Molecular Dynamics Modeling of Orientation-Induced Nucleation in Short Alkanes: Toward Molecular Modeling of Flow-Induced Crystallization in Polymers

by

Predrag Duranović

Submitted to the Department of Materials Science and Engineering in partial fulfillment of the requirements for the degree of Master of Science at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY September 2012

© Massachusetts Institute of Technology 2012. All rights reserved.

Author .................................................................
Department of Materials Science and Engineering
August 17, 2012

Certified by ............................................................
Gregory C. Rutledge
Lammot du Pont Professor of Chemical Engineering
Thesis Supervisor

Certified by ............................................................
Samuel M. Allen
POSCO Professor of Physical Metallurgy
Thesis Supervisor

Accepted by .........................................................
Gerbrand Ceder
R. P. Simmons Professor of Materials Science and Engineering
Chairman, Department Committee on Graduate Students
Molecular Dynamics Modeling of Orientation-Induced Nucleation in Short Alkanes: Toward Molecular Modeling of Flow-Induced Crystallization in Polymers

by

Predrag Đuranović

Submitted to the Department of Materials Science and Engineering on August 17, 2012, in partial fulfillment of the requirements for the degree of Master of Science

Abstract

The enhancement of the primary flow-induced nucleation rate in short chain alkanes (C20 and C150) has been examined for different levels of orientation by atomistic molecular dynamics simulations. The nucleation rate has been found to change drastically by varying average molecular orientation and temperature. For example, it is possible to accelerate nucleation kinetics by three orders of magnitude at the same temperature, but varying the average level of orientation \( P_2(\cos \theta) \). The size of the critical nucleus has been found to increase with the level of undercooling \( T_m - T \) decrease, consistent with the classical nucleation theory. Our atomistic molecular dynamics simulation model is even tractable at the small levels of undercooling, thus clearly demonstrating the effects of orientation (melt anisotropy) on nucleation kinetics when thermal nucleation is expected to be negligible. Furthermore, we calculate the influence of melt anisotropy on the growth rate. As expected, the growth rate is also altered by melt anisotropy. Furthermore, the growth rate maximum always occurs at the temperature above the nucleation kinetics maximum.

Thesis Supervisor: Gregory C. Rutledge
Title: Lammot du Pont Professor of Chemical Engineering

Thesis Supervisor: Samuel M. Allen
Title: POSCO Professor of Physical Metallurgy
Contents

1 Introduction .................................................. 11
  1.1 Back To Basics ........................................... 11
  1.2 Experimental Background: Measuring the Nucleation Rate ........ 12
  1.3 Atomistic Modeling of Nucleation in Polymer Melts ............. 13
  1.4 Thesis Approach .......................................... 15

2 Molecular Dynamics Simulation .......................... 17
  2.1 System ................................................... 17
  2.2 Method and Force Field ................................... 17
  2.3 Introducing Orientation in Molecular Dynamics Simulation ...... 19
  2.4 Order Parameter .......................................... 19
    2.4.1 Global Order Parameter ............................... 19
    2.4.2 Local Order Parameter ................................ 19
    2.4.3 Defining an Ordered Phase in Molecular Simulation ....... 21
  2.5 Characterizing Nucleation .................................. 21
  2.6 Characterizing Growth ...................................... 23

3 Results and Discussion .................................. 27
  3.1 Cluster Search Algorithm Parametrization ...................... 27
  3.2 Molecular Dynamics Simulation of Uniaxially Oriented Systems .... 28
  3.3 Nucleation from the Isotropic State .......................... 30
  3.4 Molecular Dynamics Simulation from Anisotropic n-eicosane Melts .... 32
  3.5 Temperature Dependence of the Nucleation Rate ................ 36
3.6 Temperature Dependence of the Growth Rate  

4 Conclusions and Future Work  

A Local Order Parameter Properties  

B Supplementary Data
List of Figures

2-1 An analytical example of mean-first passage time curve (MFPT) indicating the following parameters: critical nucleus size $n^*$, average induction time $<\tau^*>$ and growth regime $N_1 < N < N_2$. 

3-1 Spatial distribution of the local order parameter $S$ for an oriented and mixed system, containing about 50 \% of crystalline phase.

3-2 The largest cluster in the simulation plotted for three different values of local connectivity parameter $R_c$. The trajectories were shifted by +50 along $y$ axis for clarity purposes.

3-3 $\langle P_2 (\cos \theta) \rangle$ versus different strengths of biasing parameter $\mu$ corrected for temperature of equilibration for two C20 and C150.

3-4 Example quiescent C20 and C150 MD trajectories at 20\% under-cooling

3-5 An example on one successful nucleation trajectory from the state point $(\mu = 0.12 \: kT, T = 295 \: K)$, which corresponds to 6\% undercooling. $\langle P_2 (\cos \theta) \rangle$ maintained a steady value from the quench to a critical nucleation event. After the critical nucleation event approximately at 70 ns, the largest cluster begins to grow rapidly, with the corresponding expected increase of $\langle P_2 (\cos \theta) \rangle$. As in the quiescent case, nucleation appears to be a stochastic process, just like in the quiescent case at much larger undercooling levels. This is illustrated in Figure B-7.

3-6 Visualization of the nucleation and growth process for the state point $(\mu = 0.12 \: kT, T = 295 \: K)$. 

25

28

29

30

32

33

34
3-7 MFPT fitting of the state point ($\mu = 0.12kT, T = 295K$). The extracted parameters are: $\langle \tau^* \rangle = 37$ ns and $n^* = 125$. 

3-8 An example of low barrier crossing process, when the MFPT curve does not plateau.

3-9 MFPT curves for $\mu = 0.17kT$ at different temperatures.

3-10 Summary of all nucleation data.

3-11 Critical nucleus size as a function of temperature and bias strength.

   As the undercooling $\Delta T$ decreases, the critical nucleus size increases, consistent with the classical nucleation theory. Data is plotted for all $\mu$ values except for $\mu = 0.02kT$.

3-12 MFPT for the state point ($\mu = 0.12kT, T = 295K$) and identification of the growth regime.

3-13 Calculated linear growth rates in the growth regime $600 < N < 1000$.

3-14 Calculated linear growth rates vs. simulation temperature and biasing factor $\mu$.

B-1 Visualization of uniaxially oriented C20 molecules. Different chains are represented by different colors.

B-2 Visualization of uniaxially oriented C150 molecules. Different chains are represented by different colors. Some chain segments were continued outside of the simulation box for clarity purposes.

B-3 Histogram of induction times in C20.

B-4 Example quiescent C20 MD trajectories at 20% under-cooling.

B-5 Example quiescent C150 MD trajectories at 20% under-cooling.

B-6 The summary of induction time $\langle \tau \rangle$, growth rate $G$, the size of the critical nucleus $n^*$ and logarithm of the nucleation rate $I$.

B-7 8 simulation trajectories at $T=295K$ and biasing parameter $\mu = 0.12kT$ demonstrating stochastic nature of the nucleation process.

B-8 8 simulation trajectories at $T=280K$ and biasing parameter $\mu = 0.12kT$ demonstrating stochastic nature of the nucleation process.
B-9 16 simulation trajectories at T=290K and biasing parameter $\mu = 0.12kT$ demonstrating stochastic nature of the nucleation process
Chapter 1

Introduction

Since the first direct experimental observations in the 1960s of flow-induced crystalline phases occurring in polymeric materials, numerous theoretical and experimental research efforts [21, 23, 24, 29, 34, 30, 5] have been directed over the past several decades to understand the nucleation and growth process and the resulting microstructure that ultimately determines physical properties of the final product. It is generally known that the kinetics of nucleation and crystal growth and the resulting morphology are extremely sensitive to experimental conditions such as temperature, pressure, molecular weight distribution, flow type, imposed strain and strain rate. This complexity often leads to confusion and controversy among researchers. This thesis will focus only on the early stages of flow-induced crystallization — homogeneous primary nucleation and immediately ensuing growth. In the following sections, the basics of experimental and modeling challenges and ultimately understanding of the motivation that made the approach of this thesis different from all other simulation works, will be introduced.

1.1 Back To Basics

Any kind of flow (extensional, shear, Couette, biaxial, ...) perturbs a random-coil polymer configuration. The resulting orientation and deformation of polymer chain molecules in systems undergoing phase change affect various aspects of thermody-
namics and kinetics of the phase transition. According to the first classical theory of phase transformation (the famous Johnson-Mehl-Avrami-Kolmogorov equation), the degree of transformation $\chi$ at the instant $t$ of a new phase is:

\[-\ln (1 - \chi(t)) = E(t) \]  \hspace{1cm} (1.1)

where

\[ E(t) = \int_0^t \dot{N}(s) \left[ \prod_{i=1}^d \int_s^t G_i(z) \, dz \right] \, ds \]  \hspace{1cm} (1.2)

where $\dot{N}$ is the rate at which the new phase nucleates. $G_i$ denote linear growth rates in various directions. So now we see that accurate modeling of phase transformation requires the knowledge of the nucleation rate $\dot{N}$ and generalized growth rate $G$. In the case of flow-induced crystallization in polymers, the inability to accurately describe the effect of molecular anisotropy on both $\dot{N}$ and $G$, precludes successful application of Equation 1.1. In the following section, we will provide a brief overview of relevant experimental and modeling efforts targeted toward understanding of the first step in phase transformation — nucleation.

### 1.2 Experimental Background: Measuring the Nucleation Rate

The most widely accepted assumption is that imposing flow on polymers drastically increases the nucleation rate upon cooling below the melting temperature. The speculated increase in the nucleation rate is by many orders of magnitude; however experimentally it becomes complex, and often cumbersome, to quantitatively evaluate the influence of the flow. Flow-induced crystallization (FIC) experiments usually involve melting the polymer samples above the melting temperature, quenching to just below the crystallization temperature, usually determined by differential scanning calorimetry (DSC), and applying a short period of flow. These measurements indirectly measure the increased nucleation rate through a decrease in the crystal-
lization half-time. In situ crystallization following the flow can be monitored with common experimental techniques such as small-angle X-ray scattering (SAXS). The authors in [16] notice drastic decreases in crystallization half-time when observing signatures of thread-like nuclei in SAXS signals. They postulate that crystallization rate is unaffected and that only the density of potential flow-induced nucleation sites changes. In situ rheo-optical techniques combined with wide-angle X-ray scattering (WAXD) reveal the emergence and structure of oriented nuclei that develop upon strongly shearing an isothermal melt of polydisperse isotactic polypropylene [23]. Recent optical microscope observations have provided a more direct measurement of the polymer nucleation [6], by counting the nuclei as they emerge from shear flow and confirming the speculated increase of the nucleation rate. Janeschitz-Kriegl [32] plotted the logarithm of the number density of spherulites versus temperature for different amounts of mechanical work applied to iPP in shear flow. The concept of flow-enhanced activation of dormant precursors is another speculation to explain the huge effect of flow on the number density of spherulites. Peters et al. [17] derive the number of point-like nuclei from the rheometry experiments by modeling the system as a suspension. Alternatively, depolarized light scattering [26] or infrared spectroscopy can be employed to study the induction period prior to crystallization.

1.3 Atomistic Modeling of Nucleation in Polymer Melts

While flow-induced enhancement of nucleation and growth measurements is more than abundant in experimental literature, very little simulation work has been done to understand the kinetics of nucleation on the atomistic level in polymer melts. Molecular dynamics simulations are a powerful tool for this task. While they already have provided information about growth [35, 36] and crystallization behavior under uniaxial extension [22] their utility in examining the nucleation process is just beginning to emerge. Quite recently, Yi et al. [39, 40] dispelled a tremendous doubt that atomistic
simulations can capture nucleation events in quiescent polymer melts, by fully characterizing the nucleation process for short alkanes. While this work demonstrated the ability to characterize the nucleation rate at 20% undercooling in short alkanes, it is the first account of detecting nucleation events in complex fluids. With experimentalists' findings about tremendous nucleation rate enhancement under the influence of flow, it appears that simulating the nucleation process should become even more feasible. Here is where molecular simulations reached stumbling roadblocks. Non-equilibrium molecular dynamics (NEMD) simulations, which simulate polymer melts in flow fields, are currently under development [2, 11, 18, 10]. These simulations are usually constrained to planar elongation or shear flows and can be run indefinitely because of the existence of appropriate boundary conditions, at extremely high shear rates in order to stay within the limits of available computational time. Such shear rates are beyond the limits of linear response theory and the extrapolations of the results by many orders of magnitude is currently under debate. Unfortunately, in uniaxial flow, which potentially has a higher degree of orienting power, the size of the simulation box sets the time limit to MD simulations, as the smallest dimension will continue to diminish indefinitely. Jabbarzadeh et al. [19, 20] provide significant insight into crystallization behavior by making the comparison between the total shear and shear rate. While their simulations could have potentially yielded nucleation rates as function of temperature, strain rate and total strain, it is unclear why the authors have not identified nucleation events. In addition to NEMD simulations, a notable novel coarse-grained kinetic Monte Carlo method has been reported [14].

Despite scarcity in atomistic modeling, microrheological modeling of FIC is abundant. Many of these microrheological models demonstrated great success; however, the nucleation rate is usually either assumed or parametrized from experimental data, thus often failing to predict the behavior or properties that are not obvious from experimental data. While FIC microrheological modelling is of tremendous value, it does not provide any new information about the nucleation process on the atomistic level.
1.4 Thesis Approach

Macromolecular non-equilibrium states, commonly encountered in polymer processing, can be characterized with great precision on the most fundamental molecular level — atomic bond level — regardless of the processing history, flow field and other numerous experimental conditions. Experimental techniques such as birefringence and infrared dichroism give the aggregate averages \( \langle \cos^2 \theta \rangle \) of the polarizable or IR active structural units. X-ray diffraction spectra can fully resolve any structural unit in the crystal phase. Raman spectroscopy gives both \( \langle \cos^2 \theta \rangle \) and \( \langle \cos^4 \theta \rangle \) of the scattering unit. In addition to these moments, NMR can determine even higher moments, such as \( \langle \cos^6 \theta \rangle \) and \( \langle \cos^8 \theta \rangle \) of structural units. Therefore, spectroscopic techniques can already provide structural information regarding orientation distribution function of local bond vectors in non-equilibrium states even without performing any molecular simulations. Colhoun et al. [71] performed NMR studies of sheared polystyrene to fully reconstruct the orientation distribution function of the relaxing polystyrene sample in real time. This study further inspired Colhoun [8] to employ SGMC formalism developed by Rutledge [33] to generate the atomistic configurations that fully reconstruct the moments measured by NMR experiments. Then, Bernardin et al. [3] generated atomistic configurations to reproduce a desired value of \( \langle P_2 (\cos \theta) \rangle \). This quantity is particularly chosen because it is related to birefringence and stress-optical coefficient, both of which can be measured. In this way, molecular simulations can be used to predict properties, which is the ultimate goal of modelling. However, Mavrantzas et al. [27] developed a Monte Carlo scheme to model uniaxial orientation through a tensorial orienting field acting on the end-to-end distance conformation tensor. Instead, Bernardin [3] in his approach used the SGMC framework to bias the local bonds, as well as the end-to-end vector. These two approaches are intimately related but SGMC approach is designed to reconstruct atomistic configurations given the information on the bond level, whereas Mavrantzas’ approach relies on evoking a rheological model (such as elastic Hookian dumbbell or FENE model) to connect the biasing tensorial field with the flow rate. Therefore, depending on the model they
use, the biasing tensorial field will be different. This is not the case with the SGMC method, which only relies on the moments of the orientation distribution function. According to [3], the probability density of the species in the semi-grand canonical ensemble can be transformed in terms of Legendre polynomials:

$$\ln p \propto -\frac{1}{kT} \left[ U(r) - \sum_{k=1}^{\infty} \mu P_{2k} (\cos \theta) \right]$$  \hspace{1cm} (1.3)

For uniaxial orientation, the sum is truncated at the first non-vanishing Legendre polynomial $P_2(\cos \theta)$ as such moment can be obtained from birefrigence measurements.

The SGMC approach has also inspired this thesis, in a way of adding an extra biasing potential to a very well known force field, to introduce uniaxial orientation in molecular dynamics simulation. By using the biasing potential, we can introduce macromolecular deformation and effectively bypass any knowledge about the flow field. This approach makes this thesis different from all other NEMD approaches to the same problem. The ultimate goal of this thesis is to determine how molecular deformation, as described by $\langle P_2(\cos \theta) \rangle$, influences the nucleation and growth rates of chain molecules with varying degree of undercooling and molecular anisotropy.
Chapter 2

Molecular Dynamics Simulation

2.1 System

We simulated a system of 400 n-eicosane ($C_{20}$) chains and a system of long chain alkane $C_{150}$ in the isothermal-isobaric (NPT) ensemble at one atmosphere. Periodic boundary conditions were employed in all three directions while the simulation box was maintained isotropic and orthogonal. Molecular dynamics simulations in the NPT ensemble enable realistic system contraction, which is indispensable in accommodating density changes of the melt during nucleation and crystallization processes. Initially, we prepared an oriented system at a temperature higher then the melting point of the material $T > T_m$, and then suddenly quenched the system below the melting point $T < T_m$. Since nucleation is a stochastic process, we repeated multiple simulations starting from different initial configurations.

2.2 Method and Force Field

We used molecular dynamics simulation to create non-equilibrium oriented states at temperatures higher than the melting point of $n$-eicosane and longer chain alkanes. We run MD simulations by using open source code LAMMPS (Large-Scale Atomic/Molecular Massively Parallel Simulator) package$^1$. The equations of motion

$^1$http://lammps.sandia.gov
were integrated with the timestep $\Delta t = 5\text{fs}$. Every simulation was performed in the isothermal-isobaric (NPT) ensemble. Pressure and temperature were maintained at their set points by the Nose-Hoover thermostat and barostat, each with damping frequencies $\omega_t = 1/(1000\Delta t)$ and $\omega_p = 1/(1000\Delta t)$, respectively. While temperature tracked the set temperature very well, pressure showed greater deviations from the set point, yet it averaged precisely at the pressure set point, as expected with the systems with large internal energy virial contributions. We used the united atom force field, originally proposed by Paul, Yoon and Smith [31] and then modified in [35, 36, 25] in studies of the crystal-amorphous interface and growth in \textit{n}-alkanes. The functional form and parameters of the force field are given as:

\begin{equation}
E_{\text{bond}} = K_{\text{bond}}(l - l_0)^2
\end{equation}

\begin{equation}
E_{\text{angle}} = K_{\text{angle}}(\theta - \theta_0)^2
\end{equation}

\begin{equation}
E_{\text{torsion}} = \frac{1}{2} [k_1 (1 + \cos \phi) + k_2 (1 - \cos 2\phi) + k_3 (1 + \cos 3\phi)]
\end{equation}

\begin{equation}
E_{\text{LJ}} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^6 - \left( \frac{\sigma}{r} \right)^{12} \right]
\end{equation}

where $K_{\text{bond}} = 350\text{kcal/(mol \, \AA)}$, $l_0 = 1.53\ \text{\AA}$, $K_{\text{angle}} = 60\text{kcal/rad}^2$, $\theta_0 = 1.23\text{rad}$, $\sigma = 0.401\text{nm}$, $\varepsilon = 0.469\text{kJ/mol}$, $k_1 = 6.69\text{kJ/mol}$, $k_2 = -3.63\text{kJ/mol}$, $k_3 = 13.56\text{kJ/mol}$.

\textsuperscript{2}Wahood et al. [35] have previously evaluated the effect of using larger integration time steps during the MD simulation of \textit{n}-alkanes with this PYS force field. They found that changing $\Delta t$ from 1 to 5 fs increased the bond energy, the angle-bending energy, and the relaxation time for the chain-orientation autocorrelation function by approximately 10%. The consequence of these errors is mitigated through the use of a thermostat, such that no detectable difference in crystallization kinetics was observed for simulations with $1\text{fs} \leq \Delta t \leq 5\text{fs}$.
2.3 Introducing Orientation in Molecular Dynamics Simulation

We introduced uniaxial anisotropy in the simulation box by adding a physical biasing potential that acts on the orientation of the local chord vector \( \mathbf{u}_i = \mathbf{r}_{i-1} - \mathbf{r}_{i+1} \)

\[
U_{\text{bias}} = \frac{3}{2} \mu \cos^2 \theta_z
\]

where \( \theta_z \) is the angle between \( \mathbf{u}_i \) and biasing (flow) direction \( \mathbf{z} \). A single parameter \( \mu \) determines the strength of the biasing field, hence driving the overall orientation within the simulation box. The biasing forces acting on united atoms updated the LAMMPS force calculation by the expression:

\[
\mathbf{F}_{\text{bias}} = -\nabla U_{\text{bias}}
\]

2.4 Order Parameter

2.4.1 Global Order Parameter

In order to characterize the level of anisotropy of the entire simulation box, we monitored the global order parameter of the entire simulation box, defined as:

\[
\langle P_2(\cos \theta) \rangle = \left\langle \frac{3 \cos^2 \theta_{j,z} - 1}{2} \right\rangle_j
\]

where \( \theta_{j,z} \) is the angle between the chord vector connecting the \((j - 1)\)th and the \((j + 1)\)th bead \( (\mathbf{u}_j = \mathbf{r}_{j+1} - \mathbf{r}_{j-1}) \) and the direction of the uniaxial anisotropy, \( \mathbf{z} \). Averaging is performed over all chord vectors in the simulation box.

2.4.2 Local Order Parameter

In order to identify the local crystalline nuclei and differentiate between oriented and crystalline phases, we used the nematic order parameter. The degree of order
is characterized by a scalar $S$ ranging from $-1/2$ to 1, where 0 indicates complete disorder and 1 indicates a perfectly ordered uniaxial phase. In order to calculate the local order parameter at the beads site $r_i$, first we generate a set of local chord vectors $\Omega_i = \{u_j : |r_i - r_j| \leq R_s\}$, which are within a certain distance $R_s$ from the bead site $r_i$. The distance $R_s$ should be at least as large as the first neighbor distance and certainly smaller than the dimensions of the simulation box. This value is set to $R_s = 10 \text{Å}^3$. Then, we construct the local second rank ordering tensor at every bead site $i$:

$$S_i = \left\langle \frac{3}{2} u_\alpha u_\beta - \frac{1}{2} \delta_{\alpha\beta} \right\rangle_{u \in \Omega_i}$$  \hspace{1cm} (2.8)$$

By construction, this tensor is traceless and symmetric. Since any symmetric second-order tensor has three eigenvalues and three corresponding orthogonal eigenvectors, a Cartesian coordinate system can be found in which it is diagonal. The eigenvector corresponding to the numerically largest eigenvalue is a director $n$ which points along the average orientation, in the case of uniaxial symmetry. For the proof of the stated theorems, as well to learn more about properties of the local order parameter tensor, refer to Appendix A. For a uniaxial nematic phase, this tensor further reduces to:

$$S_{\alpha\beta} = S \left( n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta} \right)$$  \hspace{1cm} (2.9)$$

If $n$ is parallel to the $z$ axis of uniaxial orientation, the three non-zero components of $S$ are:

$$S_{zz} = \frac{2}{3} S \text{ and } S_{xx} = S_{yy} = -\frac{1}{3} S$$  \hspace{1cm} (2.10)$$

In the isotropic case $S = 0$ and in the nematic phase $0 < S < 1$. These properties indicate that $S$ is a good candidate for the local order parameter in our simulations.

---

3 We determined this number by evaluating the number of united atom sites which would be contained in a sphere of radius $R_s$. As indicated in the following chapter, our C20 simulations contain 8000 united atoms with the simulation box size of 61.27Å in equilibrium and 59.71Å in the completely crystalline state. A sphere of a radius of 10 Å would approximately encompass 12 united atoms, which is a good number for determining the local order parameter value $S$. Any increase of $R_s$ parameter value would coarsen the numerical value for the local order parameter. Conversely, any decrease in $R_s$ would lead toward erratic changes in the local order parameter values and poor estimates of local order.
with uniaxial anisotropy — it is sensitive to the direction and magnitude of the average local orientation.

2.4.3 Defining an Ordered Phase in Molecular Simulation

Identifying an imperfectly ordered crystalline phase can be computationally challenging. First, the value of the local $S$ order parameter must be evaluated at every site. Then, if two beads are neighbors (within some certain preset distance $R_c$) and their local directors $\mathbf{n}$ (which are obtained from orthogonalization of the local nematic tensor $\mathbf{S}$) are nearly parallel (within some tolerance angle $\theta_c$) and their local $S$ values exceed some critical value $S_c$), then they belong to the same cluster. By sweeping recursively through the entire simulation box outputs, a list of clusters and their respective sizes is constructed. However, parameters $S_c$ and $R_c$ must be sensibly determined for optimal cluster search outcomes. These parameters will be determined in the next chapter.

2.5 Characterizing Nucleation

The crossing of a free energy barrier in a thermally activated process is typically a rare event and thus, difficult to observe and quantify in a simulation. Nucleation is a stochastic process: it may occur after a short or a long time, or not occur at all in the limited time of a simulation. In addition to this, the location of the transition state is usually not known a priori. Several methods have been developed to estimate the critical nucleus size and average induction time from brute-force MD simulations [1]. In this work, we followed the procedure from [38] based on a very well known concept of first-hitting-time models, which are a subclass of probability survival models. The first-hitting-time is defined as the time when the stochastic process first reaches a certain threshold. In this work, first-hitting-time will be rephrased to first-passage time. The procedure of extracting the mean-first passage time (MFPT) directly from MD simulation trajectories is relatively straightforward. For each simulation, the size of the largest cluster $n$ in the system is recorded at regular intervals. After the end of
each simulation, the first-passage time curve is constructed by noting the time when a cluster of size \( n \) appears for the first time. Subsequently, the mean first-passage time for each cluster size \( n_{\text{max}} \) is simply obtained by averaging first-passage time curves obtained from multiple molecular dynamics simulations starting from different initial conditions. The strength of the method, as fully elaborated in [38], is that as long as the barrier to nucleation is sufficiently high (\( \Delta G \gg kT \)), the mean-first passage time of the largest nucleus in the system takes the following analytical expression:

\[
\tau(n) = \frac{\tau^*}{2} \left( 1 + \text{erf} \left( b(n - n^*) \right) \right) \tag{2.11}
\]

where \( n^* \) is the critical nucleus size and \( \tau^* \) is the average induction time. The parameter \( b \) is related to the Zeldovich factor \( b = \sqrt{\pi} Z \):

\[
Z = \sqrt{\frac{d^2 \Delta G(n)}{dn^2}} \frac{2\pi k_b T}{2} \tag{2.12}
\]

MFPT curves obtained from molecular dynamics trajectories are then fitted by using the Levenberg-Marquardt algorithm with bisquare weights to obtain the numerical values of \( n^* \) and \( \tau^* \). This fitting minimizes a weighted sum of residue squares, where the weight given to each data point depends on how far the point is from the fitted curve. For a sufficiently high energy barrier in a thermally activated process, we expect that the distribution of induction times follows Poisson statistics. Since we are interested in determining the mean first-passage time, we report the standard error of the mean, which is obtained by block averaging of the mean. This is different than reporting standard deviation, as that becomes relevant in describing the dispersion of individual induction times. For example, if \( N \) simulation trajectories yield \( N \) induction times, the standard error is computed by the following formula:

\[
\sigma_{\langle \tau \rangle} = \frac{1}{\binom{N}{k}} \sum_{k} \binom{1}{k} \sum_{j \in \Omega} \tau_{j} \tag{2.13}
\]
where $\Omega$ is any $k$-combination subset of $\{\tau_1, \tau_2, \ldots, \tau_N\}$. If $k = 1$ or $k = N$, the standard error reduces to standard deviations of individual observations $\tau_i$. In this work, where $N = 16$, $k$ is chosen for the block averaging of 4 independent induction times. The average nucleation rate $I$ is calculated as:

$$I = \frac{1}{<\tau^*> V} \quad (2.14)$$

where $V$ is the volume of the simulation box. The error $\Delta I$ is given by the expression:

$$\Delta I = I \times \frac{\Delta\langle\tau^*\rangle}{\langle\tau^*\rangle} = I \times \frac{\sigma(\tau)}{\langle\tau^*\rangle} \quad (2.15)$$

### 2.6 Characterizing Growth

Molecular dynamics trajectories that have nucleated during the simulation time can also give valuable information regarding the growth rate $G$. In MD simulations, the growth rate is the velocity $v$ by which the crystalline cluster is expanding radially. In the case of very short alkanes, the critical nucleus has a cylindrical shape [40]. By assuming that short chains are aligning in the orientation direction and simply adding onto a nucleus, the numerical growth rate can be easily extracted from molecular dynamics trajectories. For a visual confirmation of the cylindrical supercritical nucleus assumption, refer to Figure 3-6c in the next section, in which the supercritical nucleus appears as a slab of alkanes, with the thickness corresponding to the maximum chain contour length$^4$:

$$l \approx 20 l_0 \sin \frac{\theta}{2} \quad (2.16)$$

where $l_0 = 1.53$ Å is the length between two beads, and $\theta$ is the angle between the two adjacent bonds in the pure trans conformation of an alkane. By assuming cylindrical growth, the number of united atoms in a cylinder of length $l$ and radius $r$ is simply:

$$N = r^2 \pi l \rho \quad (2.17)$$

$^4$According to Yi et al. [40], the critical nucleus contains dangling ends, thus its shape deviates from fully extended all trans configuration.
where $\rho$ is the number density of beads (for example, in units of beads per nm$^3$) and $r$ is the cylinder radius. While $\rho$ is a direct simulation observable (density), the radius $r$ is not. Since the cluster search algorithm identifies the size of the cluster, the radius $r$ is simply:

$$r = \left( \frac{N}{\pi \rho} \right)^{1/2} \quad (2.18)$$

Taking the time derivative of Equation 2.17 gives:

$$\frac{dN}{dt} = 2rR\rho G \quad (2.19)$$

where the radial growth rate (velocity) is $G = \frac{dr}{dt}$. Simple substitution yields the expression for the growth rate:

$$G = \frac{1}{2 \left( N \rho \pi \right)^{1/2}} \frac{dN}{dt} \quad (2.20)$$

where $N$ is the largest cluster size (simulation observable) and $dN/dt$ is the inverse slope of the mean-first passage time, which can be calculated as a numerical derivative. Namely, for every mean-first passage time curve, the growth part of the curve is determined. For example, in Figure 2-1 the growth regime corresponds to a region between $N_1$ and $N_2$. The numerical derivative is calculated at all points $N_1 < N < N_2$ by linear fitting of the subregion $N - \Delta N$ and $N + \Delta N$. The standard error of the mean is calculated by block averaging.

---

5 Although the plateau appears completely horizontal, it does have a finite slope. The presence of this plateau indicates that the rate limiting step in the formation of a large cluster is the activation time to overcome the critical size and that the time required for the subsequent growth of the cluster is negligible compared to that. According to [38], in the case of low-barrier crossing, this plateau interferes with the sigmoidal shape of the mean first-passage time, indicating that nucleation is not a rate-limiting step.
Figure 2-1: An analytical example of mean-first passage time curve (MFPT) indicating the following parameters: critical nucleus size $n^*$, average induction time $\langle \tau^* \rangle$ and growth regime $N_1 < N < N_2$. 
Chapter 3

Results and Discussion

3.1 Cluster Search Algorithm Parametrization

In the previous chapter, three parameters were left to be determined: \( S_c \), the critical value of the local order parameter \( S \) above which an united atom belongs to a crystalline phase, and \( R_c \), which determines the minimum distance between two united atoms belonging to the same cluster. The tolerance angle \( \theta_c \) was set to 10° to ensure nearly parallel alignment of the local orientation directors \( \mathbf{n} \). Figure 3-1 shows the spatial distribution of the local order parameter \( S \) calculated at every united atom site in the simulation box for two melts: one consisting of a mixture of about 50% crystalline phase, and another one in which no nucleation has occurred. As expected, the first distribution is bimodal. The two peaks in the distribution correspond to a disordered but oriented melt phase and ordered crystal phase. The \( S \) value that corresponds to the minimum of the first distribution, serves as the dividing point to distinguish united atoms in the melt phase from those in the crystal phase. Therefore, this critical local order parameter value was set to \( S_c = 0.7 \). For the other parameter \( R_c \), any two crystal beads that are within a distance 1.5\( \sigma \) are considered to be in the same nucleus. The numerical value of 1.5\( \sigma \) is slightly larger than the first nearest-neighbor distance for united atoms belonging to different chains in the crystal phase. Figure 3-2 demonstrates one trajectory of the largest crystal size versus simulation time, plotted for several values of the connectivity parameter \( R_c \). While
the cluster size changes, the location of the critical nucleation event does not change significantly. Since MD trajectories were analyzed to extract induction time, the application of different numerical values of $R_c$ would not change the numerical value for induction time. Yet, it changes the cluster size, hence we kept the value of $R_c = 1.5\sigma$ consistent throughout all MD simulations.

3.2 Molecular Dynamics Simulation of Uniaxially Oriented Systems

The system was equilibrated by positioning C20 (C150) molecules randomly over a large volume and applying compressive pressure of 1 atm, thus allowing the system to equilibrate for 10 ns at the melt density. Both C20 and C150 equilibrated at
Figure 3-2: The largest cluster in the simulation plotted for three different values of local connectivity parameter $R_c$. The trajectories were shifted by +50 along $y$ axis for clarity purposes.

$920 \text{ kg/m}^3$ and $940 \text{ kg/m}^3$, respectively. Then, the biasing potential introduced in Equation 2.5 was applied to local chord vectors $u_i$. The global order parameter $\langle P_2 (\cos \theta) \rangle$ was monitored during simulation to determine the equilibrium value of $\langle P_2 (\cos \theta) \rangle$. C20 was equilibrated at $T = 320 \text{ K}$, while C150 was equilibrated at $T = 500 \text{ K}$. Figure 3-3 shows the equilibrated $\langle P_2 (\cos \theta) \rangle$ for both systems as a function of local chord vector biasing strength $\mu$. The standard error numerical values of the equilibrated $\langle P_2 (\cos \theta) \rangle$ were calculated by block averaging. The $\langle P_2 (\cos \theta) \rangle$ values calculated by this method are in a good agreement with the results of Bernardin et al. [3]. During uniaxial orientation the system density increased to densities close to $988 \text{ kg/m}^3$ for both chain lengths, which indicates closer packing of chain molecules than in the isotropic melt. Consequently, the percentage of $\text{trans}$ dihedral states also
increased, while no crystalline clusters were observed. It is interesting to notice the difference in \( \langle P_2(\cos \theta) \rangle \) at higher bias strengths. According to [3], these differences can be traced to the lower fraction of chain ends in longer chain molecules. Chain ends tend to reduce the system density while exhibiting greater orientation freedom [4]. Figures B-1 and B-3 in Appendix B provide visualization of the system anisotropy for the two chain lengths.

### 3.3 Nucleation from the Isotropic State

Before investigation of the effect of anisotropy on the nucleation rate, several quiescent \( (\mu = 0) \) MD simulations were performed after the quench to estimate the nucleation rate in C20 in the isotropic state at \( T=250 \) K, which corresponds to 20% undercooling.
Figure B-4 in Appendix B shows the time evolution of the largest cluster in the simulation box after the quench for 36 trajectories. In a typical MD trajectory, the size of the largest cluster fluctuates before a successful nucleation event occurs, a finding consistent with the classical nucleation theory. Then, the critical nucleation event occurs, and the largest cluster continues to grow rapidly until it consumes the entire simulation box. Figure B-3a clearly demonstrates the stochastic nature of the nucleation process. The average induction time for the quiescent C20 melt at 20% undercooling is calculated by fitting the simulation MFPT plots with Equation 2.11 and extracting \( \langle \tau^* \rangle \). \( \langle \tau \rangle = 75 \text{ ns} \pm 10 \) at \( T = 250 \text{ K} \). MD runs were also performed on entangled longer C150 chains at a similar level of undercooling. Since the melting point of polyethylene is 420 K, the simulations were run at 340 K. Figure B-5 shows only 16 uncorrelated runs, with much longer induction times. MFPT analysis yields \( \langle \tau \rangle = 220 \pm 20 \text{ ns} \), as shown in Figure 3-4. Also, there has been an attempt to simulate quiescent melts at lower levels of undercooling, such as 260 K in C20 and 380 K in C150, however not a single critical nucleation event was detected within 500 ns of simulation time. At that time limit, MD trajectories were terminated. For more detailed analysis about quiescent nucleation in \( n \)-eicosane systems, refer to [40].
3.4 Molecular Dynamics Simulation from Anisotropic \( n \)-eicosane Melts

After the global order parameter \( \langle P_2 (\cos \theta) \rangle \) has equilibrated above the melting point, the system temperature was dropped below the melting point to study nucleation. 16 simulations were performed for each state point \((\mu, T)\). A complete summary of all simulations performed is given in Table B-6 in Appendix B. In a typical simulation, there is a brief period of relaxation to a new metastable equilibrium\(^1\), in which the system stays until the critical nucleation event occurs. During this period, many small clusters appear and melt, which was observed in the case of isotropic melts as well. During this stage, the level of anisotropy, \( \langle P_2 (\cos \theta) \rangle \), also remains constant.

\(^1\)Orientational relaxation to a new metastable state is in the order of 100ps, while the longest Rouse relaxation time is in the order of a nanosecond. Since nucleation can be strongly accelerated by orientation, it may occur even before the longest Rouse relaxation time.
Figure 3-5: An example on one successful nucleation trajectory from the state point $(\mu = 0.12 \, kT, T = 295 \, K)$, which corresponds to 6% undercooling. \( \langle P_2 (\cos \theta) \rangle \) maintained a steady value from the quench to a critical nucleation event. After the critical nucleation event approximately at 70 ns, the largest cluster begins to grow rapidly, with the corresponding expected increase of \( \langle P_2 (\cos \theta) \rangle \). As in the quiescent case, nucleation appears to be a stochastic process, just like in the quiescent case at much larger undercooling levels. This is illustrated in Figure B-7.

Then, a critical nucleus appears and initiates the growth phase, which occurs rapidly, compared to the long induction times. This process is quantitatively demonstrated in Figure 3-5 and visually shown in Figure 3-6. The induction time, hence the nucleation rate, as well as the size of the critical nucleus can be quantitatively determined by fitting MFPT curves to Equation 2.11. Figure 3-7 demonstrates a fitting example of the state point $(\mu = 0.12 \, kT, T = 295 \, K)$. However, in cases when induction time approaches a few nanoseconds, such as at the higher level of undercooling and smaller bias, the MFPT curves take a slightly different shape, which still can be
(a) Visualization of the onset of the critical event at 70 ns.

(b) Critical nucleus becomes supercritical right after 70 ns.

(c) Supercritical nucleus continues to grow and forms a lamella of almost completely extended all-trans C20 molecules 2 ns after the critical event.

Figure 3-6: Visualization of the nucleation and growth process for the state point ($\mu = 0.12 kT$, $T = 295$ K).
fitted to Equation 2.11 but with some caution. Figure 3-8a shows one such example. Wedekind et al. encountered similar problems with their LJ systems at high supersaturation [37]. This might be a case of low-barrier crossing problem — the MFPT still increases noticeably for higher cluster sizes but without reaching a clear plateau, indicating that the growth of the cluster occurs on a similar time scale as nucleation. For low nucleation barriers, however, the overcoming of the barrier is no longer the rate limiting step for the formation of a supercritical cluster. This is what is observed as well in some of our simulations at lower temperatures. For a low barrier crossing case, the critical nucleus size decreased to $n^* = 47$, from 125 at $T=295$K. Even though the MFPT does not reach a plateau, the fit is nevertheless reasonably good around the inflection point of the MFPT curve and provides a very good estimate of the critical size. In these cases, the inflection point is visually identified and the fitting parameter range is tuned such that the fitted MFPT curve does plateau near the inflection point, as it is shown in Figure 3-8a. Wedekind et al. details this ap-
proach in [37]. At the point when the barrier to nucleation diminishes to $\Delta G \approx kT$, Wedekind et al provides a controversial argument that the phase transformation might be dominated by spinodal decomposition. However, this discussion is beyond the scope of this thesis, as it would require further analysis in order to identify critical density fluctuations wavelengths. Gee et al. [12] reported polymer melt simulations with fluctuation critical wavelengths on the order of 20 nm. This approach would entail building simulation boxes consisting of approximately several million united atoms, as it was the case in [12].

3.5 Temperature Dependence of the Nucleation Rate

A strong dispersion of induction times appears to apply only to low levels of undercooling, such as for the quench temperatures 290–295 K. For temperatures lower then 290 K at the bias strength $\mu = 0.17kT$, nucleation events appear almost immediately after the quench, thus yielding almost unmeasurable changes in induction time, which is illustrated in the Figure 3-9 as almost overlapping mean-first passage time curves at $T = 270$–280 K. Figure 3-10a shows the calculated nucleation rate for four different values of bias strengths $\mu$ and different quench temperatures. For example, at low biasing strength $\mu = 0.02$ kT, we could only observe nucleation events at temperatures 250–270K. The quoted nucleation rates were calculated by running 16 independent trajectories. For temperatures above 270K (280 and 290 K), not a single trajectory nucleated within 500 ns of simulation time, hence the induction time for those particular temperatures are certainly higher than 500 ns. Similarly, for the bias strength $\mu = 0.12$ kT, no nucleation occurred within 500 ns above 295 K. Since more interesting orientation effects on nucleation rate appear at lower levels of undercooling for a given biasing strength $\mu$, or when induction times become longer and disperse, it is beneficial to re-plot Figure 3-10a on a semi-log scale. Figure 3-10b clearly demonstrates the effect of the bias strength $\mu$ on nucleation rate — for example, at $T=280K$, the nucleation rates changes approximately 3 orders of magnitude by increasing the bias parameter $\mu = 0.02$ kT to $\mu = 0.17$ kT. Although there is
(a) MFPT fitting of the state point ($\mu = 0.12\ kT$, $T = 270\ K$). The extracted parameters are: $\langle \tau^* \rangle = 1.5\ ns$ and $n^* = 47$.

(b) Histogram of induction times demonstrates very narrow distribution of induction times.

Figure 3-8: An example of low barrier crossing process, when the MFPT curve does not plateau.
Figure 3-9: MFPT curves for $\mu = 0.17kT$ at different temperatures.

very little experimental investigation of FIC in flowing $n$-eicosane, it is worthwhile to compare the results from Figure 3-10b with some emerging rheological model predictions. One of the earliest theoretical investigations of the mechanisms of FIC was by McHugh [28]. McHugh makes a relatively simple argument that the difference in nucleation rate from the extended chain configuration, relative to that of the random coil configuration, is proportional to the exponential of the free energy change of deformation. Under this assumption, he obtains the exponential flow induced enhancement as a function of chain extension. This can be qualitatively related to our measure of anisotropy $\langle P_2 (\cos \theta) \rangle$, as chain molecules become more oriented and extended compared to their random-coil configuration, with application of the bias $\mu$. Graham et al. [13] invoke the GLaMM [15] model and theoretically derive the expected exponential enhancement of the nucleation rate as a function of the stretch.
(a) Summary of nucleation rates as reported in Table B-6.

(b) Logarithm of the nucleation rate

Figure 3-10: Summary of all nucleation data
Figure 3-11: Critical nucleus size as a function of temperature and bias strength. As the undercooling $\Delta T$ decreases, the critical nucleus size increases, consistent with the classical nucleation theory. Data is plotted for all $\mu$ values except for $\mu = 0.02\,kT$.

ratio of entanglements. Grizzuti et al. [9] recalls the theory of Lauritzen and Hoffman and uses the Doi-Edwards model to calculate the change in free energy upon orientation, which is simply added to the barrier to quiescent nucleation. And again, they derive the exponential enhancement of the nucleation rate as a function of shear rate, which shows the same qualitative trend of the nucleation rates as in Figure 3-10b.

The critical nucleus size can also be extracted from the MFPT curves. Figure 3-11 attests to the applicability of the classical nucleation theory. The size of the critical nucleus increases as $\Delta T = T_m - T$ decreases.
3.6 Temperature Dependence of the Growth Rate

For every state point \((\mu, T)\) MFPT was constructed in order to identify the growth regime. Figure 3-12 exemplifies one state point. The growth regime was identified as the region \(N > 400\) and the interval \(600 < N < 1000\) was chosen for the growth rate calculations. Figure 3-13 demonstrates the extracted linear growth rate as a function of the cluster size. \(\Delta N\) is a variable parameter in this analysis, and in this particular case was chosen as \(\Delta N = 25\), which means that the slope \(dN/dt\) from Equation 2.20 was calculated from 50 points at every cluster size data point. This is a variable parameter and it is the largest source of error in growth rate calculations. If \(\Delta N\) is chosen too small, the calculated growth rate will become more erratic, hence introduce larger standard error. If \(\Delta N\) is chosen too large, it inadequately calculates the local slope \(dN/dT\). In case of the state points \((\mu, T)\) which do now have a clear sigmoidal shape, as discussed in the previous section, the growth regime was identified as any region after the inflection point on the MFPT curve. The temperature dependence of the growth rate at every state point \((\mu, T)\) was calculated and summarized in Figure 3-14.

It is important that these linear growth rates were calculated based on primary nucleation events. Waheed et al. [35] calculated the same growth rate on the basis of the secondary nucleation, however arrived at the numerical values of the same order of magnitude as those reported in this work. It is also interesting to notice the shift of \(T_{\text{max}}\), the temperature at which the growth rate peaks, for a given \(\mu\), which also demonstrates the utility of Ziabicki’s empirical model for crystallization:

\[
G(T) = G_{\text{max}} \left[ -4 \ln 2 \left( \frac{T - T_{\text{max}}}{D^2} \right)^2 + C f_a^2 \right] \tag{3.1}
\]

and accounts for the amorphous orientation prior to quenching, by including Herman’s orientation factor \(f_a = \langle P_2(\cos \theta) \rangle\).
Figure 3-12: MFPT for the state point \((\mu = 0.12 \, kT, \, T = 295 \, K)\) and identification of the growth regime.

Figure 3-13: Calculated linear growth rates in the growth regime \(600 < N < 1000\)
Figure 3-14: Calculated linear growth rates vs. simulation temperature and biasing factor $\mu$. 
Chapter 4

Conclusions and Future Work

The modeling and conceptual understanding of flow-induced crystallization presents enormous challenges across all length and time scales. The ultimate goal of this entire research field is rational polymer product design through development of the quantitative integrative model to predict useful material properties such as strength, elasticity, optical transparency and permeability. This thesis tackles the first step of this integrative approach on the most fundamental level. Particularly, the modeling approach developed in this thesis offers a novel way of calculating the primary nucleation rate in a uniaxially anisotropic melt of a short alkane. Non-equilibrium molecular dynamics (NEMD) was used to study the dependence of the primary nucleation rate at various levels of undercooling and system anisotropy. The model is even tractable at low levels of undercooling, where FIC shows the most dramatic effects.

The main achievements of this thesis can be summarized as:

- Development of a tractable atomistic simulation method which introduces uniaxial orientation and explores homogeneous primary nucleation events at any level of undercooling $T_m - T$ within reasonable simulation time at all levels of uniaxial anisotropy, quantified by $\langle P_2(\cos \theta) \rangle$ of the system

- Interpretation of the results within classical nucleation theory

The nucleation rate was found to depend strongly (exponentially) on the level of orientation and temperature. In contrast to this finding for primary nucleation
kinetics, the linear growth rate immediately following the primary nucleation events was found to be relatively insensitive to both the level of the undercooling, and the level of uniaxial anisotropy, but still measurable. Furthermore, the critical nucleus size was found to increase with decreases in the level of undercooling, consistent with the classical nucleation theory.

The current work, as described in this thesis, is not intended to be the final word on this subject. Rather, it represents a first attempt to study, by molecular simulation, the dependence of homogeneous primary nucleation rate in oriented short alkane melts, as well as to probe the simulation time scales associated with the nucleation process, in preparation for applying the same method to longer chain molecules. The results obtained in this thesis are promising for the investigation of long chain molecules, in hopes of capturing more interesting polymer dynamics, such as chain folding and entanglements, so far unobserved in this work. However, this extension introduces significant computational challenges. For example, in order to study chain folding in long-chain molecules at realistic melt densities, the length of the fold will dictate the minimum dimension of the simulation box. This can easily increase the number of particles in the system by one to two orders of magnitude, in order to avoid finite size artifacts. Also, larger system sizes will allow studying multidimensional linear growth rate, as in more complex systems, a more challenging topological description of the nucleation and growth process will be necessary.

In addition to a simple extension of this thesis approach, the future work, or the next step in multi-scale modeling, must provide the connection between the biasing field, which was introduced in MD to simulate uniaxial orientation, with currently developing rheological models. These models tend to coarsen the atomic description from MD simulations to a different set of quantities, such as the $\langle \mathbf{R}\mathbf{R} \rangle$ (the so-called conformation tensor, where $\mathbf{R}$ is the end-to-end vector of the chain molecule) or the stretch parameter $\Lambda$ in the Rolie-Poly model, to name just a few.
Appendix A

Local Order Parameter Properties

1. $S$ is traceless.

2. In the isotropic case, $S_{\alpha\beta} = 0$

3. In a perfectly aligned nematic (all local chord vector pointing along $z$ axis):

$$S = \begin{pmatrix}
-1/3 & 0 & 0 \\
0 & -1/3 & 0 \\
0 & 0 & 2/3
\end{pmatrix} \quad (A.1)$$

4. Since $S$ is symmetric, a Cartesian coordinate system can be found in which the diagonal components are $\frac{2}{3}S$, $-\frac{1}{3}S + B$ and $\frac{1}{3}S - B$. These eigenvalues are ordered, such as $|S|$ has the biggest absolute value. The corresponding eigenvector is called a director $n$. B is biaxiality of the chord vector distribution. For a uniaxial nematic phase, $B = 0$ and $S$ simplifies to:

$$S_{\alpha\beta} = S \left( n_\alpha n_\beta - \frac{1}{3} \right) \quad (A.2)$$

Since in our MD simulations $n$ points along $z$ axis, the three nonzero components of $S$ are:

$$S_{zz} = \frac{2}{3}S \text{ and } S_{xx} = S_{yy} = -\frac{1}{3}S \quad (A.3)$$
The scalar quantity $S$ is a measure of the degree of alignment of molecules. More quantitatively, if $P(\theta) \sin \theta d\theta$ is the fraction of chord vectors which point between $\theta$ and $\theta + d\theta$, then:

$$S = \int_{0}^{\pi} \left(1 - \frac{3}{2} \sin^2 \theta \right) P(\theta) d\theta$$

In the isotropic case $S = 0$ and in the nematic phase $0 < S < 1$. In general, $-\frac{1}{2} < S < 1$, where negative values of $S$ correspond to biaxial orientation perpendicular to the director (also called perfect oblate phase).
Appendix B

Supplementary Data
Figure B-1: Visualization of uniaxially oriented C20 molecules. Different chains are represented by different colors.
Figure B-2: Visualization of uniaxially oriented C150 molecules. Different chains are represented by different colors. Some chain segments were continued outside of the simulation box for clarity purposes.
Figure B-3: Histogram of induction times in C20
Figure B-4: Example quiescent C20 MD trajectories at 20% under-cooling
Figure B-5: Example quiescent C150 MD trajectories at 20% under-cooling
Figure B-6: The summary of induction time $\langle \tau \rangle$, growth rate $G$, the size of the critical nucleus $n^*$ and logarithm of the nucleation rate $I$.

<table>
<thead>
<tr>
<th>Bias $\mu$</th>
<th>$\langle P_2(\cos \theta) \rangle$</th>
<th>$T [K]$</th>
<th>$\langle \tau \rangle [ns]$</th>
<th>$\langle G \rangle [nm/ns]$</th>
<th>$n^*$</th>
<th>$log \langle I \rangle [1/(cm^3 s)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu = 0.02 kT$</td>
<td>$0.05 \pm 0.05$</td>
<td>250</td>
<td>8.0 ± 0.1</td>
<td>0.45 ± 0.1</td>
<td>33</td>
<td>26.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>10.0 ± 0.1</td>
<td>0.45 ± 0.1</td>
<td>64</td>
<td>26.76</td>
</tr>
<tr>
<td>$\mu = 0.07 kT$</td>
<td>$0.1 \pm 0.05$</td>
<td>250</td>
<td>4.5 ± 0.1</td>
<td>0.5 ± 0.1</td>
<td>40</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>3.2 ± 0.5</td>
<td>0.8 ± 0.1</td>
<td>22</td>
<td>27.3646</td>
</tr>
<tr>
<td></td>
<td></td>
<td>270</td>
<td>5.0 ± 1.0</td>
<td>0.7 ± 0.1</td>
<td>30</td>
<td>26.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280</td>
<td>10.0 ± 1.0</td>
<td>0.6 ± 0.22</td>
<td>80</td>
<td>25.36</td>
</tr>
<tr>
<td>$\mu = 0.12 kT$</td>
<td>$0.15 \pm 0.05$</td>
<td>250</td>
<td>1.5 ± 0.5</td>
<td>1.1 ± 0.1</td>
<td>32</td>
<td>27.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>270</td>
<td>1.5 ± 0.5</td>
<td>1.3 ± 0.1</td>
<td>47</td>
<td>27.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280</td>
<td>1.8 ± 0.5</td>
<td>1.43 ± 0.2</td>
<td>55</td>
<td>27.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>290</td>
<td>6 ± 0.3</td>
<td>1.20 ± 0.3</td>
<td>80</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>295</td>
<td>37 ± 1.0</td>
<td>0.75 ± 0.3</td>
<td>125</td>
<td>26.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>200+</td>
<td>NA</td>
<td>NA</td>
<td>25</td>
</tr>
<tr>
<td>$\mu = 0.15 kT$</td>
<td>$0.2 \pm 0.05$</td>
<td>260</td>
<td>1.0 ± 0.1</td>
<td>1.4 ± 0.1</td>
<td>32</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>270</td>
<td>1.0 ± 0.2</td>
<td>1.7 ± 0.1</td>
<td>56</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280</td>
<td>2.0 ± 0.5</td>
<td>2.3 ± 0.2</td>
<td>75</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>290</td>
<td>2.5 ± 0.5</td>
<td>2.7 ± 0.2</td>
<td>85</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>6 ± 1</td>
<td>1.8 ± 0.25</td>
<td>120</td>
<td>25.36</td>
</tr>
</tbody>
</table>
Figure B-7: 8 simulation trajectories at T=295K and biasing parameter $\mu = 0.12kT$ demonstrating stochastic nature of the nucleation process.
Figure B-8: 8 simulation trajectories at T=280K and biasing parameter $\mu = 0.12kT$ demonstrating stochastic nature of the nucleation process
Figure B-9: 16 simulation trajectories at T=290K and biasing parameter $\mu = 0.12kT$ demonstrating stochastic nature of the nucleation process


Julie Kornfield, Shuichi Kimata, Takashi Sakurai, Yoshinobu Nozue, Tatsuya Kasahara, Noboru Yamaguchi, Takeshi Karino, and Mitsuhiro Shibayama.


