often too time consuming. In the simulations of chapters 4 and 5 we will observe finite size effects and show that they disappear in larger simulations, or when only low molecular weight aggregates form.

The issue of finite size effects has recently been shown to be important for planar interfaces between two coexisting macroscopic phases. For example, simulations of an oil-water interface (even in the absence of a surfactant) can depend on the size of the simulation box, both in the plane of the interface and the direction perpendicular to it [Binder et al. 1997]. This effect is caused by wrinkles in the interface. For small systems using periodic boundaries, these wrinkles are limited to normal modes of the box size. The cylindrical micelles investigated in chapters 4 and 5 are line-shaped interfaces whose flexibility is equivalent to the wrinkles in a planar interface. However, at the concentrations used in this thesis, the micelles do not connect to themselves across a periodic boundary and hence do not suffer from the same long-range sensitivity to system size as planar interfaces.

1.13 Comparing lattice models to specific systems

Physical systems have properties that operate on different time- and
length-scales. The advance of computer technology has meant that the scope of simulations has increased dramatically over the years. This has led to the development of two schools of simulation ideology. In the material specific school, the increased power of computer technology is used to investigate real-world problems with ever-increasing accuracy. In these studies, the length and time scales available for investigation, are directly tied to the cleverness of the algorithms used and the speed of the computers employed. The data generated are based on the most realist potential functions available, and are intended to provide quantitative predictions for materials design and characterization.

The other school of computer simulation is concerned primarily with the chemical physics of the system under investigation. The goal of these simulations is primarily to gain qualitative understanding of the system behavior. Generally, chemical-specific features of the problem are lumped into a small number of adjustable parameters. This allows investigation, of what the characteristic features of the system are, and whether theoretical treatments succeed in capturing the behavior of even simplified systems. The use of simplified models also allows investigation of more complex behavior on length and time scales not possible in the material specific school.

Just because a model operates at the chemical physics level, does not mean that it cannot be compared to real systems. A good example of this is the simulation of 2d athermal polymer systems. These systems should be directly
comparable to any flexible 2d-polymer system in a good solvent. The length scaling can be quantitatively compared through the use of a Kuhn segment length analysis. This is because the scaling of the dimensions of flexible polymers has long been known to be universal and independent of chemical structure – so long as the polymer is flexible and the polymer is in the liquid or random amorphous state.

Quantitative comparisons are not always possible as the chemical details of many systems are important to their specific behavior. Often long-range interactions are neglected in simplified models. This is usually because incorporation of long range interactions is computationally intensive. However, long-range interactions can significantly affect the phase behavior of systems. For example, long range interactions between micellar aggregates are responsible for macroscopic phase separation in micellar systems.

A feature of the lattice models discussed here, is that all the beads have the same volume. Hence, for quantitative comparison to be appropriate, one must find a physical system in which the molecular volumes of the “water” and “oil” are the same and they are each good (athermal) solvents for the head and tail segments of the surfactant respectively. As far as we are aware such a system has not been synthesized.

Notwithstanding these limitations, it is remarkable that the qualitative aspects of real world behavior of many complicated systems can be reproduced,
and thus be explained, by simple models.
Chapter 2: Simulation technique and 2d athermal polymers

2.1 Introduction

The properties of lattice polymer systems have been investigated by Monte Carlo techniques for over forty years [Kremer and Binder 1988]. Nevertheless, there remain certain types of fundamental scaling behaviors, such as the variation of the volume of a chain with $N$, which are still not entirely understood [des Cloizeux and Jannink 1990]. This variation of polymer dimensions with length $N$ and with concentration will be addressed in this chapter using a simple lattice model. Although lattice Monte Carlo techniques relate to a course-grained model of polymers, they are computationally simple and efficient. They can also provide "universal" information that is independent of the lattice used and depends only on the dimensionality of the system. More realistic off-lattice simulations can be used for simple short chain systems or short time scales, but they are not currently
suitable for systems that are more complicated and longer times. For example, spinodal decomposition of a polymer blend has been performed using lattice Monte Carlo methods, despite the fact that the corresponding physical time scale is of the order of $10^2$ seconds [Sariban and Binder 1989][Binder 1992]. Using molecular dynamics techniques at least $10^{13}$ integration steps would be required, which is well beyond the capability of current computer technology.

The recently proposed general reptation algorithm [Baumgartner 1992][Murat and Witten 1990][Reiter 1990] has been shown [Reiter et al. 1990] to be more efficient than traditional lattice methods for dense systems. The computational efficiency is essentially independent of polymer density; hence, this method does not slow rapidly as the density approaches unity, as has been observed for other methods [Kremer and Binder 1988]. Figure 2.1(a) shows an example of such a general reptation motion [Reiter et al. 1990].

In what follows, an alternative treatment of the general reptation algorithm is presented, which was developed independently of the previous implementations. This method is particularly suited to dense systems on close-packed lattices. It is expected to have similar computational performance characteristics to the previous implementations. The present treatment introduces the notion of a “transition state” into the algorithm, which allows
Figure 2.1 Examples of general reptation moves according to the present algorithm. (a) An end-kink general reptation as proposed previously – [Reiter et al. 1990]. (b) Newly proposed single bead pseudo-reptation using a transition state bond (ii) to perform an end bead rotation (iii). (c) Rotation of an interior bead by a pseudo-reptation along a transition state bond. (d) Transition from state (i) to state (iii) can be achieved by the two consecutive general reptations shown.
all motion attempts in the simulation to be treated in a consistent manner. The benefit of this is largely conceptual, as the dynamics of the algorithm are comparable to other versions of the general reptation approach.

In this chapter, this new implementation of the algorithm will be rigorously tested and characterized. We will confirm that the algorithm is well behaved and can accurately reproduce known results for the average dimensions of 2d polymers. We will investigate the scaling behavior of finite chains of short to intermediate chain length in both dilute and concentrated ("melt") regimes, as well as regimes of intermediate concentration. We perform the simulation on a close-packed lattice, which alleviates problems of odd-even chain length dependence of polymer properties [Watts 1974] and the parity problem associated with simulations on loose-packed lattices [Reiter et al. 1990]. In this chapter, results for simulations of two dimensional systems are reported as this dimensionality is considered to be the most crucial test case for polymer simulation algorithms [Carmesin and Kremer 1988][Carmesin and Kremer 1990]. This is due to the effect of excluded volume being largest in 2d. Extension of the algorithm to three-dimensional systems is straightforward.
2.2 Simulation technique

2.2.1 General reptation algorithm

Consider a linear chain on a triangular lattice as shown in Figure 2.1(a). A configuration change can be made by introducing a (60°) kink in the center of the chain by sliding the three beads in the directions indicated. The general reptation algorithm on close-packed lattices includes the move shown in Figure 2.1(a), its inverse move and generalizations of both. In general, one can allow for the formation of a new kink, the removal of an existing kink or the movement of an end by the general slithering motions. These moves therefore include a wide variety of configuration changes in which two or more beads slither to occupy a vacancy adjacent to the chain. The longest move is the standard reptation move and the shortest moves are general reptations of two beads. Rotations of one or more beads were added separately to this form of the algorithm [Reiter et al. 1990].

2.2.2 Transition state formulation of general reptation

In our formulation of the general reptation algorithm, the notion of a "transition state" is introduced, in which bond(s) are formed to the vacancy
before a bead is moved to fill the vacancy. The transition state consists of the vacancy, the $N$ beads of a chain, and $N$ bonds connecting the $N$ beads and the vacancy together into a linear polymer configuration. (Note that before the transition state is formed there are $(N-1)$ bonds connecting the beads together.) If an end bead attempts to move to a vacancy, the additional bond is between the vacancy and the end bead (Figure 2.1(b)(ii)). If an interior bead attempts to move to a vacancy, one of the original bonds on the chain is removed and is replaced by two bonds to the vacancy (Figure 2.1(c)(ii)), so that the transition state is, once again, a linear polymer with $(N+1)$ "beads".

The use of a transition state allows single end bead rotations (Figure 2.1(b)) and internal bead rotations (Figure 2.1(c)) to be introduced into the algorithm in a self-consistent way, as one bead pseudo-reptations. An end bead rotation occurs in Figure 2.1(b) by forming a transition state bond (ii) between a vacancy and an end bead, the end bead then slithers along the transition state bond to complete the move (iii). In this manner, all possible motions in which one or more contiguous polymer beads reptate or "slither" one lattice spacing along a transition state bond towards a vacancy are provided for. The selection as to which type of move occurs is automatic within the algorithm and is determined by the state of the system (see below).
Possible configuration changes in which a single bead moves more than one lattice spacing are not provided for as single moves, e.g. Figure 2.1(d)(i) to Figure 2.1(d)(iii) directly. This type of move, (and its generalizations in 3d) could be added as a separate type of move in the algorithm, but this is not necessary as the move can be achieved using an intermediate configuration such as that shown in Figure 2.1(d)(ii).

All the moves discussed above are consistent with the excluded volume condition, and require only a single vacancy. Consequently, it is more efficient at low vacancy concentrations to select a vacancy first and then find a bead adjacent to it\textsuperscript{12}. [de Vos and Bellemans 1975] The form of the algorithm in which a vacancy is selected first will be called the “vacancy algorithm”, and the form of the algorithm in which a bead is selected first will be called the “bead algorithm”.

\textbf{2.2.3 Vacancy algorithm}

(1) Select a vacancy \( v \) at random.

(2) Randomly select one of the (six) directions away from the vacancy.

(3) If the site in the chosen direction is occupied by a bead \( i \) of a chain \( c \), continue, otherwise reject the move.

(4) Attempt to form a transition state by making bonds from the vacancy to
chain \( c \).

(a) If bead \( i \) is an end bead, form a single transition state bond between vacancy \( v \) and bead \( i \) with probability \( 1/2 \), otherwise reject the move.

(b) If bead \( i \) is not an end, select one of its two bonds at random. If a kink can be formed by breaking that bond and forming two transition state bonds to the vacancy (one from each of the beads that were connected by the broken bond), then continue, otherwise reject the move.

(5) Select a second bead \( j \) at random from the \( N \) beads on chain \( c \). (Bead \( i \) may be selected again.)

(6) Determine whether bead \( j \) can be removed from the chain.

(a) If bead \( j \) is a (60°) kink in the transition state then continue

(b) If bead \( j \) is an end then continue with probability \( 1/2 \), otherwise reject the move.

(c) If bead \( j \) is not an end or a kink in the transition state, then reject the move.

(7) Reptate the portion of the chain, between the vacancy and bead \( j \), by one bead along the contour of the chain defined by the transition state, so that a bead moves into the position of the vacancy.
When a move is rejected, the transition state bond(s) to the vacancy are removed and the chain is restored to its original configuration; the “time” counter is incremented irrespective of whether the move was successful, to provide unbiased sampling.

2.2.4 Examples of simulated motion

To illustrate how the simulation steps are implemented in practice, consider the successful move shown in Figure 2.1(b), it will be assumed that all the “at random” choices result in the correct decision to achieve the move shown. The vacancy in Figure 2.1(b)(i) is selected in step (1) and the direction chosen in step (2) is toward the end bead. A single transition state bond is formed in step (4)(b) with probability 1/2 as bead i is an end. The bead selected in step (5) is the same bead (i.e. j=i). Bead j is a kink in the transition state (Figure 2.1(b)(ii)) and slithers along the transition state bond (to the vacancy) to form the state in Figure 2.1(b)(iii). The inverse move follows the same steps but has a transition state that differs from the one shown in Figure 2.1(b)(ii).

For the move shown in Figure 2.1(c), the vacancy is selected in step (1). The direction chosen in step (2) could either be towards bead i=3 or 4 (the third and fourth beads from the left in Figure 2.1(c)(i)) but in either case, the bond
Figure 2.2 The two ways of generating a particular transition state.

chosen in step (4)(b) must be the third bond from the left, to form the two transition state bonds shown in Figure 2.1(c)(ii). (Figure 2.2 illustrates the two ways of forming a single transition state kink.) Bead \( j = 3 \) is selected in step (5) and the kink slithers to the position of the vacancy with probability 1 (Figure 2.1(c)(iii)). Again, the inverse move follows the same steps but the transition state will differ in arrangement. Note that bead \( j \) always slithers in a successful move, but bead \( i \) only slithers to the position of the vacancy if it is between bead \( j \) and the vacancy in the transition state. The move shown in Figure 2.1c does not appear to be included in the general reptation moves of any of the previous algorithms.
2.2.5 Bead algorithm

The vacancy algorithm can be changed to a "bead algorithm", which is more suitable for dilute systems, by changing steps (1) to (3):

(1) Select a bead $i$ on a chain $c$ at random.

(2) Randomly select one of the (six) directions away from bead $i$.

(3) If the site in the chosen direction is a vacancy $v$, then continue, otherwise reject the move.

The remaining steps of the bead algorithm are the same as for the vacancy algorithm.

2.3 Requirements for a well behaved algorithm

2.3.1 Microscopic reversibility & detailed balance

Microscopic reversibility is guaranteed as every possible move has an inverse move. The condition for detailed balance can be shown to hold by considering the matrix of conditional probabilities shown in Table 2.1.
TABLE 2.1. Conditional probabilities for each type of move in the
vacancy algorithm for $N$-bead polymers in a lattice with $N_v$ vacancies.

<table>
<thead>
<tr>
<th></th>
<th>Remove Kink</th>
<th>Move End</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add Kink</td>
<td>$1/(6NvN)$</td>
<td>$1/(12NvN)$</td>
</tr>
<tr>
<td>Move End</td>
<td>$1/(12NvN)$</td>
<td>$1/(24NvN)$</td>
</tr>
</tbody>
</table>

The conditional probabilities for each step are: $1/N_v$ for step (1), where $N_v$ is the number of vacancies in the lattice; $1/6$ for step (2); $1/2$ for step (4)(a); $1$ for step(4)(b); $1/N$ for step (5); $1$ for step (6)(a); $1$ for step (6)(b)(i); and $1/2$ for step (6)(b)(ii). In step 4(b), the probability of forming a kink from a bond which is not at an end of the chain is twice that for an end bond as either of the two beads which are joined by the bond can be selected in step (2).

Hence, there are four different types of move depending on whether the vacancy will become a kink, or an end; and whether bead $j$ is a kink, or an end. The conditional probabilities for each type of move are shown in Table 2.1. The probabilities are conditional upon the assumption that the vacancy and beads $i$ and $j$ are in a configuration where the move is possible. The inverse of every
move is either the same type of move or the corresponding move on the opposite side of the diagonal. As the entries in Table 2.1 form a symmetric matrix, the probabilities of any move and its inverse are the same, and the conditions for detailed balance are satisfied. The situation is simpler for polymers that have no ends (e.g. ring polymers) as only kink-kink moves are possible.

2.3.2 Ergodicity of isolated chains

A previous form of the general reptation algorithm has been proven ergodic for isolated single chains on hypercubic lattices [Reiter 1990], with the exception of a parity problem if only two-site motions are used. These results apply in principle to any lattice type. The only requirement for an isolated chain not to be frozen in the present algorithm is that the chain has an active bond or end. This means that there must be a vacancy adjacent to either an end or two consecutive beads on the "exterior" of the chain. This would appear to be possible for any isolated chain in 2 or 3 dimensions. To formally prove that the method is ergodic, one must show that a sequence of moves can be made which will bring the chain into a fully extended configuration [Reiter 1990], so that any arbitrary configuration can be reached due to microscopic reversibility.
2.3.3 Non-ergodicity of dense systems

To date, there has been no investigation of the ergodicity (or otherwise) of the general reptation algorithms for many chain systems. For the present algorithm, in the limit that the fractional segment density \( \rho \) tends to one, there are frozen configurations for finite size lattices, which means that the present algorithm is not strictly ergodic. However, the number of configurations excluded by the nonergodicity can be expected to be small. For example, consider the partial configuration shown in Figure 2.3(a). In this configuration, there are no single moves in which a bead can move to the central vacancy, as there are no bonds (or ends) adjacent to it. If all the vacancies in the lattice are similarly inactive, then the whole system will be frozen. However, if not all the vacancies are inactive, then configuration changes are possible, the system is not frozen, and each vacancy may be only temporarily inactive. For example, if a vacancy is adjacent to any bond (or end) of the chain (at a position not shown in Figure 2.3(a)), then the unfrozen configuration shown in Figure 2.3(b) can be generated by a single move. The central vacancy in Figure 2.3(b) is now active, as it is adjacent to a bond.

As the probability that a given vacancy is inactive is much less than one
Figure 2.3 (a) A partial configuration which would be frozen at high densities if there are no other vacancies in the lattice. Motion to state (b) is possible if there is another vacancy adjacent to either an end or a bond of the chain (at a position not shown in (a)).

(<0.02)* the probability that all the vacancies in the lattice are simultaneously

*An upper bound estimate for the probability that an isolated vacancy is inactive can be made as follows, with the assumption that the bond orientations of the six beads surrounding the chain are not correlated. All six of the beads must not be ends for the vacancy to be inactive, so each bead must have two bonds that are not adjacent to the vacancy. The probability that the first bond of the first bead is not adjacent to the vacancy is $P_{11}=3/5$ as there are
inactive will decrease rapidly as the number of vacancies is increased. Hence, the number of inaccessible (frozen) configurations can be expected to become negligible as the number of vacancies increases. In the many-chain simulations reported here more than 100 vacancies were normally used so that the a priori probability of all of them being inactive, simultaneously, is vanishingly small.

five directions for the bond which are not directed towards the vacancy, only three of which make the bond not adjacent to the vacancy. The probability that the second bond of the first bead is not adjacent to the vacancy is \( P_{21} = 2/4 \). Similarly, \( P_{12} = P_{13} = P_{14} = P_{15} = 3/4 \), as we know that the preceding bead does not have a bond towards the current bead, and \( P_{22} = P_{23} = P_{24} = P_{25} = 2/3 \). Finally, \( P_{16} = P_{26} = 1 \) as we know that first and fifth beads do not have bonds directed towards the sixth bead. The combined probability is \( (3/5)(1/2)^5 \approx 0.02 \) which is much less than one. Including correlations between the bonds of the six surrounding beads will tend to decrease this value further, as directions for non-adjacent bonds will be blocked by other beads.
2.4 Simulation setup

2.4.1 Initial conditions

In all the simulations reported here, the lattice was a rhombus with periodic boundary conditions employed along the \(a\) and \(b\) lattice directions of the triangular lattice. The polymer chain(s) were initially placed on the lattice fully stretched in the \(x\)-direction.

2.4.2 Data collected

An ensemble average of \(N_E\) independent simulation runs was performed. The mean-square end-to-end distance, \(<R^2(t)\>\), was determined using:

\[
\langle X^2(t) \rangle = \frac{1}{N_E N_p} \sum_{i=1}^{N_E} \sum_{j=1}^{N_p} \left( x_i^\mu(t) - x_j^\mu(t) \right)^2
\]

(2.1)
\[ \langle Y^2(t) \rangle = \frac{1}{N_k N_p} \sum_{i=1}^{N_k} \sum_{j=1}^{N_p} \left( y_{i}^{jk}(t) - y_{i}^{jk}(t) \right)^2 \]  \hspace{1cm} (2.2),

and

\[ \langle R^2(t) \rangle = \langle X^2(t) \rangle + \langle Y^2(t) \rangle \]  \hspace{1cm} (2.3).

where \( N_p \) is the number of polymer chains in the lattice, \( x_i^{jk}(t) \) is the \( x \) coordinate of bead \( i \) of polymer \( j \) at time \( t \) in simulation run \( k \). In the vacancy algorithm described above, the (intensive) unit of time is one Monte Carlo step per vacancy (MCS/V), and in the bead algorithm, the time is measured in Monte Carlo steps per bead (MCS/B). The motion attempts in the present algorithm are non-local and are not intended to correspond to thermally activated motions in any physical polymer system. Hence, the dynamics of the algorithm, in its present form, are accelerated with respect to the dynamics of real systems, and are not intended to reproduce those of any physical polymer system. The \( x \) and \( y \) components of \( \langle R^2(t) \rangle \) were calculated separately to aid in determining when equilibrium was reached and as a check that the simulation did not favor the \( x \)-direction, which is along a primitive lattice vector whereas the \( y \)-direction is not. The mean-square radius of gyration was calculated.
similarly.

After the completion of an equilibration period, the mean-square displacement of the center of mass of the chains $<\Delta R_{CM}^2(t)>$ and the autocorrelation function $C_R(t)$ of the end-to-end distance vector $R(t)$ were determined using the following form:

$$C_R(t-t_0) = \frac{\langle R(t-t_0) \cdot R(t_0) \rangle}{\langle R^2 \rangle} \quad (2.4).$$

The relaxation time $\tau_R$ associated with this autocorrelation function may be thought of as being proportional to the average time that it takes the end-to-end vector to rotate 90°.

### 2.5 Results for dilute systems

#### 2.5.1 Isolated chains – SAW’s

Simulations of isolated $N$-bead chains of up to length $N=100$ were performed using the bead modification of the algorithm to verify that the simulation gives the expected values for static properties and to investigate the dynamics of the algorithm in this case. For the $N \leq 50$ simulations $N_E=10,000$ runs were averaged; for the $N=100$ simulation only $N_E=1000$ runs
Figure 2.4 Raw data from simulation of. (a) Approach to equilibrium of the ensemble average values for SAWs of length N=50. The error bar indicates the 95% confidence interval.

were averaged owing to the long execution time of this simulation. All the simulations reported here have the excluded volume condition imposed so that each lattice site may only contain a single bead. For isolated chains this is equivalent to the well-studied self-avoiding walk (SAW).

2.5.2 Equilibrium

In the simulations, the polymers are initially fully extended in the x-direction and the quantity \( <X^2(t)> - <Y^2(t)> \) decreases rapidly from its initial
value of \( N^2 \) to the equilibrium value of zero (Figure 2.4). The time when this quantity first crosses zero, \( \tau_{XY} \), can be used as an indication of when the ensemble average reaches equilibrium to within the accuracy of the simulation results. Note that the radius of gyration and the mean square end-to-end distance approach equilibrium more rapidly than the quantity \( <X^2(t)> <Y^2(t)> \). Equilibrium properties were calculated after \( t_0 = 12 \ 500 \) MCS/B for this \( N=50 \) simulation, which appears to be a conservative estimate of when equilibrium is reached (Figure 2.4).

2.5.3 Equilibrium results

The relaxation time, \( \tau_R \), was calculated from the slope of the long-time linear portion of a semi-log plot of the end-to-end autocorrelation function, \( C_R(t) \) (which was determined during the steady state period \( (t \geq t_0) \)). As can be clearly seen in Figure 2.5 the long time decay of the autocorrelation function is given by a single exponential.

The center of mass diffusion coefficient, \( D_{CM} \), was determined (Figure 2.6) from the slope of a plot of the mean-square center of mass displacement as
Figure 2.5 Determination of the relaxation time $\tau_R$ from a weighted least-squares fit to the linear portion of the plot of $ln(C_R(t))$ versus time $t$ (MCS/B) for SAWs of length $N=50$. The error bars indicate the 95% confidence interval.

As a function of time using

$$\langle \Delta R_{CM}^2(t) \rangle \sim 4D_{CM}t$$ \hspace{1cm} (2.5),

in the time from $t = 2500$ MCS/B to $t = 25000$ MCS/B.

As the deviations of the simulation data from the fitted straight line are too small to be seen, the differences between the simulation and fitted values
Figure 2.6 Calculation of the center of mass self-diffusion coefficient, $D_{CM}$, from the slope of the mean-square displacement $<\Delta R_{CM}^2(t)>$ as a function of time for SAWs of length $N=50$. The error bars indicate the 95% confidence interval.

are also shown in Figure 2.6. These differences are well within the uncertainties in the region in which the fit was made. The mean-square displacement in this region is much greater than the mean-square radius of gyration $<R_g^2>=34.9$ indicating that the long-time limit of the diffusion coefficient is measured.
2.5.4 Comparison with known static results

The equilibrium values for $<R^2>$ were compared with values determined by exact numeration [Rapaport 1985a] for $N \leq 20$. The simulation values agreed with the literature values within uncertainty limits, e.g., for $N=20$, $<R^2>=61.21\pm0.07(61.191)$, where the exact value is shown in brackets.

Following the approach of [Rapaport 1985b] the functional form of $<R^2>$ can be expressed in a Taylor series expansion as

$$\frac{\langle R^2 \rangle}{(N-1)^{2\nu}} \approx A + B(N-1)^{-1} + O((N-1)^{-2})$$  \hspace{1cm} (2.6),

where $(N-1)$ is the number of bonds in the chain. We use $2\nu=1.5$, which is the accepted value in the literature [Rapaport 1985ab][Madras and Sokal 1988] for 2d self-avoiding random walks (SAWs). The validity of this assumption can be determined from the quality of the linear fit for large $N$. The fitted values $A=0.7152\pm0.0027(0.7145\pm0.0036)$ and $B=0.45\pm0.07(0.43)$ for $N \geq 20$ are in good agreement with the values in brackets obtained from simulations of much longer chains of up to length $(N-1)=2400$ on the triangular lattice [Rapaport 1985b]. The value obtained for the mean-square radius of gyration was $A=0.0998\pm0.0005(0.1002\pm0.0004)$ for $N \geq 30$, also in good agreement with the
value obtained previously [Rapaport 1985b]. In an analogous way, all other properties investigated here (Table 2.2) were fitted to a form similar to that of Eq. (2.6), with exponents selected to fit the expected asymptotic power law behavior of the property.

**TABLE 2.2. Assumed scaling exponents and parameters**

for the $p=0$ simulations c.f. equation (2.6)

<table>
<thead>
<tr>
<th>Scaling Exponent</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;R^2&gt;$</td>
<td>2v=1.5</td>
<td>0.7152±0.0027</td>
</tr>
<tr>
<td>$&lt;R_g^2&gt;$</td>
<td>2v=1.5</td>
<td>0.0998±0.0005</td>
</tr>
<tr>
<td>$\tau_R$</td>
<td>2</td>
<td>1.141±0.013</td>
</tr>
<tr>
<td>$D_{CM}\tau_R/&lt;R_g^2&gt;$</td>
<td>0</td>
<td>0.63±0.03</td>
</tr>
<tr>
<td>$D_{CM}$</td>
<td>-0.5</td>
<td>0.055±0.002</td>
</tr>
</tbody>
</table>

If simulations of long ($N>>100$) chains are performed, the exponent in all the power laws discussed herein could be accurately obtained from the slope of a log-log plot of the property versus $N-1$. For short chain systems, the power law
behavior is modified by the leading order scaling corrections. For example, the estimate for 2ν obtained from a log-log plot of \( <R^2> \) vs \((N-1)\) for \(N\geq20\) is 1.489\pm0.005 at the 95% confidence level. This estimate does not include the assumed value of 1.5, indicating that small (but significant) finite length effects are present for chains of this length.

### 2.5.5 Dynamic properties

Estimates of the scaling of the relaxation time for linear isolated chains using the previous general reptation methods were made using an extensive measurement of time (MCS), resulting in \( \tau \sim N^\gamma \) with \(\gamma=3.1\) [Murat and Witten 1990] and \(\gamma=3.05\) and 3.03 [Reiter 1990]. These values should be reduced by one to correspond to the intensive unit of time (MCS/B) used here, as there are \(N\) beads in an isolated chain system. The slope of a log-log plot of \(\tau_R\) vs \((N-1)\) is 2.03\pm0.02 (95% confidence), for the \((N\geq20)\) simulations conducted here. We use \((N-1)\) to be consistent with Eq. (2.6) and with theoretical predictions that generally use the number of bonds as a measure of chain length. Of course, the difference between \(N\) and \((N-1)\) becomes negligible as \(N\) increases. The exponent is close to two and is consistent with the literature values so it is reasonable to assume that the true limiting form is \(\tau_R \sim N^2\) for long chains.
Figure. 2.7 Dilute solution properties: scaling of the equilibration and relaxation times.

The values for $\tau_{R}/(N-1)^2$ are shown in Figure 2.7; the line is a least-squares fit to the data points for $N \geq 20$. The goodness of fit to the simulation data for $N \geq 20$ indicates that the assumed scaling of the relaxation time is consistent with the simulation data. The equilibration time, $\tau_{XY}$, is also shown in Figure 2.7. The equilibration time and the relaxation time both appear to scale with $(N-1)^2$, which suggests that relaxation from extended configurations is similar to relaxation from equilibrium configurations. Note, that since the relaxation times are plotted on a linear scale, the precision of the data required is much greater than that required for the more usual log-log plots.
All the values for $\tau_{XY}$ are less than $2.5(N-1)^2$ so a conservative estimate of $t_0=5N^2$ MCS/B (i.e. $t_0 \approx 5\tau_R$) was used as the starting point for determination of equilibrium properties in each of the simulation runs.

2.5.6 Comparison of simulation dynamics with polymer theory

Previous developments [Tanford 1961][de Gennes 1979][Doi and Edwards 1986] have shown that the relaxation time $\tau_R$ of the end-to-end vector, which corresponds to the first relaxation time in polymer theories based on the mode picture of polymer dynamics, exhibits the same characteristic time as rotation of a solid Brownian sphere of radius $R$ within the Kirkwood approximation. In this case, the dimensionless quantity $D_{CM}\tau_R/R_g^2$ should be independent of chain length. This quantity, which is a ratio of the reorientation time to the translational self-diffusion time, is plotted as a function of polymer length in Figure 2.8. For $N \geq 20$, the dimensionless quantity $D_{CM}\tau_R/R_g^2$ is independent of chain length to within statistical uncertainties (Figure 2.8). If the assumed scalings for $R_g^2$ and $\tau_R$ are correct, then the diffusion coefficient should scale as $D_{CM} \sim N^{-0.5}$. The slope
Figure 2.8 Scaling of the dimensionless quantity with polymer length for both dilute and concentrated solution conditions.

of a log-log plot of $D_{CM}$ vs $(N-1)$ is $-0.576\pm0.016$ in this range, which shows that although the simulation data are consistent with the proposed scaling, the form of the scaling cannot be determined conclusively from our simulations of short chains ($N\leq100$).

2.6 Results for concentrated systems

2.6.1 Solution conditions - melt

A series of simulations was conducted at a segment density of $\rho=0.99$ on
a 100 x 100 lattice for \( N \leq 50 \). In all cases the lattice was 99% filled with polymer segments so the simulations could be interpreted as a very concentrated polymer solution or as a polymer melt. For each of these simulations \( N_E = 50 \) simulations were averaged. In addition, an \( N = 100 \) simulation was conducted on a 200 x 200 lattice with \( N_E = 10 \) runs averaged. The large lattices were used to reduce any finite size effects in the simulation results and the equilibrium radius of gyration was always less than one tenth of the lattice size in the \( x \) direction. In all cases the simulation data were examined as outlined above in relation to isolated chains to ensure that equilibrium was reached and that the mean-square displacement and the log of the autocorrelation function were linear in the regions used to calculate \( \tau_R \) and \( D_{CM} \).

2.6.2 Equilibrium dimensions in the melt

The static properties of the 2d melts were found to be consistent with the scaling law \( \langle R^2 \rangle \sim (N-1)^{2v} \) where \( 2v = 1 \). This is in agreement with results obtained by Carmesin and Kremer [1990] for 2d melts using the bond fluctuation method. The values for \( 2v \) obtained from log-log plots were 1.04\( \pm \)0.01 and 1.07\( \pm \)0.02 for \( \langle R^2 \rangle \) and \( \langle R_e^2 \rangle \) for \( N \geq 30 \) which again shows that
there are still significant finite length effects. The ratio \( <R^2>/<R_e^2> \) in the limit \( N \to \infty \) is the ratio of the \( y \)-intercepts and is \( 5.39 \pm 0.04 \) which is also consistent with the results from the bond fluctuation method, but not with the value of 6 for Gaussian chains.

2.6.3 Simulated melt dynamics

Since all elementary polymer motions in the present algorithm require only a single vacancy to occur, it seems reasonable to assume that the length dependence of the asymptotic scaling of the relaxation time for the vacancy algorithm (at constant density) will be the same as for the bead algorithm. Hence, we will assume that \( \tau_R \sim N^2 \) for polymer melts at constant density. The values for \( \tau_R/(N-1)^2 \) were plotted as a function of \( 1/(N-1) \) (c.f. as was done in Figure 2.7 for the dilute solution case) and a least squares fit to the data for \( N \geq 20 \) was made (see Table 2.3).

The goodness of fit to the simulation data for \( N \geq 20 \) was found to be comparable to that shown in Figure 2.7, indicating that the assumed scaling of the relaxation time is consistent with the simulation data. The difference between the exponent obtained from a log-log plot (1.87±0.03) and the assumed value of 2 can be explained by the first order correction to scaling.
**TABLE 2.3.** Assumed scaling exponents and parameters for the
\( \rho=0.99 \) simulations c.f. equation (2.6)

<table>
<thead>
<tr>
<th>Scaling Exponent</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt;R^2&gt;)</td>
<td>2v=1</td>
<td>1.691±0.0002</td>
</tr>
<tr>
<td>(&lt;R_g^2&gt;)</td>
<td>2v=1</td>
<td>0.314±0.002</td>
</tr>
<tr>
<td>(\tau_R)</td>
<td>2</td>
<td>57.9±2.3</td>
</tr>
<tr>
<td>(D_{CM}\tau_R/&lt;R_g^2&gt;)</td>
<td>0</td>
<td>0.32±0.03</td>
</tr>
<tr>
<td>(D_{CM})</td>
<td>-1</td>
<td>0.00173±0.00007</td>
</tr>
</tbody>
</table>

The equilibration times, \(\tau_{XY}\), also appear to scale with \(N^2\) and a conservative estimate of \(t_0=500N^2\) MCS/V \((t_0=10\tau_R)\) was used as the starting point for determination of equilibrium properties in each of the simulation runs in the ensemble. The (intensive) time is measured in MCS/V so that the number of computer steps performed per unit time is independent of the length of the polymers at constant vacancy concentration for a constant size lattice. The
relationship found for 2d melts using the bond fluctuation method was 
approximately [Carmesin and Kremer 1990] \( \tau_{R_g} \sim N^2 \rho^2 \), where \( \tau_{R_g} \) is the 
relaxation time of the radius of gyration, which has the same length 
dependence as that assumed here for \( \tau_R \).

2.6.4 Length independence of dimensionless quantity

The dimensionless quantity \( D_{CM} \tau_R / \langle R_g^2 \rangle \) is again constant to within the 
accuracy of the simulation data for \( N \geq 20 \) (Figure 2.8). This indicates that in 
polymer melts the relaxation time is proportional to the time taken for a 
polymer to diffuse a mean-square distance equal to the mean-square radius of 
gyration, as expected. This is the same independence that was found for 
isolated chains but the constant of proportionality is smaller by a factor of two. 
This indicates that rotation-in-place is more highly favored for 2d concentrated 
polymers than in the dilute case. This is consistent with the observation that 
polymers in 2d melts form compact disks [Carmesin and Kremer 1990].

2.6.5 Scaling of the diffusion constant

Given the length independence of the dimensionless quantity
\[ D_{CM} \tau_R / <R_g^2> \], even for short chains (Figure 2.8), and the proposed exponents in the scaling relationships for \(<R_g^2>\) and \(\tau_R\) are 1 and 2, respectively, we can conclude that the exponent in the scaling relationship for \(D_{CM}\) should be -1. The diffusion coefficient for 2d polymer melts using the bond fluctuation method is also thought to be approximately consistent with [Carmesin and Kremer 1990] \(D \sim N^{-1}\) for melts.

The relationship \(D_{CM} \sim N^x\) with \(x=-0.809\pm0.025\) is found from a log-log plot of \(D_{CM}\) vs \((N-1)\). The difference from the assumed value may be explained by the large second order corrections noted above. An alternative interpretation which is consistent with the observed length independence of the dimensionless quantity \(D_{CM} \tau_R / <R_g^2>\) is that \(\tau_R \sim N^{2\beta}\) and \(D_{CM} \sim N^{2(\nu-\beta)}\) where \(\beta\) (like \(\nu\)) depends on whether the system is dilute or concentrated. For dilute systems the assumed values of \(\nu=3/4\) and \(\beta=1\) are consistent with the exponents obtained from log-log plots. For concentrated systems the assumed values are \(\nu=1/2\) and \(\beta=1\), but values determined from log-log plots are \(\nu=0.54\) and \(\beta=0.94\) so that \(2(\nu-\beta)=-0.80\), consistent with \(x\) above. Again, investigation of long \((N>>100)\) systems will be needed to determine which value is correct. In the absence of a theoretical justification for the alternative, we will assume that \(\beta=1\) for both dilute and concentrated systems. A summary of all the fits to
the assumed asymptotic scaling and first order corrections in the form of Eq. (2.6) are given in Table 2.3.

2.7 Results for intermediate systems

2.7.1 Concentration dependence

The concentration dependence of the static and dynamic properties of 2d athermal polymers was investigated for polymer chains of length \(N=20\) and \(N=50\) on a 100x100 lattice with periodic boundary conditions. In all cases for \(\rho>0\) the vacancy algorithm was used with \(N_E=50\) runs being averaged. For \(\rho=0\) the bead algorithm was used as discussed above. The equilibration of the system and the goodness of the fits used to obtain the diffusion coefficient and the relaxation time were verified as before.

Figures 2.9 and 2.10 summarize the static and dynamic properties of the athermal polymer system as a function of the segment density \(\rho\). The scaled relaxation times are shown in Figure 2.9 as a function of density. In addition to being scaled to reflect the asymptotic scaling, they are also scaled by the vacancy concentration \(\phi_v = 1 - \rho\) to reflect the proportion of the motion attempts per bead which are not rejected because a second vacancy is found in
Figure 2.9 Variation of the scaled relaxation time with density for polymers of length $N=20$ and $N=50$.

the direction chosen away from vacancy $v$ in steps 2 and 3 of the vacancy algorithm. A similar effect is found in the $N=1$ system (the so-called minimally interacting lattice gas) which has been studied extensively [Kehr and Binder 1986][Nelson et al. 1991][Nelson and Wei 1992]. Using this scaling, the values plotted for each of the chain lengths reflect the number of moves attempted by the computer, for a fixed lattice size, independent of the vacancy concentration.
Figure 2.10 Variation of the dimensionless quantity $D_{CMT}/\langle R_g^2 \rangle$ with density for polymers of length $N=20$ and $N=50$.

2.7.2 Comparison with other algorithms

The results shown in Figure 2.9 are similar to the concentration dependence observed for previous forms of the general reptation algorithm on cubic and face centered cubic lattices, which were shown to be more efficient than other traditional algorithms [Reiter et al. 1990], such as the standard reptation algorithm.
2.7.3 Static and dynamic properties

The data in Figure 2.9 are approximately given by the dashed line $0.54(1 + \phi_c)$. The value of 0.54 is the extrapolated limit of the relaxation time in the melt ($\rho=0.99$) as $N \rightarrow \infty$. The longer than expected relaxation times for high $\rho$ are probably due to correlations between consecutive motions of the vacancies. These correlations occur because there is a finite probability that a move is the inverse of the previous move. This effect can be expected to decrease as the length of the chain is increased and as the number of vacancies is increased. The probability of a particular type of move occurring scales like $1/(N_c N)$ (see Table 2.1). This explains why the deviations are largest for the shorter chains at high density.

The dimensionless quantity $D_{CM} \tau_R / \langle R_g^2 \rangle$ (Figure 2.10) tends towards a constant value of about 0.34 (solid line) as the density increases. The dashed lines are guides for the eye. The overlap threshold density $\rho^*$, for the crossover between dilute and semi-dilute behavior is given approximately by [de Gennes 1979] $\rho^* = N^{-0.5}$ which has values $\rho^* = 0.22$ and $\rho^* = 0.14$ for the $N=20$ and $N=50$ systems respectively. These values are shown as stars in Figure 2.10 and are approximately halfway between the limiting values for dilute and semi-dilute solution, as might be expected. In the limit $N \rightarrow \infty$, $\rho^*$ tends to zero and we expect that the dimensionless quantity will approach a constant limiting value.
for all densities greater than zero.

In the limit \( N \rightarrow \infty \), we have simple scaling forms for \( \langle R_e^2 \rangle \) and \( \tau_R \), and the dimensionless quantity is independent of both length and concentration for \( \rho > 0 \), so the form of \( D_{CM} \) can be determined. These relationships are

\[
\langle R_e^2 \rangle \approx 0.317 \frac{N}{\rho}, \quad \tau_R \approx \frac{0.54(1 + \phi_v)N^2}{\phi_v}, \quad \frac{D_{CM} \tau_R}{\langle R_e^2 \rangle} \approx 0.34, \quad D_{CM} \approx \frac{0.2\phi_v}{1 - \phi_v^2}N \quad (2.7).
\]

These proposed limiting forms may be confirmed by simulating systems of longer chains.

### 2.8 Empirical Scaling Relations

#### 2.8.1 Existing scaling predictions

An asymptotic scaling prediction [de Gennes 1979][Bishop et al. 1983] is available for polymer chains in \( d \) dimensions as a function of both length and concentration of the form

\[
\langle R^2(N, \rho) \rangle \sim A(X)N^{2\nu} \quad (2.8).
\]
This is valid in the limit $N \to \infty$. $X$ is a scaling variable defined by $X \sim \rho / \rho^*$, where $\rho^* \sim (N-1)/<R_{SAA}^d>$ is the overlap threshold density at which the chains begin to interfere with each other, $<R_{SAA}^2> \sim (N-1)^{2v}$ is the mean-square end-to-end distance of isolated chains of length $N$, and $d$ is the dimensionality of the system. We will define $X$ as being $X \equiv (N-1)^{d_v-1} \rho$, so that $X = \sqrt{(N-1)} \rho$ for the 2d systems studied here, as $v=3/4$ for isolated chains in 2d. Whereas $N$ is a measure of chain length in the system, $X$ is a measure of diluteness relative to the condition of chain overlap, and hence accounts for the combined effect of chain length and concentration. As $X$ goes to infinity, so does $N$; however, the converse is not necessarily true. $A(X)$ is a function which should become independent of $N$ as $N \to \infty$.

When both $X$ and $N$ tend to infinity [Bishop et al. 1983], $A(X) \sim X^{-(2v-1)(d_v-1)}$, which for our 2d systems gives $A(X) \sim 1/X$ which can be combined with Eq. (2.8) to give

$$\langle R^2(N, \rho) \rangle \sim \frac{N}{\rho} \quad (2.9),$$

as $X \to \infty$. This power law behavior has been shown to occur for polymers on the 2d square lattice as $X$ becomes large [Dickman 1989]. This is seen on a log-log
plot of $<R^2>/N$ versus density. Similar behavior is observed when the data obtained here are plotted in the same fashion.

2.8.2 Reformulation of scaling predictions

By analogy with the approach of Rapaport [1985ab] (see above), Eq. (2.9) can be rearranged by noting that $<R^2>\sim N$ as $p\to 1$. First order corrections to the scaling as $X\to\infty$ could, in principle, be obtained by plotting $p<\sqrt{R^2}>/N$ versus $1/X$, but much larger values of $X$ than those found here would be required.

An alternative approach is possible. Note that Eq. (2.8) can be rewritten as

$$\frac{\langle R^2(N,\rho) \rangle}{\langle R_{S\perp}^2 \rangle} \sim A(X) \quad (2.10),$$

in the limit $N\to\infty$, where $<R_{S\perp}^2>\sim N^{2\nu}$. $<R^2> / <R_{S\perp}^2>$ has been plotted previously [Bishop et al. 1983] for both 2d and 3d polymer systems. However, in the limit $X\to\infty$, $A(X)\sim 1/X$. Hence, if we plot the inverse quantity $<R_{S\perp}^2> / <R^2>$ versus $X$ we expect that a linear regime will be found for large $X$. The curves in Figure 2.11 are least squares fits to the simulation data for
polymers of length $N=50$ to a function of the form

$$\frac{\langle R_{SW}^2 \rangle}{\langle R^2 \rangle} = \alpha X + \exp(-\beta X) \quad (2.11).$$

The values for $\alpha$ and $\beta$ are given in Table 2.4.

**TABLE 2.4.** Empirical scaling parameters

<table>
<thead>
<tr>
<th></th>
<th>$R^2$ (N=20)</th>
<th>$R^2$ (N=50)</th>
<th>$R^2$ (N→∞)</th>
<th>$R_s^2$ (N=20)</th>
<th>$R_s^2$ (N=50)</th>
<th>$R_s^2$ (N→∞)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.429</td>
<td>0.434</td>
<td>0.427</td>
<td>0.312</td>
<td>0.320</td>
<td>0.321</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.406</td>
<td>0.393</td>
<td>-</td>
<td>0.285</td>
<td>0.278</td>
<td>-</td>
</tr>
</tbody>
</table>

Expected errors for these values are of the order of ±0.005.

This gives the following functional form for $A(X)$

$$A(X) = \frac{1}{\alpha X + \exp(-\beta X)} \quad (2.12).$$
Figure 2.11 Fits of the proposed empirical scaling relation to the mean-square dimensions of the polymers as a function of both concentration and length. The solid curves are least-squares fits to the simulation data for N=50. The straight lines indicate the extrapolated values of $\alpha$ for the existing scaling relation, which is only valid for large $X$.

Extrapolations of the $N=50$ fits correctly predict the $N=100$ data points (at $X \approx 10$ in Figure 2.11). In addition, the straight lines in Figure 2.11 indicate the values of $\alpha$ for polymers of infinite length obtained from the melt data; these values are consistent with those obtained from the $N=50$ fits (see Table 2.4). Hence, fits for the comparatively short length of $N=50$ appear to be already in the long chain length limit for the empirical scaling formulae. The empirical
relation (2.12), appears to be the first reported empirical formula for the scaling function $A(X)$ for 2d polymers for all values of $X$ and finite $N$.

2.9 Conclusion

A new treatment of the general reptation algorithm has been used to investigate the scaling of static and dynamic properties of 2d athermal polymers, using an approach which includes the first order analytic correction to scaling for finite length polymer chains. Using this approach it has been possible to confirm that the asymptotic scalings of all the investigated properties are consistent with simple power law forms. The scalings of the static properties are consistent with previous results in 2d and the scalings of the dynamic properties are of the same form as the approximate relationships proposed for the bond fluctuation method in 2d. The computational efficiency of the vacancy form of the present algorithm is approximately independent of concentration, in agreement with what was determined for the previous implementations of the general reptation algorithm. This indicates that it is well suited to investigation of equilibrium thermodynamic properties of polymer systems.

The simulation data for these relatively short chains are consistent with
the scaling of $\tau_R \sim N^2$ for both dilute and concentrated systems, after consideration of scaling corrections. However, it is interesting to note that scaling $\tau_R$ by $N^{2\beta}$ and $D_{CM}$ by $N^{2(v-\beta)}$ with $\beta$ less than one, successfully captures the observed behavior for these short chains and also reproduces the expected length independence of $D_{CM}\tau_R/\langle R_g^2 \rangle$. Simulations of chains with $N>>100$ would be required to demonstrate that $\beta$ approaches unity for large $N$.

Empirical scaling formulae have been proposed for the mean dimensions of 2d athermal polymers. These formulae account for variations in mean polymer dimensions as a function of length over the whole concentration range from dilute solution conditions to a concentrated melt. The form of the formulae should be applicable to any 2d athermal polymer system, and may be directly applicable to 3d athermal polymers and polymers in a good solvent as well.

Combination of the empirical scaling relation with the fit to the relaxation time shown in Figure 2.9 and the concentration independence of the dimensionless quantity shown in Figure 2.10 provides a quantitative prediction for all the static and dynamic properties of the polymers discussed herein, both as a function of length and concentration throughout the semi-dilute regime for polymers as short as $N=50$. 

129
Chapter 3: Self-assembled star copolymers in dilute solution

3.1 Introduction

Star polymers have attracted much attention in recent years owing to their unique properties. Much of the work has focused on homopolymer stars but star copolymers have an even richer range of existing and potential applications in such diverse fields as drug delivery and other biological applications, separation processes, viscosity modification and materials design.

3.1.1 Regular stars

The properties of star polymers in which all the arms are homopolymers of the same type are reasonably well understood [Grest 1994, 1996]. A blob model for the arms of the star polymer, based on de Gennes scaling approach [de Gennes 1979] for linear polymers, has been developed [Daoud and Cotton 1982, Birshtein and Zhulina 1984, Birshtein et al. 1986]. The star is considered to consist of three regions: an inner, melt-like, extended core region;
an intermediate region resembling a concentrated solution; and an outer, semi-dilute region. The arms of the star are considered to be constrained to lie within a cone emanating from the core of the star. Results from molecular simulations have been shown to be consistent with scaling models for properties such as the mean-square radius of gyration, monomer density profiles, center-to-end distribution functions, and the relaxation of shape fluctuations [Grest 1994]. These results were for good, θ, and poor solvent conditions and were found to compare favorably with experiments on many-arm stars in dilute solution conducted by Burchard [1983], Roovers and coworkers [1972, 1974, 1983, 1989, 1993], Huber et al. [1984] Toporowski and Roovers [1986], Khasat et al. [1988], Bauer et al. [1989] and Zhou et al. [1992].

3.1.2 Amphiphilic stars

Amphiphilic star copolymers have been synthesized by a variety of techniques by Tsitsilianis [1993], Winnik [1992], Saunders et al. [1992], Kanaoka et al. [1992], Ishizu and Uchida [1994][1995], Floudas et al. [1996], Zhou and Smid [1993] and Chen and Smid [1996]. These fall into two main types, heteroarm (or miktoarm) star copolymers of the form AₓBᵧ, which have x arms of type A blocks and y arms of type B blocks and homoarm star block copolymers of the type (AB)ₙ in which there are n arms each of which is an AB
block copolymer.

Condensed phases of polystyrene-polyisoprene \((AB)_n\)-type stars with \(n=4\) to 41 arms have been investigated recently experimentally by Ishizu and Uchida [1994, 1995] and by Floudas et al. [1996] and via computer simulation [Floudas et al. 1996]. Ordered lamellar, cylindrical and bicontinuous cubic structures were found to form in the condensed phase.

Aqueous solution behavior of three and four armed stars with poly(ethylene oxide) (PEO) arms capped with hydrophobic end-groups have shown [Zhou and Smid 1993] that the arm ends tend to associate, and that above a critical star concentration the system phase separates into a dilute phase and a condensed gel phase. In the dilute phase, intramolecular association was dominant whereas in the gel phase intermolecular association was more prevalent. Three-armed stars with hydrophobic cores and PEO arms were found [Chen and Smid 1996] to form micelles in aqueous solution above a critical micelle concentration (cmc).

Solubilization of polycyclic aromatic compounds in solutions containing \((AB)_n\) poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) stars with \(n=2\) and \(n=4\) was investigated both experimentally and using self-consistent mean-field lattice theory by Hurter and coworkers [1992, 1993ab]. It was found that the \(n=2\) stars formed larger micellar aggregates than the \(n=4\) stars of the same molecular weight. This was attributed to steric hindrance within the
hydrophobic core of the low molecular weight \( n=4 \) micelles.

In this chapter we investigate dilute solution behavior of two variants of amphiphilic star block copolymers of the form \((AB)_n\), (see Figure 3.1) in which different ends of the AB block copolymer arms are attached to the center of the star. Of particular interest, are the conformations of hydrophilic-core \((AB)_n\) stars whose outer hydrophobic blocks tend to aggregate in solution.

3.2 Model and simulation technique

3.2.1 Lattice model in 3d

The general reptation method [Nelson et al. 1997a] discussed in chapter 2 was modified to operate on a face centered cubic (fcc) lattice. Conformation changes of the polymers were weighted using standard Metropolis sampling techniques.

3.2.2 Molecular architecture

The stars investigated here have \( 12 \leq n \leq 42 \) identical linear diblock AB copolymer arms. The solvent is a good (athermal, \( \chi=0 \)) solvent for one of the blocks, and the other block is solvophobic with \( \chi>0 \). For ease of discussion, we
Figure 3.1. A typical conformation of a 12-arm hydrophilic-core star at a \( \chi \)-value of 0.5. Each arm of the star is an AB diblock copolymer with \( N_A=20 \) hydrophilic beads (lighter color) and \( N_B=20 \) hydrophobic beads (darker color). The axes indicate the center of the star.

will assume that the solvent is water and that it is a good solvent for the
“hydrophilic” ($\chi=0$) block. The other block with $\chi>0$ will be designated “hydrophobic”. These labels are arbitrary and the model can equally apply to other systems with comparable $\chi$-parameters.

In the “hydrophilic-core” stars, the block attached to the center is hydrophilic and the outer block is hydrophobic. For the “hydrophobic-core” stars, the block attached to the center is hydrophobic and the outer block is hydrophilic. Figure 3.1 shows a hydrophilic-core star diblock copolymer. The origin of the axes shown in Figure 3.1 corresponds with the central branch point of the star. The star has 12 arms, each of which is of length $N=40$ with $N_A=20$ hydrophilic beads (lighter color in Figure 3.1) and $N_B=20$ hydrophobic beads (darker color in Figure 3.1). A hydrophilic solvent, “water”, fills the remainder of the lattice. The pairwise interaction strength between hydrophobic/hydrophilic beads is set to $\varepsilon$, and the hydrophilic/hydrophilic and hydrophobic/hydrophobic interactions are set to zero. A single Flory-Huggins $\chi$-parameter

$$\chi = \frac{z\varepsilon}{kT}$$

characterizes the system, where $z=12$ is the coordination number of the lattice, $k$ is the Boltzmann constant and $T$ is the temperature.

136
3.2.3 Initial conditions

The stars are constructed with the end of the first arm being placed at the center of the star. The next eleven arms are placed at the eleven unoccupied nearest neighbor sites of the central bead. Each of these arms extends in a nearest neighbor direction away from the center of the star. For 18-arm stars, the 6 additional arms are added in the next available nearest neighbor sites. For the 24-arm stars and 42-arm stars, this process is repeated. The result is that all stars discussed here have small compact cores, in which the beads are closely packed.

The beads touching the center of the star were fixed during the simulations so that no diffusion or rotation of the center of the star was possible. This was not considered to be a significant limitation as dilute solution behavior is represented by isolated stars and intermolecular interactions are not important.

3.3 Results for 12-arm stars

3.3.1 Equilibration and data collection

Hydrophilic-core and hydrophobic-core stars with \( n=12 \) arms were
Figure 3.2. Configurational energy of 12-arm hydrophilic-core and hydrophobic-core stars as a function of solution conditions as characterized by $\chi$.

Initially equilibrated for a period of 50,000 Monte Carlo steps per bead (MCS/B) at a solvent quality given by $\chi=0.5$ ($\theta$-solvent) followed by a data collection run of 500,000 MCS/B at the same solvent conditions. At the end of this run the star was equilibrated at a poorer solvent quality of $\chi=1.0$ for 50,000 MCS/B and a data collection run of 500,000 MCS/B was run at these solvent conditions. This procedure was repeated up to $\chi=4.0$ (poor solvent conditions). The solvent conditions were then made better incrementally to retrace the progression in the opposite direction, starting at $\chi=3.75$ and
Figure 3.3. Weight average globule aggregation number of 12-arm hydrophilic-core and hydrophobic-core stars as a function of solution conditions as characterized by $\chi$.

decreasing in 0.5 increments initially (see Figures 3.2 to 3.4). For each solvent condition the time-average configurational energy per hydrophobic bead $<E>$ of the star molecule was calculated (Figure 3.2), together with the time-average aggregation number $<\alpha>$ of the arms (Figure 3.3), and the root mean square radius of gyration $<R_g>$ of the star as a whole (Figure 3.4). The arms are considered to form an aggregate when one or more of the hydrophobic beads of distinct arms are touching each other.
Figure 3.4. Radius of gyration of 12-arm hydrophilic-core and hydrophobic-core stars as a function of solution conditions as characterized by $\chi$.

3.3.2 Comparison of hydrophilic- and hydrophobic-core stars

There is no apparent hysteresis in the plots for the configurational energy and aggregation number, which suggests that the data obtained were representative of equilibrium values. The configurations of the hydrophobic-core star are consistent with the scaling model [Daoud and Cotton 1982] [Birshtein and Zhulina 1984] for stars at all solution conditions, as the star retains approximate spherical symmetry and each arm of the star can be
considered to lie within a cone emanating from the center of the star. Both the configurational energy $<E>$ and radius of gyration $<R_s>$ of the hydrophobic-core star decrease gradually as $\chi$ is increased, consistent with the observation that the central hydrophobic melt-like region becomes more compact and develops a more well-defined interface as $\chi$ is increased.

### 3.3.3 Aggregation transition

The hydrophilic-core star shows a dramatic change in configurational energy $<E>$ as the solvent quality is reduced (higher $\chi$), having a clear inflection point at $\chi \approx 2$ see Figure 3.2. This transition point corresponds to a dramatic change in the dimensions of the hydrophilic-core star as measured by the radius of gyration (see Figure 3.4) as the arms aggregate to form a single globule with an aggregation number of 12, the maximum possible for a 12 arm star (Figure 3.3). The aggregation number of the hydrophobic-core star is identically equal to the number of arms as the hydrophobic blocks touch each other at the center of the star by construction.

A typical configuration of the hydrophilic-core star at a $\chi$-value of 2.5 is shown in Figure 3.5. The single hydrophobic globule is clearly visible. Once the hydrophilic-core star forms a single hydrophobic globule, its energy $<E>$ is

141
Figure 3.5. An aggregated conformation of the 12-arm hydrophilic-core star shown in Figure 3.1 at a $\chi$-value of 2.5. The axes indicate the center of the star.

comparable with that of the hydrophobic-core star at the same solution conditions (Figure 3.2). For a compact hydrophobic region, $\langle E \rangle$ is essentially the surface energy of that region, indicating the equivalence between the two
types of star.

At high temperatures (low \( \chi \)), the radius of gyration of the hydrophilic-core star is large and at low temperatures (high \( \chi \)), the radius of gyration of the hydrophilic-core star is reduced by a factor of three, indicating that dilute solutions of this polymer could be used as a temperature dependent viscosity modifier. This can be contrasted with the hydrophobic-core star, whose size shows no dramatic change with solution conditions.

3.3.4 Scaling models

The behavior of the hydrophilic-core star cannot be modeled adequately by the scaling model developed by Daoud and Cotton [1982] and Birshtein and Zhulina [1984], as each arm is not confined to a cone centered on the core of the star. A more appropriate model would have the hydrophobic blocks confined to a compact spherical globule and the hydrophilic blocks constrained to have one end attached to the center of the star with the other end attached to the surface of the hydrophobic globule.
3.4 Results for stars with more arms

3.4.1 Multi-globule conformations

Similar simulations were run for stars with 24 and 42 arms and qualitatively similar results to those shown in Figures 3.2 to 3.4 were obtained. For example, the average aggregation number as a function of χ is shown in Figure 3.6 for the n=12, 24 and 42 arm hydrophilic-core stars. The main difference between the simulations was the conformation of the hydrophilic-core polymer at poor solvent conditions. The 24-arm star formed two approximately equal hydrophobic globules, each with an aggregation number of about 12, separated from each other by the center of the star to form a linear arrangement. The 42-arm star formed three approximately equal hydrophobic globules in a planar triangular configuration as shown in Figure 3.7.

3.4.2 Arm length variation

The effect of varying the length of the hydrophilic block, \( N_A \), was briefly investigated using 18-arm hydrophilic-core stars all with \( N_E=20 \) (not shown). It was found that all the stars with \( N_A=10, \) 20 and 30 reversibly formed a
Figure 3.6. Average aggregation numbers of 12-, 24-, and 42-arm stars as a function of solution conditions $\chi$. Above $\chi=2.2$ these have one-, two-, and three-globule conformations respectively.

two-globule conformation for $\chi>2.2$, on the timescale of the simulations, in a manner similar to the 24-arm star shown in Figure 3.6. However, small deviations from the linear arrangement of the two-globule conformations were observed to increase with increasing $N_A$, indicating that the aggregated state becomes more flexible as the length of the hydrophilic block is increased.
Figure 3.7. A three-globule conformation of a 42-arm hydrophilic-core star at a $\chi$-value of 2.5. Each arm of the star is an AB diblock copolymer with $N_A=20$ hydrophilic beads (lighter color) and $N_S=20$ hydrophobic beads (darker color). The axes indicate the center of the star.
3.4.3 Excluded volume globule repulsion

The linear form of the two-globule 18- and 24-arm stars and the triangular form of the three-globule 42-arm star are caused by an effective repulsion between the arms in different globules. The globules are repelled to positions separated from each other by the maximum possible distance given the constraint that they are attached to the center of the star. This repulsion is caused by excluded volume effects between the beads of the hydrophilic blocks attached to the center of the star. The arms connected to one globule extend from the center of the star in the direction of the globule to which they are attached, and tend to exclude any hydrophilic blocks of other globules from the same space. The number of configurations available to the hydrophilic blocks attached to a second globule is increased if they avoid the space occupied by the arms of the other globule.

As more arms are added to a globule, the entropy of the hydrophilic blocks on a per arm basis decreases due to excluded volume effects. This can be understood by considering a simple situation in which fixed length linear polymer chains connect two points $c$ and $g$ in space. Point $c$ can be taken to be the center of the star and point $g$ can be taken to be the globule. If there were no excluded volume effects, any number of chains could connect $c$ and $g$ and
the entropy per chain would be independent of the number of chains. However, excluded volume effects reduce the number of configurations available per chain as the number of chains connecting $c$ and $g$ is increased. This is because any given chain is always excluded from the space occupied by the others so that a new chain added between $c$ and $g$ will have to go around the chains already there.

As shown in Figure 3.6, the average aggregation number of the globules formed by the $N_A=20$, $N_B=20$ arms considered here is between 12 and 15 for the 12-, 24- and 42-arm stars. Enthalpy will favor an arrangement of globules with small surface area, such as a single spherical globule. It is only the arrangement of the hydrophobic beads that determines the enthalpy of our model stars, as the hydrophilic bead interactions are the same as for the solvent. The arrangement of the hydrophilic blocks in the solvent does not affect the enthalpy of the star but can affect its entropy.

### 3.4.4 Free energy considerations

At the temperature $T$ at which the globules form ($\chi=2.2$) there is a trade-off between the enthalpy $H$ favoring larger globules (lower $H$) and the entropy $S$ favoring smaller globules (larger $S$). This can be seen by considering the Gibbs free energy $G$.
\[ G = H - TS, \]

which must be minimized at equilibrium. As the temperature is decreased (increasing \( \chi \) in our model) the magnitude of the entropy term in the free energy decreases so that the preferred globule size will increase. Figure 3.6 shows an example of this. The average aggregation state of the 42-arm star shows a slight shoulder at an aggregation number of about \( <a> \geq 10 \) at \( \chi \geq 1.9 \). This corresponds to configurations in which there are four relatively loosely aggregated globules. As the temperature is decreased further, the conformation changes to one with three globules.

This process of a decreasing number of globules with decreasing temperature is expected to continue, with the 42-arm star conformation changing to a two-globule conformation as the temperature is decreased and with a single-globule conformation being favored at some still lower temperature. These two- and one- globule conformations of the 42-arm star were never observed to form spontaneously during the simulations reported here.

The conformation of the 42-arm star shown in Figure 3.7 (at \( \chi = 2.5 \)) has three globules in a planar triangular configuration. The effective repulsion caused by excluded volume effects keeps the globules from touching each other and coalescing. Another possible mechanism for changing the aggregation state of the polymer is similar to Ostwald ripening, in which an arm detaches.
from a small globule and then "diffuses" to a larger globule and is absorbed into it. This is a rare event in the simulations for $\chi > 2.2$ as evidenced by the lack of variation in $<a>$ above $\chi = 2.2$ seen in Figure 3.6, indicating that the arms remain associated with a particular globule at these solvent conditions and do not desorb and move to another globule. The three-globule conformation of the 42-arm star is effectively "frozen in" on the timescale (rate of cooling) of the present simulations for $\chi > 2.2$.

3.5 Non-reversible simulations of a 42-arm star

3.5.1 Other possible low energy conformations

As the conformations of the 42-arm hydrophilic core star with less than three globules were kinetically excluded from the reversible simulations discussed above, we developed a method to generate a single-globule 42-arm star in order to investigate its properties and to confirm the intuitive ideas outlined in the previous section. This method is completely artificial and is not intended to mimic any real physical process.

3.5.2 Preparation of a one-globule 42-arm star

We started with an $N=40$ 42-arm star in which all the arms are
completely hydrophobic. This star was equilibrated at a $\chi$-value of 3, and formed a single compact globule. The composition of the star was then modified by changing the central beads of each arm from hydrophobic to hydrophilic. This makes a compact hydrophobic globule with a centrally located hydrophilic core (of 42 beads, one on each arm). The new star was then equilibrated and the next bead on each of the arms was converted into a hydrophilic bead, so that each arm now had a two-bead inner hydrophilic block and a 38-bead hydrophobic outer block. This process was repeated until an $N_A=20$, $N_B=20$ star was formed. During this process the hydrophobic globule moved away from the center of the star and eventually formed a hydrophobic globule conformation of spherical shape, comparable with the arrangement of the 12-arm star shown in Figure 3.5.

This star was then equilibrated at $\chi=4$, and the data shown in Figures 3.8 and 3.9 were obtained by heating (decreasing $\chi$) the one-globule star. At the heating rate of the simulations the single globule with an aggregation number of $\langle n \rangle=42$ was stable for $\chi>2.6$, as shown in Figure 3.8.

3.5.3 Preparation of a two-globule 42-arm star

As the temperature was lowered to a value corresponding to $\chi=2.6$, the
Figure 3.8. Average aggregation number from simulations of specially prepared 42-arm hydrophilic-core stars with (1)- (2)- and (3)-globule conformations.

A single globule became an elongated prolate spheroid with the ends turned towards the center of the star in a banana-like shape. This globule broke approximately in the center forming two globules with an average aggregation number of about 20 (see Figure 3.8). The two globules migrated to form a linear configuration with the center of the star. This two-globule conformation was equilibrated at $\chi=4.0$ and the two-globule data shown in Figures 3.8 and 3.9 were obtained by heating the two-globule star.
Figure 3.9. Configurational energy of specially prepared 42-arm hydrophilic-core stars with (1)- (2)- and (3)-globule conformations.

3.5.4 Variation of properties with conformation

The plots for the one-globule and two-globule configurations shown in Figures 3.8 and 3.9 represent an irreversible process on the timescale of the simulations. Once the $\chi$-value was lowered past 2 the properties became comparable with the earlier three-globule results; cooling the star by raising the $\chi$-value results in the properties retraced the original (reversible) three-globule curve (c.f. Figure 3.6) rather than their original path. Once the three-
globule conformation is formed at about $\chi=2$, a local minimum in free energy is reached and spontaneous formation of the two- and one-globule configurations does not occur on the timescale of the present simulations.

The single-globule conformation has a configurational energy less than the two-globule conformation, which has a lower energy than the three-globule conformation (Figure 3.9). This confirms that the two-globule and one-globule conformations should be favored at sufficiently low temperatures.

### 3.6 Potential applications

#### 3.6.1 Macromolecular amphiphiles

The hydrophilic-core stars would seem to be a good candidate for applications requiring a high molecular weight amphiphile. A dilute solution of the hydrophilic-core star block copolymer can sustain well-defined hydrophobic regions under certain solution conditions and no hydrophobic region under other solution conditions, in a manner similar to low molecular weight amphiphiles that form micelles.

The distinction between these stars and the hydrophobic-core stars and miktoarm stars is that the star has a configuration in which all the hydrophobic blocks are well dispersed (see Figure 3.1), whereas the hydrophobic blocks of the hydrophobic-core stars and miktoarm stars are
permanently adjacent to each other at the core of the star forming a (small) region of increased hydrophobic block concentration at all solution conditions. Thus, hydrophilic-core stars may be expected to exhibit a more dramatic transition between states that have well-defined hydrophobic regions (high $\chi$) and those that lack well-defined hydrophobic regions (low $\chi$) than the other star architectures.

3.6.2 Non-dilute behavior

The results discussed here are only applicable to dilute star solutions in which the stars do not aggregate with each other in an intermolecular manner. However, it seems reasonable to suggest that the stars which form a single hydrophobic globule, such as that shown in Figure 3.5, would behave in a similar manner to the short linear amphiphiles with a similar overall shape (see Chapter 4), forming micellar aggregates at higher star concentrations. At still higher concentrations, a condensed phase would probably form as has been observed experimentally for stars with three and four arms [Zhou and Smid 1993]. The solubility of the hydrophilic core stars should depend on the molecular weight of the star, the number of arms and the fraction of hydrophilic segments in the arms.

Stars that form multi-globule conformations in dilute solution would
probably tend to form condensed phases more easily. The structure of the dilute conformation may be related to the condensed phase and allow selection of a particular morphologies in the condensed phase. For example, the three-globule star may preferentially form cylinders packed in a triangular array.

3.7 Conclusion

A simple model of $(AB)_n$ star copolymers has been investigated using an fcc-lattice model. It has been found that hydrophilic-core stars, in which the inner blocks are hydrophilic and the outer blocks are hydrophobic, undergo a symmetry breaking, aggregation transition. The hydrophobic blocks are separated from one another in a relatively good solvent and aggregate into one or more compact globules in a poor solvent. The number of compact globules formed can be affected by the preparation history of the star, at least on the time scales available in the simulations presented here. The size of the polymer, as measured by the radius of gyration, decreases dramatically through this transition and the spherical symmetry of the stars is destroyed, making scaling models which assume that each arm is confined to a cone inappropriate. No such transition occurs for hydrophobic-core stars in which the inner blocks are hydrophobic and the outer blocks are hydrophilic.

Experimental verification of this aggregation transition may be
obtained for dilute solutions of hydrophilic-core stars by methods sensitive to the radius of gyration of the polymer such as light or neutron scattering.
Chapter 4: Self-assembled micelles

4.1 Introduction

Recently, there have been a number of studies of micelle formation using computer simulations of course grained bead-type models. The motivation for using simplified mesoscopic models is that the computational requirements for equilibrating models that are more realistic are too demanding, at present, primarily due to the long time scales involved in self-assembling systems. In addition, a relatively large system size is required to accommodate even a modest number of micelles. Fortunately, there appear to be universal properties of aggregate formation and structure that are similar for many different surfactant systems [Smit et al. 1991], it is these properties which the simplified models are intended to investigate. The very simplicity of the model can be an asset in determining which microscopic properties are responsible for observed aggregate characteristics.

Lennard-Jones interaction model to investigate the properties of oil-water-surfactant systems using molecular dynamics techniques. This approach is an elegant one, but suffers from the disadvantage that the motion of all the molecules, including the solvent, must be included explicitly in the simulation, even when the system is dilute. This has meant that true equilibrium is difficult to attain.

A significant reduction in the complexity of the problem can be made by moving to a lattice model where the detailed structure of the solvent need not be considered explicitly. Lattice sites not otherwise occupied are implicitly filled with solvent beads. In dilute systems, the volume fraction of surfactant is typically less than about 10% so that an order of magnitude fewer particles need be explicitly considered in the simulation.

In previous simulations [Desplat and Care 1996, Gottberg et al. 1997], the size distributions of relatively small micelles with aggregation numbers less than 100 were modeled using an empirical approach based on the dilute solution excess chemical potential determined from the measured size distribution. In this chapter, we investigate distributions of equilibrium aggregates of up to 500 surfactants and fit their size distributions to widely accepted phenomenological theories that assume the micelles have spherical and cylindrical shapes.
In determining the size of the system to be simulated, Larson [1992] has noted that it is the number of aggregates in the simulated system that is of importance in determining finite size effects. Consequently, we chose a small surfactant occupying four lattice sites and a large lattice size. Recent results [Desplat and Care 1996] are consistent with the relatively smooth single-peaked micellar size distributions reported here. In what follows, we compare our results with the simple thermodynamic models that assume spherical and cylindrical micellar shape.

4.2 The simulated system

4.2.1 Molecular architecture

The simulations reported here were conducted on a face centered cubic lattice with periodic boundary conditions implemented along the three lattice directions in the usual way. The surfactants used here occupy four lattice sites and are linear symmetric $H_2T_2$ molecules comprising two "hydrophilic" head beads ($H$) and two "hydrophobic" tail beads ($T$). The remainder of the lattice is filled with "water" beads ($W$). This provides a simple Flory-Huggins type model [Flory 1954] for the system. The pairwise interaction energies were chosen to be $\epsilon_{HH}=\epsilon_{TT}=\epsilon_{WW}=\epsilon_{HW}=0$ and $\epsilon_{HT}=\epsilon_{WT}=\epsilon$, so that the head and water beads
interact as if they were identical to each other [Larson 1988-1996]. With these values, the lattice energy can be thought of as an excess energy of mixing. Hence, the system is characterized by a single $\chi$-parameter:

$$\chi = \frac{z}{T'} \quad ; \quad T' = \frac{k_B T}{\epsilon}$$

where $z=12$ is the coordination number of the lattice, $T'$ is a scaled temperature, $k_B$ is the Boltzmann constant and $T$ is the temperature.

A form of the general reptation algorithm was used for moving the surfactants through the lattice. Details of the bead algorithm used here are given in chapter 2. Standard Metropolis sampling techniques were used to determine whether a motion attempt should be accepted.

4.2.2 Physical Interpretation

The simulated surfactants are not directly comparable to any real surfactant systems, but qualitative comparison with short-length non-ionic surfactants is justified. For example, the hydrophobic tail may be compared with an alkane chain of up to about $C_{20}$ length if each bead is considered to represent one Kuhn segment length. (A more direct physical interpretation of
the hydrophobic tail is of a rigid “rod” formed by two moieties connected by a fixed-length bond.) In our simulated system, all configurations of an isolated surfactant have the same energy, so that the diffusion coefficient of an isolated surfactant is independent of temperature. (Longer surfactants have temperature dependent diffusion coefficients due to energy differences between isolated configurations.) Consequently, we equilibrated the system from the start at the desired temperature, rather than annealing the system slowly from a higher temperature.

4.3 Temperature dependence

4.3.1 Small system

In order to investigate the temperature dependence of the system and to select a temperature for the main simulation run, we ran a number of simulations on much smaller lattices (20x20x20) at the same volume fraction (7.5%) as the main simulation. On this smaller lattice, there were only 150 surfactants in the system. Figure 4.1 shows the resulting size distributions of the micelles for scaled temperatures ranging from $T'' = 2.0$ to $T'' = 2.4$. Each
Figure 4.1 Variation of the micellar size distribution with scaled temperature $T'$ (interaction strength) in a small 20x20x20 system with a surfactant volume fraction of 7.5%. Finite size effects are apparent in the $T' = 2.0$ distribution (see text).

Point on the graph represents an integer aggregation number; no smoothing of the distribution was performed. The definition of an aggregate (micelle) is a collection of surfactant molecules whose tail blocks are touching each other. The values plotted in Figure 4.1 are the volume fraction of surfactant at a given state of aggregation. The average of this distribution therefore corresponds to the weight average aggregation number of the aggregates.
4.3.1 Micelle formation

At the highest temperature $T'' = 2.4$ there is a slight shoulder in the size distribution at an aggregation number of about 20, indicating that micelles are just barely stable at this temperature. For the $H_2T_2$ surfactants used here, this scaled temperature corresponds to a value of $n_r \chi = 10$, where $n_r$ is the number of tail beads. Previous studies [Larson 1992] using surfactants of different sizes at fixed $\chi$ found that micelles did not form at $n_r \chi = 8$, while micelles did form at $n_r \chi = 12$ or higher.

As the temperature is lowered to $T'' = 2.2$, a well-defined peak occurs in the size distribution, indicating separation of the surfactant population into micelles and isolated surfactants or premicelles. As the temperature is lowered further to $T'' = 2.0$ ($n_r \chi = 12$), the separation between premicelles and true micelles becomes more distinct, as exemplified by the deepening of the minimum in the distribution at an aggregation number of about 10. At this temperature, the distribution becomes more polydisperse as the fraction of surfactant in larger aggregates increases. This temperature of $T'' = 2.0$ was chosen for the large simulation. Lowering the temperature further to obtain an even greater separation slows down the simulation dramatically. This slowing down is because the rate of desorption of a monomer from a micelle is a thermally activated process governed by the desorption energy.
4.3.3 Finite size effects

The $T' = 2.0$ distribution has three peaks at aggregation numbers of about 40, 90 and 125. One possible configuration of the 20x20x20 system consists of three aggregates of roughly equal size (ca. 40) in equilibrium with the 25 surfactants with an aggregation number of less than 10 (i.e. the monomers and premicelles). The small but well-defined peak at an aggregation number of about 125 corresponds to configurations of the system wherein a single micelle of aggregation number ca. 125 is in equilibrium with the remaining 25 non-micellar surfactants. Micelles larger than this size are unable to form due to the finite-size of this small simulated system. As we demonstrate below, the peaks at 90 and 125 are due to the small size of the system, and they disappear in the larger simulations.

4.4 Equilibration

4.4.1 Larger system

The main simulation run was conducted on a 60x60x60 lattice with a volume fraction of 7.5% surfactant as before. The simulation was equilibrated
Figure 4.2 Approach to equilibrium for the 60x60x60 surfactant system with a volume fraction of 7.5%. The configurational energy $E(t)$ approaches its equilibrium value (horizontal line) approximately three times faster than the average aggregation number $a(t)$.

for $2.7 \times 10^{10}$ Monte Carlo steps, or $1.67 \times 10^6$ Monte Carlo steps per surfactant bead (MCS/B). The temperature during this time was held constant at $T' = 2.0$. The configurational energy of the system reached its equilibrium value approximately three times faster than did the average aggregation number, see Figure 4.2. Hence, we used the time development of the average aggregation number to determine when the micelles had grown to their equilibrium size. The conformational energy is not as sensitive to the form of
the size distribution, as there is only a relatively small conformational energy
difference between two moderately large aggregates, and the larger aggregate
which they may form by coalescence. Note that in Figure 4.2 there are long
time scale fluctuations in the average aggregation number that are
proportionately much larger than the fluctuations in the configurational
energy.

4.5 Correlations at equilibrium

4.5.1 Autocorrelation function

Once we have determined that the system is at equilibrium, there
remains the question of how long it takes the system to evolve from a given
configuration to a statistically independent configuration. An estimate of this
time is required to determine how long the simulation must run to sample the
complete size distribution representatively. An estimate of this time can be
obtained from the autocorrelation function for the aggregation number of a
surfactant.

\[ \rho_{\infty}(t) = \frac{\langle a(t)a(t'+t) \rangle - \langle a \rangle^2}{\langle a^2 \rangle - \langle a \rangle^2} \]
Figure 4.3 Semi-log plot of the single surfactant-aggregate autocorrelation function $\rho_{sa}(t)$ vs time $t$. The slope long-time linear portion for $t>30,000$ MCS/B is used to determine the characteristic time.

where $a(t)$ is the aggregation number of a surfactant at time $t$ (in MCS/B) and the average is over all surfactants and all times $t'$. The semi-log plot of $\rho_{sa}(t)$ vs time $t$ shown in Figure 4.3 has a long-time linear portion for $t>30,000$ MCS/B. The slope of this portion can be used to determine a characteristic time, $\tau_{sa}$, for the single surfactant-aggregate autocorrelation function. During this time period $\rho_{sa}$ is proportional to $\exp(-t/\tau_{sa})$. The value obtained for $\tau_{sa}$ was found to be 23,900 MCS/B. This time can be related to the rate at which monomers desorb from a micelle.
4.5.2 Representative sampling time

The requirements for obtaining a "smooth" distribution relate to the size of the system and the value for $\tau_{aa}$. An order of magnitude estimate for the time required to obtain a smooth distribution can be determined by considering the fluctuations in the size of a given micelle. A time averaged size distribution of a micelle can be expected to be a Gaussian distribution for short times, centered on the initial size. The width of this peak will increase with time in a manner similar to a diffusive process, so that the time required for the width of the distribution (as measured by the standard deviation of the Gaussian) to reach a value of $\sigma$ will require a time proportional to $\sigma^2 \tau_{aa}$. The time required for the distribution to become smooth is that required for the peaks from separate micelles to overlap. For the peaks to overlap, $\sigma^2$ needs to be made proportional to $\langle \alpha^2 \rangle / N_{mic}$, which is a measure of the mean-square distance between single micelle peaks in the distribution. $N_{mic}$ is the average number of micelles in the system, which can be estimated as $N_\alpha \langle \alpha \rangle$, where $N_\alpha$ is the number of surfactant molecules in the system.

Hence, the time required to obtain a smooth distribution can be estimated as
\[ \tau_{\text{dust}} \sim \frac{\langle a \rangle \langle a^2 \rangle \tau_{\text{dust}}}{N_s}. \]

Using this relation, \( \tau_{\text{dust}} = 1 \times 10^6 \) MCS/B for the large simulation. The smoothness of the distribution in Figure 4.4 can be attributed to the length of the simulation being significantly larger than \( \tau_{\text{dust}} \).

4.6 Micellar size and shape distributions

4.6.1 Size distribution

After the equilibration period, the properties of interest were averaged over a period of 4.583x10^6 MCS/B (c.f. \( \tau_{\text{dust}} \) calculated above). Over this time the system was sampled 11,000 times at regular intervals. The equilibrium size distribution for the 60x60x60 lattice system shown in Figure 4.4 is similar to that shown in Figure 4.1 for the 20x20x20 lattice at the same temperature and concentration. However, the secondary peaks in the size distribution at aggregation number of about 90 and 125 (Figure 4.1) have now disappeared, confirming that these peaks were artifacts of small system size. The system contains 4050 surfactants and ca. 70 aggregates. The distribution is smooth.
Figure 4.4 Micellar size and shape distributions in a larger 60x60x60 system at $T^*=2.0$ with a surfactant volume fraction of 7.5%. $X_g$, $Y_g$, and $Z_g$ are the ordered components of the radius of gyration tensor for aggregates of size $n$.

and has a single peak at an aggregation number of about 40 with a long tail to higher aggregation numbers. This type of distribution is considered to be in qualitative agreement with experiment [Mackie et al. 1996, Wennerstrom and Lindmann 1979, He et al. 1993] and recent lattice simulations [Desplat and Care 1996]. However, recent off-lattice simulations of a similar surfactant did not produce a significant number of aggregates with aggregation numbers larger than ca. 50 [Gottberg et al. 1997].
4.6.2 Shape distribution

To investigate the structure of the micelles the radius of gyration tensor was calculated for the aggregates:

\[
R_g^2 = \begin{pmatrix}
\langle xx \rangle & \langle xy \rangle & \langle xz \rangle \\
\langle yx \rangle & \langle yy \rangle & \langle yz \rangle \\
\langle zx \rangle & \langle zy \rangle & \langle zz \rangle
\end{pmatrix} - \begin{pmatrix}
\langle x \rangle \langle x \rangle & \langle x \rangle \langle y \rangle & \langle x \rangle \langle z \rangle \\
\langle y \rangle \langle x \rangle & \langle y \rangle \langle y \rangle & \langle y \rangle \langle z \rangle \\
\langle z \rangle \langle x \rangle & \langle z \rangle \langle y \rangle & \langle z \rangle \langle z \rangle
\end{pmatrix}
\]

Where \( x, y \) and \( z \) are the Cartesian coordinates of each bead in the surfactant aggregate. This tensor can be diagonalized into the form:

\[
R_g^2 = \begin{pmatrix}
X_g^2 & 0 & 0 \\
0 & Y_g^2 & 0 \\
0 & 0 & Z_g^2
\end{pmatrix}
\]

where the diagonal elements are ordered so that \( X_g > Y_g > Z_g \). This transformation is a rotation of the micelle so that the principal axes of the radius of gyration tensor coincide with the (Cartesian) coordinates axes, and \( X_g^2 \), \( Y_g^2 \) and \( Z_g^2 \) are the ordered eigenvalues of the mean-square radius of gyration tensor. These values characterize the size of the micelles in each of
the principal directions. The root mean square values of the radius of gyration tensor are shown in Figure 4.4.

For comparison, note that for a cylinder of length $2L$ and radius $R$, $Y_g$ and $Z_g$ are equal to each other and proportional to $R$, and $X_g$ is proportional to $L$. The simulation data are consistent with the observation that the peak in the distribution centered at an aggregation number of ca. 40 is comprised of "spherical" micelles. (The instantaneous shapes of the micelles are not perfectly spherical, and the inequality of the three principle components of the radius of gyration tensor is maintained by the ordered averaging.)

In the size range from 40-80 the micelles grow in one direction to form spherically-capped cylinders, with approximately the same minimum dimension as the 40-spheres. As the micelles grow longer, the cylinders become flexible and $X_g$ falls below the linear form expected for rigid cylinders. This flexibility also explains why $Y_g$ and $Z_g$ increase from the constant value expected for rigid cylinders as the micelles become more worm-like. These observations were also confirmed by visualization and inspection of snapshots of the system (e.g. see Figure 4.7).

4.6.3 Theories for spheres and cylinders

The size distributions were fitted to simple theories that assume the
micelles are spherical and cylindrical (for example, see Israelachvili [1991]).

The aggregate distribution is split into two components.

\[
C_N = C_N^s + C_N^c
\]

where \( C_N^s \) is the volume fraction of surfactants in spherical micelles of aggregation number \( N \) and \( C_N^c \) is the volume fraction of surfactants in cylindrical micelles of aggregation number \( N \).

The main peak in the distribution is fitted to a Gaussian distribution which is expected from a simple model\(^{21}\) for spherical micelles:

\[
C_N^s = C_M \exp\left(\frac{-(N - M)^2}{2\sigma^2}\right)
\]

where \( M \) is the most probable aggregation number for the spherical micelles with peak height \( C_M \) and \( \sigma \) is the width of the Gaussian distribution.

The long tail in the distribution is fitted to an exponential distribution\(^{21}\) for cylindrical micelles of the form:

\[
C_N^c = \beta \exp(-\alpha N)f(N)
\]
where \( f(N) \) is a matching function of the form:

\[
f(N) = \begin{cases} 
0 & N \leq M \\
\frac{C_M - C_N^s}{C_M} & N > M 
\end{cases}
\]

The matching function has a value of unity at large aggregation numbers and smoothly takes the cylindrical micelle distribution to zero at an aggregation number of \( M \). At values lower than \( M \) there can be no cylindrical micelles by definition.

Figure 4.5 shows the fit to the data from the 7.5% surfactant volume fraction simulation. For \( n<40 \) the fitted distribution is comprised entirely of spherical micelles. In the range \( n=40 \) to \( n=70 \) the distribution is a mixture of spherical and cylindrical micelles. For \( n>70 \) the fitted distribution is due solely to cylindrical micelles. The inset to Figure 4.5 shows the micelle distribution for \( n \) in the range from 50 to 200 on a semi-log plot. The linear region for \( n>70 \) on the semi-log plot corresponds to the exponential distribution for cylindrical micelles. The simple model used here assumes that the distribution is comprised entirely of fully formed micelles and monomers only. This does not
Figure 4.5 Micellar size distribution fitted to the forms expected for spherical and cylindrical micelles in the 7.5% surfactant volume fraction simulation. Inset is the size distribution in the range n=50 to n=200 on a semi-log plot to show the exponential tail of the cylindrical micelles.

account for the pre-micelles in the aggregation range n=2 to n=40, which are not well-developed spheres.

4.6.4 Micellar growth

Another simulation at a surfactant volume fraction of 15% was also performed on a 60x60x60 lattice. The results were fitted to the same aggregate model and the result is shown in Figure 4.6. Once again the distribution fits
Figure 4.6 Micellar size distribution fitted to the forms expected for spherical and cylindrical micelles in the 15% surfactant volume fraction simulation. Inset is the size distribution in the range $n=50$ to $n=500$ on a semi-log plot to show the exponential tail of the cylindrical micelles.

The cylindrical micelle model for $n > 70$ (see inset). As the surfactant concentration is increased the distribution becomes broader, with the excess surfactant moving into the long cylindrical tail of the distribution. A number of micelles were extracted from this system and are shown in Figure 4.7. These micelles were oriented to have their two largest dimensions in the plane of the page. As can be seen, the larger micelles are not simply colliding spherical micelles but are fully developed flexible worm-like micelles that may have one
Figure 4.7 Micelles taken from a single snapshot of the 15% surfactant volume simulation. They have aggregation numbers of 42, 91, 125 and 269 (starting at the lower left and proceeding clockwise).

or more branch-points. The \( n=269 \) micelle has a single branch-point and was the largest aggregate at the time the snapshot was taken. The fact that the
larger aggregates are not exactly the rigid cylinders assumed in the theory does not appear to affect the fits in Figs 3 and 4 significantly. The semi-log plots confirm the expected exponential decay to a good approximation.

4.7 Conclusion

Equilibration of simulated micellar systems is better monitored using the average aggregate size rather than the configurational energy of the system. The surfactant aggregate autocorrelation function can be used to estimate how long a simulation must be run to sample the equilibrium configuration space of the system representatively. Thermodynamic models of micelles usually assume that the micelles have a well-defined geometric shape. Our results confirm this assumption for self-assembled micellar aggregates, whose size distributions are found to be consistent with the simple thermodynamic models for micelles of spherical and cylindrical shape in equilibrium with each other.
Chapter 5: Solubilization of oil in micelles

5.1 Introduction

Dilute solutions of surfactants are commonly used to solubilize hydrophobic compounds in aqueous solution. A familiar example is dishwashing, where household detergents (surfactants) are used to dissolve oil and grease in water. The ability of surface-active agents to solubilize hydrophobic molecules is central to understanding an extremely wide range of natural systems from subcellular biological to transcontinental geological systems [Gelbart and Ben-Shaul 1996]. Industrial applications range from enhanced oil recovery and cleanup of ground water contaminated with hydrophobic pollutants, to stabilizing cosmetics and foodstuffs. Medical applications range from drug delivery to providing understanding of basic biological processes.

Recently, molecular dynamics simulations [Karaborni et al. 1993, 1994, Esselink et al. 1994] and experiments [McClements and Dungan 1995, Dam et al. 1996, Weiss et al. 1997] have been conducted to investigate the dynamics of
oil solubilization by surfactant solutions. In the simulations, three mechanisms were identified for transport of oil molecules from a (bulk) oil droplet to the hydrophobic cores of the micelles [Karaborni et al. 1993]. If a surfactant coated oil droplet is considered to be a "micelle", then the mechanisms for transfer of oil from one micelle to another can be summarized as "desorption followed by capture" and "micellar coalescence/breakup". In the first, an oil molecule desorbs from a micelle and diffuses to another micelle surface where it is captured in its hydrophobic region. This mechanism is most important for small oil molecules whose solubility in (pure) water is not vanishingly small. The second mechanism occurs when two micelles collide so that their hydrophobic regions touch and oil molecules can be exchanged between them without the oil having to desorb into the water. If the two micelles break apart quickly then a soft collision (as discussed by [Karaborni et al. 1993]) has occurred.

The simulations [Karaborni et al. 1993, 1994, Esselink et al. 1994] were of the initial solubilization process, and hence were far from equilibrium. Hence, the effect of the solubilized oil on equilibrium micellar structure was not investigated. Extensive equilibrium studies of oil-water-surfactant systems have been conducted by Larson in recent years [Larson 1988, 1989, 1992, 1994, 1996] using a lattice model. The rich phase behavior of (mainly) ordered condensed phases of systems with high (>20%) surfactant concentrations was
successfully demonstrated using this model. The structure and properties of disordered systems with low oil and surfactant concentrations has gone largely unexplored.

In this chapter, a lattice model similar to that of Larson [1988, 1989, 1992, 1994, 1996] is used to investigate, for the first time, the effect of small amounts of oil on the equilibrium microstructure of dilute (7.5% by volume) surfactant solutions. A new thermodynamic ensemble is introduced for these simulations and it is used to guarantee that the equilibrium microemulsion is stable with respect to emulsification failure (appearance of a bulk oil phase), and the partition coefficient between the micellar solution and a bulk aqueous phase is measured directly.

5.2 The simulated system

5.2.1 Two-box simulation technique

The main simulation box (the micelle box) is a face centered cubic (fcc) lattice the usual periodic boundary conditions applied (see Figure 5.1). The lattice contains a symmetric H₂T₂ surfactant, which has two "hydrophilic" head beads (H) and two "hydrophobic" tail beads (T). Single-bead “oil”
Figure 5.1 Two-box simulation within the Helmholtz ensemble. The water box contains water (not shown) and oil (black beads). The micelle box contains oil, water and H₂T₂ surfactant (The hydrophilic head beads (H) are white and the hydrophobic tail beads (T) are gray). Oil and water molecules can exchange between the two simulation boxes with the constraint that the volume of each box does not change.
molecules (O) are also present and the remainder of the lattice is filled with water beads (W) (not shown in the figures). The oil molecules interact with the other beads as if they were hydrophobic tail beads. The hydrophilic/hydrophobic nearest neighbor interactions are set to $\epsilon$ and all other interactions are set to zero as has been done previously in chapters 3 and 4 [Nelson et al. 1997b, 1997c]. This makes the oil a good (athermal) solvent for the tail blocks of the surfactant (e.g. hexane and a C$_{12}$ surfactant tail) and the water a good solvent for the head beads. The general reptation method of chapter 2 and [Nelson et al. 1997a] is used to make configurational changes in the simulation. A combination of the bead and vacancy algorithms is used to move the oil and surfactant molecules through the lattice.

5.2.2 Adding oil to the simulation

The simulation in chapter 4 used the bead algorithm of the general reptation method to move the surfactants through the lattice. A successful move produces displacement of the water beads that are assumed to fill the remainder of the lattice. When single-bead oil molecules are added to this system, they can be moved by the bead algorithm as if they were vacancies. The bead algorithm for moving the surfactant does not provide for movement of oil beads that are not adjacent to surfactant molecules. Hence, the oil beads
must be explicitly moved through the lattice by swapping places with neighboring water beads so that they can diffuse through the water phase. If an oil bead attempts to move to a site occupied by a surfactant molecule, the vacancy algorithm is used to move the oil bead and the surfactant, with the oil bead playing the role of a vacancy.

5.3 The Helmholtz Ensemble

In addition to the micelle box, a water box is set up that is of the same size as the micelle box (with periodic boundary conditions) but contains no surfactant (Figure 5.1). The oil beads in the water box are made to move by exchanging places with neighboring water beads. Oil beads, in the micelle box and the water box, are also selected randomly for exchange with a randomly selected water bead in the other simulation box. Boltzmann weighting factors are calculated for the initial and final states of all trial moves so that the Metropolis sampling technique [Metropolis et al. 1953] can be applied, and the chemical potentials of the oil and the water are the same in both boxes. Although the two simulation boxes are not in physical contact, this arrangement is thermodynamically equivalent to having them in contact but separated by a rigid diathermal semi-permeable membrane that allows water and oil to pass but is impermeable to the surfactant. The term "Helmholz Ensemble" is introduced for this method here.
If volume moves are added to the simulation method described above, with the constraint that the pressure difference between the boxes \( \Pi = P_1 - P_2 \) is specified, then the ensemble becomes the thermodynamically distinct Gibbs Ensemble developed by Panagiotopoulos [1987a, 1987b, Panagiotopoulos et al. 1988]. In the Gibbs ensemble, it is only the total volume of the two boxes \( V = V_1 + V_2 \) that is held constant. In the isothermal-isobaric Gibbs ensemble both boxes are held at a specified pressure \( P = P_1 = P_2 \). Thus, in the Gibbs ensemble, the pair of variables that are specified for each box is \((T, P)\) and in the Helmholtz ensemble, the independent pair for each box is \((T, V)\), (just as for the Helmholtz free energy). This distinction can also be illustrated by considering the limiting case in which one of the boxes is infinite in size. Under these limiting conditions: the Gibbs ensemble becomes equivalent to the \((\mu, P, T)\) ensemble for box 1, if box 2 is infinite; while the Helmholtz ensemble becomes equivalent to the \((\mu, V, T)\) ensemble for box 1, if box 2 is infinite.

5.3.1 Applicability to other systems

The Helmholtz ensemble is well suited to use with lattice models but is not limited to them. The only requirement is that the boxes have constant volume. Thus extension to off lattice systems is straightforward procedurally. For lattice systems, the Gibbs ensemble is troublesome to implement because
small changes in system volume are desired, but it is difficult to add less than an entire plane of lattice sites to the box size. The Helmholtz ensemble is straightforward to implement in lattice simulations because no change in box volume is required. In addition, it can be easily applied to molecules larger than a single lattice site if there is a monomeric solvent (or voids) present. For example, we could double the molecular weight of our oil molecule to be two connected oil beads. The constant volume exchange between the water box and the micelle box can be achieved by selecting an oil molecule in one box and two adjacent water beads in the other box and the simulation method can proceed as before.

5.3.2 Comparison with grand-canonical ensemble

An alternative approach that has been used in similar surfactant systems [Larson 1996] employs a single simulation box in the grand-canonical ensemble. In that approach, oil beads are converted into water beads and *vice versa* using a Boltzmann weight that has the desired chemical potential difference between oil and water $\Delta \mu$ added to it. However, this open system method does not work well for chemical potential differences close to that between bulk water and oil phases. Under these conditions, the system is able to fluctuate between the mostly water phase on one side of the phase diagram
and the mostly oil phase on the other side of the phase diagram causing large uncertainties in measured properties. An additional complication is that one must provide the desired chemical potential difference as an input to the simulation.

5.3.3 Emulsification failure

Oil/water concentration fluctuations in the two-box simulation are limited by the constraint that the amount of oil/water in the combined system is constant throughout a simulation. This has the advantage that we can approach the phase boundary closely without sampling the two phases that can coexist across a tie line on the phase diagram. With this method, it is also possible to move past the coexistence line into a supersaturated region of the phase diagram, where the concentration of the oil in the water box is higher than its equilibrium solubility.

The water box is a simple oil-water system with no surfactant. If the measured concentration of oil in the water box is below the equilibrium oil solubility, then we are assured that the micelle box is a stable microemulsion not subject to "emulsification failure". Emulsification failure occurs [Gelbart and Ben-Shaul 1996] when all the oil in an emulsion cannot be solubilized in the water phase so that a bulk phase of oil coexists with the microemulsion at
\textit{equilibrium}. In this study we are also interested in determining the partition coefficient of the oil between the micellar system and a bulk water phase. The Helmholtz ensemble has the advantage that the concentration of oil in each phase can be measured directly, to calculate the partition coefficient.

\section*{5.4 Simulation results}

\subsection*{5.4.1 Equilibrium oil solubility}

The free energy of mixing for a dilute solution of oil in water with concentration $x$ on a lattice can be written as:

$$\frac{\Delta G_{\text{mix}}}{k_B T} = \chi x (1-x) + x \ln(x) + (1-x) \ln(1-x)$$

using the mean-field approximation for the enthalpy of mixing and the ideal solution expression for the entropy of mixing; $k_B$ is the Boltzmann constant, $T$ is the temperature and $\chi = z \varepsilon / k_B T$ is the Flory-Huggins $\chi$-parameter for our lattice system with coordination number $z$ and interaction strength $\varepsilon$. For all the simulations reported here, $\chi=6$, and the free energy has a minimum at $x=0.00255$, which is the equilibrium solubility of the oil in water. The mean-
field and ideal entropy of mixing approximations are justified a posteriori by the low value of $x$ obtained (both these approximations become very good at low concentrations).

The Helmholtz ensemble can easily be applied to this binary system of oil and water beads. The phase equilibrium between the two bulk phases can be investigated by filling the main simulation box with oil (the oil box) and filling the water box with pure water. The simulation proceeds as described above with the simplification that there is no surfactant in the oil (micelle) box. The equilibrium oil concentration (solubility) of the oil in water was determined and a value of $x=0.00254 \pm 0.0001$ was obtained (c.f. theoretical prediction of $x=0.00255$), confirming that the Helmholtz ensemble can be used to investigate bulk phase equilibria.

This oil/water phase equilibrium simulation is a simple two component system. However, the identical simulation can be reinterpreted as a single component system if the water beads are interpreted as a vacuum. The simulation is then of a condensed (liquid) phase in equilibrium with its own vapor. The only particles that transfer between the boxes in this case are the oil particles (a void is left behind when an oil particle is transferred from one box to the other).
5.4.2 Equilibration

All the simulations reported in this chapter were conducted with a surfactant volume fraction of 7.5% - the same value as was used for the more dilute system discussed in chapter 4 [Nelson et al. 1997b]. The amount of oil in the combined two-box system was the only independent variable that was varied. A preliminary simulation was conducted on a 40x40x40 lattice simulation with 9600 oil molecules (15% of the volume of the micelle box) and 1200 surfactant molecules (7.5% of the volume of the micelle box). This system was equilibrated until a single oil droplet formed in the micelle box. The oil content in this system was then adjusted as described below to generate initial configurations with large aggregates. The advantage of starting with large aggregates is that their stability can be determined for various solution conditions without having to wait for them to form spontaneously.

The amount of oil in the micelle box was reduced by performing simulations in which oil transferred to the water box could not return to the micelle box. Once the desired oil concentration in the micelle box was reached, the surplus oil in the water box was removed from the simulation. Equilibration then proceeded with the oil particles being allowed to exchange between the two simulation boxes in the normal way prescribed by the Helmholtz ensemble method. During equilibration, the instantaneous average
Figure 5.2 Approach to equilibrium of the micellar aggregation state of a two-box simulation with an oil/surfactant molecular ratio of 1/10. The dashed line indicates the equilibrium value (see text).

The aggregation number of the system was monitored to gauge when equilibrium was reached. As discussed in chapter 4 and [Nelson et al. 1997b], the time development of the average aggregation number of the system is significantly more sensitive to deviations from equilibrium than the configurational energy.

Figure 5.2 shows how the aggregation state of a system with 120 oil molecules develops with time. The initial large aggregates break up spontaneously into smaller micelles that diffuse apart and spread out randomly throughout the micelle box until the equilibrium value of 55.8 (dashed line) is reached at about $2 \times 10^5$ Monte Carlo steps per (oil or
surfactant) bead (MCS/B). The large jumps in Figure 5.2 illustrate that the micellar coalescence/breakup mechanism for oil transport (observed in the previous non-equilibrium simulations [Karaborni et al. 1993, 1994, Esselink et al. 1994]), also operates in our model system. The desorption followed by capture mechanism is also possible as the oil has a significant solubility in water. The main simulation was started using the ultimate configuration of the equilibration simulation and was run for much longer (10⁷ MCS/B), to collect the equilibrium data (such as the dashed line in Figure 5.2).

5.4.3 Oil partitioning

The ability of surfactant solutions to dissolve more oil than aqueous solutions is quantified by the partition coefficient $K$

$$K = \frac{c_m}{c_w}$$

where $c_m$ is the concentration of oil in the micelle box and $c_w$ is the concentration of oil in the water box. The partition coefficient is shown in Figure 5.3 as a function of oil concentration for the systems investigated. Small system (20x20x20) values are shown as squares and large system (40x40x40) values are shown as circles. Also shown is the total oil/surfactant
Figure 5.3 Partition coefficient of oil between a 7.5% surfactant volume micellar solution and bulk water phase, as a function of oil concentration in the water phase. Circles are from a larger system (40x40x40) and squares are from a smaller system (20x20x20). Also shown are the total oil/surfactant molecular ratios in the two-box simulation, which can be used as a key to go between discussions where we use the oil concentration in the water box to characterize the system and those where we use the total oil/surfactant ratio. The vertical line indicates the phase boundary for emulsification failure.
molecule. This makes the volume fraction of surfactant tails and oil molecules approximately equal in the micelle box.

The behavior shown in Figure 5.3 is comparable to that found experimentally [Christian and Scamehorn 1989]. At low oil concentrations, the partition coefficient increases slowly with \( c_w \), but it increases rapidly as \( c_w \) approaches the bulk solubility. The large values of the partition coefficient indicate that the surfactant system is able to solubilize many times more oil than the bulk water phase in the water box. As we will show later, most of the oil is contained within the oily region formed by the tails of the micelles.

### 5.4.4 Low oil concentrations

Figure 5.4 shows the size distributions of 40x40x40 simulations of dilute oil-water-surfactant systems with small amounts of added oil. The ratios of oil to surfactant in the combined two-box system range from zero (results from ref. [Nelson et al. 1997b]) to a ratio of 2/5. The definition of an aggregate is modified from that used in ref. [Nelson et al. 1997b] to account for the presence of oil molecules. An aggregate is now defined as a collection of oily surfactant tails and oil molecules that are touching each other. It is no longer necessary for all the surfactant tails of an aggregate to touch each other.
Figure 5.4 Changes in the micellar size distribution as small amounts of oil are added. Numerical values indicate the oil/surfactant molecular ratio in the two-box simulation.

directly, they could now be joined by a connected region of oil molecules. The aggregation number of an aggregate is still defined as the number of surfactant molecules in the aggregate.

The peak in the distributions shifts to higher aggregation numbers, indicating that the spherical aggregates become larger as oil is added. This is expected and the oily core of the micelle is expanded by the absorbed oil, thereby increasing the surface area available for the surfactant molecules. The height of the peak decreases with oil concentration while the width (full width
Figure 5.5 Changes in the micellar size distribution as larger amounts of oil are added. Numerical values indicate the oil/surfactant molecular ratio in the two-box simulation.

at half maximum) increases, and there is an increasing proportion of surfactant in the tail portion of the distribution \((n \geq 100)\) as the amount of added oil increases. As we saw in chapter 4, this exponential tail contains cylindrical micelles [Nelson et al. 1997b]. All these changes are consistent with the swelling and growth of micelles upon addition of small amounts of oil.
5.4.5 Dramatic micellar growth

Adding more oil to the system significantly alters the micellar size distribution. Results from systems with oil/surfactant ratios of 2/3 and 1/1 are shown in Figure 5.5. The scale of the horizontal axis has been doubled because there are now a significant number of aggregates with aggregation numbers larger than 200.

Figure 5.6 shows only the data from the simulation with equal numbers of oil and surfactant molecules together with the 1/10 oil/surfactant ratio simulation. The scale of the horizontal axis has been increased six-fold (relative to Figure 5.4) to show the long tail of the 1/1 distribution, which has an average aggregation number of about 300. There is a large amount of scatter in the distribution, so that the true shape of the size distribution can not be determined precisely. For example, the width of the peak at low aggregation numbers is not clear in the figure. This scatter is caused primarily by the width of the distribution. As we have seen previously in chapter 4 [Nelson et al. 1997b], the time required to obtain a smooth distribution can be estimated as

\[ \tau_{\text{dist}} \sim \frac{\langle a \rangle \langle a^2 \rangle \tau_{\text{aa}}}{N_s}, \]
Figure 5.6 Comparison of micellar size distributions in two-box simulations with oil/surfactant molecular ratios of 1/10 and 1/1.

where $\langle a \rangle$ is the average aggregation number, $\langle a^2 \rangle$ is the mean-square aggregation number $\tau_{aa}$ is the characteristic time for desorption of a monomer from a micelle and $N_s$ is the number of surfactant molecules in the simulation.

If we compare the simulations with oil/surfactant ratios of 1/10 and unity (see Figure 5.6), we find that $N_s$ is the same for both, $\tau_{aa}$ has similar values, but $\langle a \rangle$ is over 5 times larger and $\langle a^2 \rangle$ is over 30 times larger. Hence, we can estimate that the higher oil concentration simulation will need to execute for more than 150 times longer to obtain the same smoothness in the
size distribution as the lower oil concentration simulation. The data in Figure 5.6 were generated from $5 \times 10^{10}$ Monte Carlo steps (or $8.3 \times 10^6$ MCS/B for the oil/surfactant=1/1 simulation) and took thirteen days of execution time on kumera.mit.edu (an IBM RS/6000 model 370). Hence, we estimate that a smooth distribution would require five years to be produced using the same machine!

5.4.6 Micellar shape distribution

The shapes of the aggregates of different sizes can be determined from the principal moments of the radius of gyration tensor (see chapter 4 and [Nelson et al. 1997b]). The oil beads are included in the determination of the average shape of the aggregates. Figure 5.7 shows the shape distribution obtained from the simulation with an oil/surfactant ratio of 1/1. True micelles begin to form at an aggregation number of about 50 and the three components of the radius of gyration tensor are approximately equal, indicating that these small aggregates are roughly spherical. The instantaneous shapes of the micelles are not perfectly spherical and the principle components are ordered before averaging, so only small fluctuations in shape are required to account for the differences between the three values in Figure 5.7 at an aggregation number of about 50.
Figure 5.7 Micellar shape distributions in a two-box simulation with an oil/surfactant molecular ratio of 1/1. \( X_g, Y_g \) and \( Z_g \) are the ordered principle components of the radius of gyration tensor.

In the size range from 50-300, the micelles grow in one direction to form spherically capped cylinders, with approximately the same minimum dimension as the 56-spheres. For comparison, note that for a cylinder of length \( 2L \) and radius \( R \), \( Y_g \) and \( Z_g \) are equal to each other and are proportional to \( R \), while \( X_g \) is proportional to \( L \). As the micelles grow longer, the cylinders become flexible and \( X_g \) falls below the linear form expected for rigid cylinders. This flexibility also explains why \( Y_g \) and \( Z_g \) increase from the constant value
Figure 5.8 Snapshot of a micellar aggregate (n=288) taken from the final configuration of the two-box simulation with an oil/surfactant molecular ratio of 1/1. Also shown are single surfactant and oil molecules. The darkest beads are oil, the lightest are surfactant head beads, and the intermediate shade represents surfactant tail beads.
Figure 5.9 Snapshot of a branched micellar aggregate (n=429) taken from the final configuration of the two-box simulation with an oil/surfactant molecular ratio of 1/1. The colors are the same as in Figure 5.8.

expected for rigid cylinders as the micelles become more worm-like. These
Figure 5.10 An alternate view of the micellar aggregate shown in Figure 5.9.

observations were also confirmed by visualization and inspection of snapshots of the system (e.g. see Figures 5.8, 5.9 and 5.10). As the size of the micelles increases further, they become more thread-like and may contain one or more branch points. The largest aggregate in Figures 5.9 and 5.10 contains 429
surfactant molecules and has a well-defined branch point.

The size distributions of the micelles containing oil are qualitatively similar to the distributions in chapter 4 for surfactant-only micelles [Nelson et al. 1997b], having a peak of spherical micelles in equilibrium with an exponential tail of cylindrical micelles. In the surfactant only systems, the aggregation number of the spherical peak remains approximately constant as the micelles grow upon addition of more surfactant, whereas the spherical peak shifts to higher aggregation numbers as oil is added to the micelles here. Another difference is that adding oil to a 7.5% surfactant solution produces greater micellar growth than adding an equal concentration of surfactant molecules. For example, the average aggregation number of the 1/1 oil/surfactant system is more than three times that of the 15% surfactant-only solution in chapter 4 [Nelson et al. 1997b], and the mean-square aggregation number is more than ten times larger.

5.4.7 Prediction of oil location in micelles

It has long been recognized that oil molecules mix with the tails of surfactant monolayers [Fowkes 1962]. More recently, Aveyard et al. [1990] proposed a physical model of oil solubilization in surfactant monolayers based on indirect experimental evidence. The model is based on ideas of Mitchell and
Ninham [1981], in which effective cross-sectional areas $a_H$ and $a_T$ are assigned to the head and tail of the surfactant. A packing factor may then be defined as

$$p = \frac{a_T}{a_H}.$$

The cross-sectional areas, and the packing factor $P$, can be affected by the local environment of the head and tail groups. Hence, $P$ is not determined solely by molecular structure of the surfactant. (If this were the case, $P$ would be exactly one for our symmetric $H_2T_2$ surfactant.)

As an example, consider our symmetric surfactant adsorbed at a planar interface between oil and water. The surfactant is symmetric and the solution conditions for the head and tail are equivalent (good solvent conditions), so the packing factor will be unity. However, for a surfactant located in a surfactant-only micelle, the heads are in a good solvent but the tails are in a concentrated solution (or melt) of themselves (with higher concentration). Hence, the tails have an effective cross-sectional area that is lower than that of the heads and the packing factor is less than one, indicating that the surfactant prefers a positive curvature. As oil is added to the tail region, the concentration of the tail beads is gradually reduced, and the effective cross-sectional area increases until complete saturation occurs and a planar interface is preferred.
Figure 5.11 Cloud points of 0.5 wt. % aqueous solutions of \( \text{C}_{12}\text{E}_6 \) as a function of nonane added. Data from Aveyard et al. [1990].

These ideas were used to provide a molecular level explanation for the change in cloud point of dilute solutions of the nonionic surfactant \( \text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_6\text{OH} \) (commonly referred to as \( \text{C}_{12}\text{E}_6 \)) upon addition of the oil nonane. The concentration of the \( \text{C}_{12}\text{E}_6 \) surfactant was held constant throughout the experiments, as it is in our simulations. As oil is added to the surfactant solution, the cloud point drops sharply until a minimum is reached at a relatively low oil/surfactant ratio (Figure 5.11). The cloud point then increases and levels off as saturation is approached.
The molecular level explanation proposed by Aveyard et al. [1990] for this behavior is as follows. The oil is initially solubilized in the tail regions of the micelles, increasing the value of $P$ towards unity. The micelles then become more asymmetrical (cylindrical) to reduce the overall surface curvature. This results in increased inter-micellar attractions that reduce the cloud point of the solution. As more oil is added, the micelles begin to form a central pool of oil and the aggregates are transformed into spherical microemulsion droplets with an accompanying increase in the cloud point. No direct microscopic evidence for this proposal was given. Aveyard et al. [1990] also discussed the effect of alkane length. Longer alkanes tend only to give an increase in cloud point with concentration, indicating that alkane penetration into the tail region of the interfacial layer is stronger for shorter alkanes.

Our model system has no long-range attractive forces between the micelles. Hence, the experimental cloud point behavior is unlikely to be reproducible in our simulations. However, the structural changes are believed to be due to local packing effects in the oily tail region of the micelles, these effects have been shown to be reproducible in our simple model system as discussed above.
5.4.8 Observed location of oil in micelles

The number of oil molecules in micelles of different sizes is shown in Figure 5.12. The amount of oil solubilized in the micelles is directly proportional to the surfactant aggregation number for aggregates larger than about 70. Hence, the oil is absorbed uniformly into the tails of micelles of all sizes. This means that the effective cross-sectional area of the tail groups $a_r$ is increased for all aggregates, which explains the growth of the cylindrical micelles to reduce interfacial curvature.

These simulation results thus provide direct confirmation for the microscopic model of aggregate growth upon oil solubilization proposed by Aveyard et al. [1990]. They also serve to confirm that the particular chemical details of the solute, solvent and surfactant system studied by Aveyard et al. are not necessary for micellar growth, but rather, it can be caused by simple (universal) packing changes in the surfactant tail region of the micelles upon addition of low molecular weight oil that is a good solvent for the tails.

It is also clear from Figure 5.12 that the tail region of the micelles is not yet saturated with oil. If the tail regions were saturated, well-defined oil pools would form in the larger aggregates. These spherical aggregates would then have larger oil to surfactant ratios than indicated by the linear fit shown in
Figure 5.12 Distribution of oil molecules in micellar aggregates of different sizes in the two-box simulation with an oil/surfactant molecular ratio of 1/1. The straight line is a least squares fit to the data.

...the figure. Hence, the simulations results lie within the initial downward portion of the cloud point curve of Figure 5.11 that was attributed to asymmetric micellar growth. The subsequent development of large spherical aggregates is not observable in our small scale simulations due to finite size effects.

5.4.9 Emulsions and finite-size effects

The 1/1 oil/surfactant ratio simulation discussed above is the highest oil
concentration simulation that does not appear to be affected significantly by the finite size of the simulation box. (This is not completely certain due to the large statistical uncertainties in its aggregate size distribution shown in Figure 5.6.) Finite size effects in the simulation of self-assembling oil-water-surfactant systems are particularly troublesome. The obvious problem is that the largest aggregate that can form is determined by the number of molecules in the box. This can be a significant limitation if many aggregates of large size are expected at equilibrium. A more subtle effect is that the maximum aggregate surface area to volume ratio may be limited by the size of the simulation box (at fixed composition).

As an example of this, consider the preliminary simulation used here to generate initial configurations. The 9600 oil molecule simulation suffers from both these finite size effects. Firstly, the surfactant-coated oil droplet is the largest possible in a 7.5% surfactant, 15% oil system of this size, so no information on the equilibrium size distribution is available, except the trivial fact that aggregates of at least this size are possible. Secondly, and more significantly, the oil droplet is not representative of any equilibrium microemulsion droplet at the same solution conditions. The small simulation box simply does not contain enough surfactant molecules to coat the outside of a 9600 molecule oil droplet properly. One indication of this is that the oil concentration in the water box (0.00267) is significantly higher than the
equilibrium oil solubility (0.00255).

5.4.10 Monomer concentrations (cmc)

It is a commonly made assumption in theories of micellar systems and microemulsions that the concentration of monomers (surfactants with an aggregation number of unity) in the water micro-phase is constant [Gelbart and Ben-Shaul 1996], [Israelachvili 1991]. Figure 5.13 shows that the monomer concentration of our model decreases significantly as the oil concentration in the water box increases.

The decrease in the bulk monomer concentration is not due to excluded volume effects as the volume fraction of the aggregates only changes slightly. The decrease reflects the change in aggregate geometry with oil concentration. The larger aggregates at higher oil concentrations have lower average curvature due to micellar growth. Increasing the length of the cylindrical micelles reduces the fraction of surfactant in the higher curvature spherical end caps. In addition, the minimum dimension of the aggregates increases as more oil is added. Both these effects serve to lower the chemical potential of the surfactant, which prefers low curvature interfaces. This is reflected in the lowering of the monomer concentration.
Figure 5.13 Surfactant monomer concentration of micellar systems (of constant total surfactant concentration) as a function of oil concentration in the bulk aqueous phase. Squares are from (20x20x20) systems and circles are from (40x40x40) systems. The vertical line indicates the phase boundary for emulsification failure.

An additional contributing factor is that the oil molecules are single beads with no water loving head group attached. This means that the oil beads are able to move freely throughout the interior and surface of the oily core of the micelle, which serves to increase the packing efficiency of the oily core and help smooth any roughness in the surface. Longer oil molecules are perhaps less likely to be able to fill small defects efficiently in the interior or surface of
the oily tail region. Finally, these results indicate that the critical micellar concentration (cmc) or critical microemulsion concentration (cµc) of our short surfactant decreases strongly with increasing oil concentration.

5.4.11 Single site representation of oil

Recently, the appropriateness of a single site representation of oil molecules in lattice models of oil-water-surfactant systems was questioned [Larson 1996]. It was speculated that this representation is such an extreme divergence from reality that even qualitative comparisons could not be made to the phase behavior of real systems when oil is present. In contrast, the present simulation results serve to confirm that a single site representation (of low molecular weight oil) is sufficient to reproduce qualitatively, experimentally-inferred microstructural changes in dilute nonionic surfactant solutions as small amounts of low molecular weight oil are added to the system.

5.5 Conclusion

When oil is added to a surfactant simulation, there is an additional degree of freedom that may allow coexisting phases to appear. To reduce the chance of this occurring, and to measure the oil partition coefficient between
the micellar phase and a bulk aqueous solution, a two-box simulation method has been developed. This method utilizes a thermodynamic ensemble for simulations, which has been termed the "Helmholtz Ensemble". The name signifies that for each box the variables \((T,V)\) are specified. This ensemble has been shown to be useful for investigating coexisting phases in lattice simulations and is also applicable to off-lattice simulations. The Helmholtz ensemble used here has two constant volume boxes at the same temperature: a micelle box containing oil, water and surfactant; and a water box containing oil and water but no surfactant. In the simulation, oil and water can exchange between the two boxes at constant system volume.

A significant advantage of the Helmholtz ensemble is that the equilibrium concentration of oil in the water box, and hence the partition coefficient, can be measured directly. This ensemble provides a valuable means for probing the chemical potential of oil in micellar systems, equilibrium microemulsions and nonequilibrium emulsion droplets. A simple test for emulsification failure (or the appearance of a bulk oil phase) in the oil-in-water surfactant system is whether the concentration of oil in the water box is above the limit of solubility. As long as this concentration is below the solubility limit, it is guaranteed that the system is stable with respect to emulsification failure. Such guarantees concerning phase behavior are
impossible using the traditional single box simulation method in the canonical ensemble.

The effect of solubilized oil on the equilibrium microstructure of a dilute micellar system is investigated for the first time via simulation. It is found that small amounts of solubilized oil can produce dramatic one-dimensional growth of the micelles. Asymmetric growth upon addition of oil, has previously been proposed as an explanation for experimentally observed changes in the macroscopic phase behavior of dilute surfactant solutions as oil was added. The proposal was based on a phenomenological model of surfactant behavior based on the "packing factor" (or effective intrinsic curvature) but it was not based on any direct measurements of the changes in the microstructure of the surfactant solutions. The simulation results therefore serve to confirm not only the microscopic interpretation of the macroscopic phase behavior, but also the phenomenological model upon which the microscopic interpretation was based. This phenomenological model does not yet appear to have gained widespread use.

According to this phenomenological model (as confirmed via simulation), oil added to the solution is preferentially absorbed into the oily tail region of the micelles. This reduces the local tail concentration in the oily core of the micelle, and thus increases the effective cross-sectional area of the tails. The packing factor is then increased and the surfactant prefers interfaces with

217
lower overall curvature. Consequently, the micelles grow in one dimension to become the elongated worm-like structures observed in the simulation.

This growth is quite dramatic and the average micellar size increases many-fold until the aggregates become branched worm- or thread-like micelles. The simulation results also serve to confirm that micellar growth is not necessarily due to the precise chemical nature of the surfactant, oil or solvent, but rather, it can be caused by simple (universal) packing changes in the surfactant tail region of the micelles as small oil molecules (that are a good solvent for the surfactant tails) are added to the solution.
Chapter 6: Summary and recommendations

6.1 Summary*

Self-assembled polymer and surfactant systems can take milliseconds or longer to reach equilibrium. The typical size of the self-assembled aggregates (micelles) is from tens to thousands of molecules, or even higher. These two factors combine to provide a significant challenge, if one is to investigate the collective behavior of large numbers of molecules, and the structures that they spontaneously form at equilibrium. The surfactant systems form "complex fluids" that have rich phase behavior due to the wide variety of aggregate microstructures that they form. In this thesis, these challenges are met by adopting a simplified lattice model, in which the intermolecular and intramolecular interactions are reduced to a single interaction parameter. The only inputs to the simulation are the structure of the molecules and their interactions, the concentrations in the system, and its temperature. No

* an "Illustrated Summary" is available on the world wide web at http://www.circle4.com/phd/
assumptions need to be made \textit{a priori} about the aggregate sizes or shapes.

An alternate form of the general reptation algorithm is developed for moving polymers in lattice Monte Carlo simulations. This algorithm is shown to be ideal for simulating polymer and surfactant systems. The computational efficiency of the algorithm is shown to increase with system density, in contrast to earlier algorithms that slow down dramatically in dense polymer systems. This new algorithm is rigorously tested by simulating two-dimensional athermal polymer systems (good solvent conditions). The new algorithm is shown to quantitatively reproduce known polymer dimensions - to an accuracy of better than one part in a thousand. The algorithm is then used to investigate the self-segregation of two-dimensional polymers in concentrated solutions or melts. This collective behavior cannot be explained by traditional polymer theories that neglect the effects of excluded volume in concentrated systems. The segregation is caused by entropic effects that occur because of the excluded volume condition. The polymer dimensions are measured at all concentrations and new empirical formulae are provided. These are the first formulae that successfully predict the dimensions of polymers of finite length at all concentrations.

The conformations and self-assembly of three-dimensional (AB)$_n$ star block copolymers in dilute aqueous solution are then investigated. The A and B blocks in each arm can be either hydrophilic or hydrophobic. The
hydrophobic-core stars, in which the inner blocks are hydrophobic and the outer blocks are hydrophilic, are found to behave as predicted by current theoretical models. However, hydrophilic-core stars, in which the inner blocks are hydrophilic and the outer blocks are hydrophobic, are found to behave in a manner incompatible with current theoretical treatments. The outer hydrophobic blocks aggregate into one or more globules away from the center of the star, thus breaking the spherical symmetry assumed in the theoretical treatments. Entropic effects in the core of the star cause the globules to separate from one another so that the three-globule conformation has a planar triangular arrangement of the globules, with the star's center located in the middle of the triangle. Specially prepared, low-energy, single-globule conformations, of the forty-two armed hydrophilic-core star were also investigated. It was found that while they were stable at low temperatures (high $\chi$), they underwent a spontaneous and irreversible decomposition into two-globule and then three-globule conformations as the temperature was raised.

This type of star polymer has not yet been synthesized, but has been shown to have many interesting properties. In separation processes, drug delivery and other biological applications, its properties as a macromolecular amphiphile could prove useful. The molecule can undergo a dramatic change in size as the temperature is increased (or the solution conditions changed) so
that it has potential applications as a viscosity modifier. Finally, because of the well-defined shape of the multi-globule conformations, these molecules should form ordered condensed phases whose structures may be selected by changing the architecture of the molecule. In this way, polymeric materials with a predetermined microstructure might be designed a priori.

By conducting large-scale simulations of many thousands of surfactant molecules, it is found that one should monitor the aggregate size distribution carefully to determine when equilibrium is reached. In many previous studies, this was not done, and the reported size distributions were not truly representative of equilibrium values, and did not match the predictions of theory. The mathematical forms of the size distributions reported here are found to closely correspond with the predictions of the phenomenological theories that assume spherical and cylindrical aggregate shapes. This is somewhat surprising, as the self-assembled aggregates deviate significantly from the assumed shapes. The "spherical" micelles are not perfectly spherical, the short "cylindrical" micelles are not rigid cylinders but have a flexible worm-like structure, and finally the largest aggregates are not only highly flexible but can have one or more branch points. Notwithstanding these deviations in actual structure from that assumed by the theoretical treatments, the accuracy with which the theoretical predictions follow the observed behavior is truly striking - indicating that the general approach of
the phenomenological theories may actually be better than anticipated. This provides a new explanation for their success in predicting experimental behavior. An estimate is also provided for how long a simulation should be run to representatively sample a size distribution at equilibrium. This estimate is based on the "dynamics" of the Monte Carlo simulation and is related to the rate at which single surfactant molecules desorb from a micelle. This estimate successfully predicts the increased time required to sample a broad size distribution in a (relatively) small sized simulation.

When oil is added to the surfactant simulation, there is an additional degree of freedom added to the system, which may allow coexisting phases to appear in the small simulation box. In order reduce the chance of this occurring, and to measure the oil partition coefficient between the micellar phase and a bulk aqueous solution, a two-box simulation method is developed. This method utilizes a thermodynamic ensemble for simulations, which I call the "Helmholtz ensemble". The name signifies that for each box the variables \((T,V)\) are specified. This can be compared with the previously developed "Gibbs ensemble" where \((T,P)\) can be specified. This ensemble is shown to be useful for investigating coexisting phases in lattice simulations and is also applicable to off-lattice simulations. In the simulation, oil and water can exchange between the two boxes at constant system volume. A significant advantage of this method is that we can directly measure the equilibrium concentration of
oil in the water box, and hence the partition coefficient. As long as this concentration is below the solubility limit for the oil in water, we are guaranteed that the system is stable with respect to emulsification failure (or the appearance of a bulk oil phase). Such guarantees concerning phase behavior are impossible using the traditional single box simulation method in the canonical ensemble. The effect of solubilized oil on the equilibrium microstructure of a dilute micellar system is investigated for the first time. It is found that small amounts of solubilized oil produce dramatic growth of the micelles.

Asymmetric growth upon addition of oil, has previously been proposed as an explanation for experimentally observed changes in the macroscopic phase behavior of dilute surfactant solutions as oil was added. The simulation results therefore serve to confirm not only the microscopic interpretation of the macroscopic phase behavior, but also the phenomenological model that the microscopic interpretation was based on. As oil is added to the system, it is preferentially absorbed into the tail region of the micelles, reducing the local tail concentration in the core of the micelle, and thus increasing the effective cross-sectional area of the tails. The surfactant then prefers interfaces with lower overall curvature - such as the worm-like structures observed in the simulation. This phenomenological model does not yet appear to have gained widespread use.
6.2 Recommendations for future work

As mentioned in chapter 1, the lattice models used here are intended to model real systems in a qualitative way, with the main aim being to gain a better understanding of the behavior of self-assembled polymer and surfactant systems, without any a priori assumptions about the size, shape or even the existence of any aggregates that may form. Scaling concepts may be used to relate the empirical formulae of chapter 2 in a quantitative way to the dimensions of any flexible (2d) polymer systems in a good (athermal) solvent. The results of chapter 3 give qualitative predictions for the changes in conformation of (AB)n star block copolymers of in dilute aqueous solutions with varying values of χ, and the results of chapters 4 and 5 serve to confirm the microscopic predictions of phenomenological theories of dilute micellar solutions, and to provide additional insights into their detailed behavior. These are examples of what the approach used in this thesis is suited for.

A relatively obvious extension of the work in chapter 5 would be to investigate the effect of increasing the molecular weight of the oil in the oil-water-surfactant system, to determine whether the oils molecular weight affects the structure of the aggregates in the manner inferred from changes in the systems macroscopic phase behavior. The qualitative properties of other
classes of self-assembled systems, such as amphiphilic copolymers and (simplified) proteins, could also be investigated in a manner similar to that used here, so that whole classes of systems can be investigated and the results are not limited to a specific chemical compounds.

The Helmholtz Ensemble has been shown to be a valuable tool for investigating the behavior of multicomponent systems on lattices and should find wide applicability as a simulation technique.
References


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234
