## The effect of local chain stiffness on oligomer crystallization from a melt

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While the process by which a polymer crystal nucleates from the melt has been extensively studied via molecular simulation, differences in polymer models and simulated crystallization conditions have led to seemingly contradictory results. We make steps to resolve this controversy by computing low-temperature phase diagrams of oligomer melts using Wang-Landau Monte Carlo simulations. Two qualitatively different crystallization mechanisms are possible depending on the local bending stiffness potential. Polymers with a discrete bending potential crystallize via a single-step mechanism, whereas polymers with a continuous bending potential can crystallize via a two-step mechanism that includes an intermediate nematic phase. Other model differences can be quantitatively accounted for using an effective volume fraction and a temperature scaled by the bending stiffness. These results suggest that at least two universality classes of nucleation exist for melts and that local chain stiffness is a key determining factor in the mechanism of nucleation.

### I. INTRODUCTION

Given the scale of production and the ubiquity of semicrystalline polymers, polymer crystallization remains one of the most important, and most challenging, fundamental problems in polymer science [1]. Despite decades of study, the mechanism by which a crystal first nucleates in a polymer melt remains controversial [2]. The conventional theory, Classical Nucleation Theory (CNT), treats the transition between polymer melt and a crystal nucleus as a single-step transition [3]. However, for the most widely studied case of polyethylene (PE) crystallization, there are numerous experimental observations of mesoscale precursors prior to crystal formation [4-12]. Subsequently, as shown in Fig. 1, a number of researchers have proposed multi-step theories of polymer crystal nucleation [13–16]. For example, Olmsted et al. proposed that a metastable liquid-liquid phase separation intervenes to assist nucleation [13], and Strobl et al. [14] and Milner [15] separately proposed that PE crystallizes via a nematically-aligned intermediate.

The multi-step theories of nucleation by Olmsted, Strobl, Milner, and others rely on the existence of specific (but different) low-temperature thermodynamic behavior as a necessary (but not sufficient) condition. Consequently, although kinetics are critical to the process of polymer crystallization and the resulting microstructure, a study of the thermodynamics of polymer crystallization is necessary for evaluating the plausibility of these theories. Additionally, a better understanding of polymer crystallization thermodynamics will provide context for understanding kinetic effects. Finally, all theories of polymer nucleation predict that free energy barriers dominate system dynamics, and we recently showed that equilibrium methods can be used to calculate free energy landscapes (FELs), providing values of free energy barriers and identifying metastable states [17]. Knowl-



FIG. 1. Schematic of free energy landscape separating a metastable melt from the crystal resulting from CNT, a single-step mechanism, and newer theories postulating two-step phase transitions.

edge of the phase diagram is a necessary pre-requisite for determining FELs. We argue, therefore, that the low-T equilibrium behavior of long-chain molecules continues to require attention, despite the importance of kinetics.

In this manuscript, we use Wang-Landau Monte Carlo (WLMC) simulations [18, 19] to construct low-T equilibrium phase diagrams of a homopolymer melt for several different models of polymers. Unfortunately, even equilibrium simulations of polymer crystallization are numerically costly, so we are presently limited to relatively small systems composed of short chains. We are particularly interested in the existence and location of intermediate phases, such as a nematic phase, that may assist the nucleation process. Here, we focus specifically on how the "virtual chemistry" (i.e., the molecular potentials) of the polymer affects the phase diagram. We find that, at least for these relatively small systems, the bending stiff-

ness of the chain plays a critical role in determining the equilibrium phase behavior.

### A. The Current State of Molecular Simulations of Polymer Crystal Nucleation

Molecular simulations appear ideally suited to directly address the mechanism of primary nucleation for polymers, but the simulation literature contains significant disagreements. For example, several research groups modelled crystallization of a united-atom model of PE and found evidence that supports the single-step transition described by CNT, including a cylindrical critical nucleus and a lack of nematic ordering before crystallization [20–25]. On the other hand, other researchers have observed nematic ordering in simulations of n-alkanes and PE [26, 27], as well as a non-cylindrically shaped nucleus, providing evidence for a two-step transition [3, 26– 31]. Simulations of flow-induced crystallization of PE also provide evidence that chain orientation plays a role in nucleation [32–34].

There are at least two significant issues to consider when seeking to resolve these apparent discrepancies in the literature. First, one must consider the role that kinetics play in the crystallization process, and more specifically, in simulations. Polymer crystallization is a notoriously non-equilibrium process, though exactly which effects are due to thermodynamics and which are due to kinetics remain a subject of vigorous debate [24, 25, 29, 30].

Because kinetics are so important, most simulation studies use non-equilibrium molecular dynamics (NEMD) to study nucleation. In NEMD, a polymer melt is equilibrated above the melting point  $T_m$ , and then instantaneously quenched to a temperature  $T_c < T_m$ , where it crystallizes. Since homogeneous nucleation is a rare event in a dense melt [35], a large degree of supercooling  $S = (T_m - T_c)/T_m$  is used [36] to reduce the nucleation time to the order of nanoseconds [20-22, 37-46]. Consequently, nucleation rates in NEMD are highly accelerated relative to experiments [47], and the rapid crystallization rates in simulations are believed to significantly impact the nucleation mechanism [23–26]. Thus, one reason for the apparent contradictions could be different kinetic protocols, leading to qualitatively different crystallization behavior.

A second possible reason for the discrepancy could be the differences between the molecular potentials. A numerical polymer model can be thought of as its *virtual monomer chemistry* [48], and thus the relation between molecular potentials and crystallization behavior is related to the question of "universality" in polymer crystallization. The principle of universality in polymer physics applies when chain-level degrees of freedom dominate the physical behavior independent of monomer chemistry [49], and this concept is widely invoked for more coarse-grained phenomena such as block copolymer self-assembly and entanglement dynamics. Its usefulness for polymer crystallization is more complicated because there are some phenomena, such as crystal structure, that are monomer dependent and thus clearly not universal, but others, such as the formation of folded lamellae, appear to be common to nearly all polymer chemistries.

The simulations of PE cited above employ various (all-atom or united-atom) force fields including Paul-Yoon-Smith (PYS) [50], OPLS [51, 52], Flexible Williams (FW) [53], Shinoda-DeVane-Klein (SDK) [54, 55], TraPPE [56], and Siepmann-Karaboni-Smit (SKS) [57]. All of these models are parameterized for the well-studied system of monodisperse linear n-alkanes, and at first blush, it seems surprising that the equilibrium crystallization behavior of these models could be qualitatively different. Nevertheless, there are important differences in the degree of coarse-graining between some of these models, and coarse-graining can indeed produce important effects on phase behavior [26, 39, 58]. Therefore, it is possible that some of these different numerical model "chemistries" could belong to different universality classes of crystallization.

### B. Our Approach

In the present work, we use equilibrium simulation methods to investigate the crystallization phase behavior of several model polymers. Our objective is to catalogue which monomer "chemistries" lead to a given "universality class" of equilibrium crystallization behavior. Equilibrium methods eliminate the need for a kinetic protocol that has made it difficult to interpret and compare simulations of polymer crystal nucleation in the literature. By avoiding one of the key sources of variation between simulations in the literature, we are free to focus on examining how differences in molecular potentials lead to different crystallization thermodynamics.

Note an important caveat when connecting the results that follow with the nucleation theories discussed at the outset. The *equilibrium universality class* (phase behavior and FEL) is not equivalent to the *dynamic universality class* for nucleation; the latter involves dissipative processes that may, for example, lead to the kinetically preferred formation of a metastable state. However, we hypothesize that it is a necessary condition for two systems to reside within the same equilibrium universality class. Stated less abstractly, a phase diagram must be compatible with a given nucleation theory (one-step or two-step), but the existence of a compatible phase diagram is not positive proof of a nucleation mechanism.

Unfortunately, even neglecting kinetics, simulating polymer crystallization is numerically expensive, and it is difficult and costly to calculate phase diagrams of dense melts containing long chains with accurate molecular potentials. Indeed, these limitations widely impede progress in the field. Therefore, we resort here to two simplifying assumptions in order to make progress. First, we use short oligomers. Shorter chains significantly reduce simulation costs, which are substantial due to low-temperatures, large nucleation barriers, and extended chains. In particular, a crystalline state consisting of fully extended chains requires a relatively large simulation box (compared to simulations of a melt) to avoid unphysical self-interactions. Using short chains therefore limits the required size of the box, helping to reduce finite-size effects. We obtain valuable results despite the relatively short chains, and we anticipate future progress in our abilities to reach larger system sizes as we improve our methods.

Second, we use relatively simple molecular potentials. The use of simple polymer models may also appear unwise, because, as discussed, the details of crystallization necessarily depend on atomic-level structure. However, we use simple models because they are less expensive to simulate, they facilitate comparison with prior work [17, 59–64] and possible generalization.

The rest of the paper proceeds as follows. We detail our methods in Section II, with Section II A explaining the polymer models and parameters, and Section II B detailing the protocol for constructing phase diagrams. The main results are contained in Section III, beginning with the identification of the low-T phases and phase transition temperatures in Section III A. We then present the phase diagrams of the various models and the effect of bending stiffness on phase behavior in Section III B. After ascertaining the impact of the bending stiffness, we explore the effects of excluded volume on phase behavior in Section III C. We then offer brief concluding remarks and a perspective for future research in Section IV.

### II. METHODS

Our WLMC simulations consist of a melt of  $N_c = 125$ chains that contain  $N_b = 10$  beads per chain in a periodic box of volume V. They generate representative melt configurations and a density of states  $\Omega(U)$  as a function of potential energy U.  $\Omega(U)$  is post-processed to compute a heat capacity  $C_V(T)$  and temperature profiles of various crystalline and nematic order parameters (OPs) [17, 65–67]. We performed WLMC simulations at different volume fractions,

$$\phi = \frac{\pi a^3 N_c N_b}{6V} \tag{1}$$

where a is the bead size, in the range  $\phi \in [0.2, 0.5]$  to obtain phase diagrams as a function of both T and  $\phi$ .

We focus on two different families of polymer models, shown in Fig. 2, based on the way local chain stiffness is calculated: (i) a "discrete stiffness" family employing a discontinuous bending potential that has recently been used in several studies of oligomer crystallization [17, 59, 67], and (ii) a "continuous stiffness" family of models (equivalent to a Kratky–Porod or wormlike chain [68]) consisting of polymers whose stiffness



FIG. 2. Schematic of the two families of bending stiffness: discrete and continuous.

comes from a harmonic bending potential between adjacent bonds. The model of a polymer chain must also include a bonding potential  $U_{\text{stretch}}$  and a non-bonded (excluded volume) pair potential  $U_{\text{pair}}$ . We examine multiple models for  $U_{\text{stretch}}$  and  $U_{\text{pair}}$  within each of the two families. For  $U_{\text{stretch}}$ , we study rigid-rod and harmonic bonding potentials with a bond length scale  $l_0$ , whereas for  $U_{\text{pair}}$ , we employ hard-bead and soft repulsive (Weeks-Chandler-Anderson, WCA) non-bonded potentials characterized by the parameter  $\sigma$ . There are no attractive interactions in the models discussed here. Several authors have provided evidence that attractive interactions are of secondary importance for the qualitative phase behavior [37–40, 59, 60, 69], and we leave a deeper investigation of this issue to future work.

The following sections detail the methods we used to collect, analyze, and interpret our results. Section II A describes the coarse-grained polymer models and their potentials in greater detail. Then, Section II B details the protocol for determining phase diagrams, including a descriptions of the order parameters that we use. Further methodological details are found in the Supplemental Material (SM) [70] (see also references [18, 19, 59, 64, 71–90] therein).

### A. Polymer Models and Parameterization

We use a coarse-grained model that has been estimated to be roughly equivalent to about four  $CH_2$  monomers of polyethylene for one coarse-grained bead [52]. While this unfortunately sacrifices atomic-level accuracy, these models allow one to capture important polymer physics including connectivity, excluded volume, and chain stiffness. The latter is especially important for our present purposes as we seek to understand what is *universal* about the crystallization behavior among several different polymer models.

A polymer model is defined by the total potential energy,

$$U_{\rm tot} = U_{\rm bend} + U_{\rm stretch} + U_{\rm pair} \tag{2}$$

where  $U_{\text{bend}}$  is the bond angle bending energy,  $U_{\text{stretch}}$  is the bond length stretching energy, and  $U_{\text{pair}}$  is the nonbonded (pairwise) potential energy. In this paper, we study eight different polymer potential variations: two for each of the potentials (bending, stretching, and nonbonded) in Eq. 2.

The family of polymer models is defined by the bending potential, which accounts for polymer chain stiffness. The continuous stiffness (i.e., wormlike) potential is a harmonic bending potential between adjacent bonds,

$$U_{\text{bend}} = \sum_{i=1}^{N_c(N_b-1)} u_{\text{cont}}(\theta_i)$$
(3)

$$u_{\rm cont}(\theta_i) = \epsilon_{\theta}(1 - \cos \theta_i) \tag{4}$$

where

$$\boldsymbol{l}_i = \boldsymbol{r}_{i+1} - \boldsymbol{r}_i \tag{5}$$

is the bond vector between bead i and its neighbor along the backbone of the chain,  $l_i = |l_i|$  is the bond length,

$$\theta_i = \frac{\boldsymbol{l}_i \cdot \boldsymbol{l}_{i-1}}{l_i l_{i-1}} \tag{6}$$

is the bond angle, and  $\epsilon_{\theta}$  is the bending elasticity. The discrete stiffness (i.e., square-well) potential is given by

$$U_{\text{bend}} = \sum_{i=1}^{N_c(N_b-1)} u_{\text{disc}}(\theta_i) \tag{7}$$

$$u_{\rm disc}(\theta_i) = \begin{cases} -\epsilon_\theta & \theta_i \le \theta_s, \\ 0 & \theta_i > \theta_s \end{cases}$$
(8)

where  $\theta_s = \cos^{-1}(0.9)$  is a critical upper bound on bond angles that are favored. Both types of potentials incentivize chains to adopt extended conformations.

Each model family (continuous or discrete stiffness) has four different possible combinations of stretching ("rod-like" and "spring") and nonbonded ("hard-sphere" and "soft-sphere") potentials. The rod-like stretching potential is given by

$$U_{\text{stretch}} = \sum_{i=1}^{N_c(N_b-1)} u_{\text{rod}}(l_i) \tag{9}$$

$$u_{\rm rod}(l_i) = \begin{cases} \infty & l_i \neq l_0 \\ 0 & l_i = l_0 \end{cases}$$
(10)

where  $l_0$  is the equilibrium bond length. Eq. 10 only allows constant bond lengths, which we set to be the size of the nominal bead diameter *a*. The spring stretching potential is harmonic and is given by

$$U_{\text{stretch}} = \sum_{i=1}^{N_c(N_b-1)} u_{\text{spring}}(l_i)$$
(11)

$$u_{\rm spring}(l_i) = \frac{\epsilon_l}{2} \left( l_i - l_0 \right)^2 \tag{12}$$

where  $\epsilon_l = 600k_BT/a^2$  is the bond spring constant and  $l_0 = a$ . Polymers that use Eq. 12 have bonds that fluctuate around  $l_0$  to a degree that depends on the strength of  $\epsilon_l$ .

The hard-sphere nonbonded potential accounts for purely repulsive excluded volume interactions and is given by

$$U_{\text{pair}} = \sum_{i=1}^{N_c N_b} \sum_{j=1}^{N_n(i)} u_{\text{hard}}(r_{ij})$$
(13)

$$u_{\text{hard}}(r_{ij}) = \begin{cases} \infty & r_{ij} < \sigma \\ 0 & r_{ij} \ge \sigma \end{cases}$$
(14)

where  $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$  is the distance between beads *i* and *j*,  $N_n(i)$  are the number of neighbors of bead *i* with a nonzero pairwise potential, and  $\sigma$  is the hard-bead diameter which is set equal to *a*. The soft-sphere nonbonded potential is the purely repulsive Weeks-Chandler-Anderson (WCA) potential given by

$$U_{\text{pair}} = \sum_{i=1}^{N_c N_b} \sum_{j=1}^{N_n(i)} u_{\text{WCA}}(r_{ij})$$
(15)

$$u_{\text{WCA}}(r_{ij}) = \begin{cases} 4\epsilon_{ij} \left[ \left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6 \right] + \epsilon_{ij} & r_{ij} < 2^{1/6}\sigma \\ 0 & r_{ij} \ge 2^{1/6}\sigma \\ (16) \end{cases}$$

where  $\epsilon_{ij}$  and  $\sigma$  are the WCA pair potential energy and length scale, respectively. The value of  $\sigma$  in the WCA potential is set to  $2^{-1/6}a$  so that the effective bead diameter is commensurate with the equilibrium bond length  $l_0$ , ensuring that crystallization is possible [64, 87] (details available in the SM [70]). Notably, neither of these nonbonded potentials include attractive interactions. We neglect them here for simplicity, but we note that several studies suggest that their effect is a simple shift of the temperature-dependence of the phase diagram [37– 40, 59, 60, 69]. A summary of the parameters for each potential are given in Table I.

Dimensional analysis reveals that there are six dimensionless groups that could control the phase behavior. At minimum, this includes the dimensionless volume fraction  $\phi$ , the bond length-bead diameter aspect ratio  $l_0^* = l_0/a$ , and the reduced temperature  $T_r = k_B T/\epsilon_{\theta}$ . In addition, if the model uses a WCA nonbonded potential (instead of a hard-sphere potential) then there is a dimensionless bending stiffness scale,  $\epsilon_{\theta}^* = \epsilon_{\theta}/\epsilon_{ij}$ , if the model includes a harmonic stretching potential (instead of the rigid-rod potential) then there is a dimensionless spring stiffness  $\epsilon_l^* = \epsilon_l/(\epsilon_{ij}a^2)$ , and if the model includes a discrete stiffness bending potential (instead of the continuous potential) then  $\cos \theta_s$  is also a group.

Where appropriate, we set  $\cos \theta_s = 0.9$ ,  $l^* = 1$  and  $\epsilon_l^* = 600$ , and did not explore other values of these groups. We chose  $\cos \theta_s = 0.9$  to enable comparisons with Refs. 59 and 17 and to facilitate nematic alignment.

TABLE I. Summary of parameters for the various potentials used in the study.

Bendi	ng Potential		
	$ heta_s$		
Discrete (D)	$\cos^{-1}(0.9)$		
Continuous (C)	N/A		
Stretching Potential			
	$\epsilon_l$	$l_0$	
Rod (R)	N/A	a	
Spring $(S)$	$600\epsilon_{\theta}/a^2$	a	
Nonbonded Potential			
	$\epsilon_{ij}$	$\sigma$	
Hard $(H)$	N/A	<i>a</i>	
WCA $(W)$	$\epsilon_{ heta}$	$2^{-1/6}a$	

TABLE II. Naming scheme for polymer models.

Systematic Name	Shorthand
DRH (Discrete, Rod, Hard)	Model A
DRW (Discrete, Rod, WCA)	
DSH (Discrete, Spring, Hard)	
DSW (Discrete, Spring, WCA)	
CRH (Continuous, Rod, Hard)	Model B
CRW (Continuous, Rod, WCA)	
CSH (Continuous, Spring, Hard)	
CSW (Continuous, Spring, WCA)	Model C

If  $l^* \neq 1$  the bonds are incommensurate with the bead diameter and crystallization is inhibited [64, 87]. A large value of  $\epsilon_l^*$  gives stiff springs; soft springs are physically unrealistic for studying crystallization and our preliminary testing suggested that phase behavior was relatively insensitive to this parameter.

The more interesting dimensionless groups are  $\phi$ ,  $\epsilon_{\theta}^*$ , and  $T_r$ , and we produce phase diagrams in  $\phi$ - $T_r$  space with volume fractions  $\phi \in [0.2 - 0.5]$ ,  $T_r \in [0, 0.5]$ , and  $\epsilon_{\theta}^* \in \{0.1, 1, 10\}$ . The high- $\phi$  simulations are quite dense; for comparison, the volume fractions of random and maximum close-packed configurations of hard spheres are 0.64 and  $\pi/(3\sqrt{2}) \approx 0.7405$ , respectively [91].

Finally, because there are numerous combinations of potentials, it is useful to define a systematic naming scheme for the models. We define our scheme based on the choice of potentials in the polymer model, following the order: bending potential (discrete or continuous), stretching potential (rods or springs), and nonbonded potential (hard or WCA). For example, a model with a discrete bending potential (Eq. 7), rod-like bonds (Eq. 9), and a hard-sphere nonbonded potential (Eq. 13) is labelled the DRH model. Because they are used frequently in this paper, the DRH model, the CRH model, and the CSW model are also labeled Models A, B, and C respectively for ease of reference. The naming scheme and shorthand names are summarized for clarity in Table II.

## B. Procedure for Constructing Phase Diagrams

The entropy obtained from a WLMC simulation can be used to compute heat capacity and order parameter profiles as a function of temperature, enabling the identification of phases and phase transitions. By sweeping volume fraction in different simulations, one can construct phase diagrams in the  $\phi$ - $T_r$  plane. This section presents a brief overview of the procedure for the creation of these phase diagrams, including details of the order parameters used to identify the phases. Note that we have also previously identified these phases in a system nearly identical to Model A using real space images and two-dimensional structure factors [17, 67].

Specifically, we observe three phases in this system: a disordered melt phase (I), a nematic phase (N), and a crystal phase (C). We use two order parameters,  $f_{\rm cryst}$ and  $P_2$ , to quantify crystalline and nematic order in these phases.  $f_{\rm cryst}$  represents the fraction of crystalline beads based on the well-known Steinhardt order parameter [17, 65, 66], and  $P_2$  is the second Legendre polynomial, a measure of nematic order [17].

We use heat capacity and order parameter curves to locate the relevant phase transition temperatures: isotropic-nematic (IN), isotropic-crystal (IC) and nematic-crystal (NC). The constant-volume heat capacity is given by

$$\langle C_V(T) \rangle = \frac{\langle U^2(T) \rangle - \langle U(T) \rangle^2}{k_B T^2} \tag{17}$$

where the moments of U are calculated using

$$\langle U^n(T)\rangle = \frac{\sum_i U_i^n \exp(\ln\Omega_i - U_i/k_B T)}{\sum_i \exp(\ln\Omega_i - U_i/k_B T)}$$
(18)

and  $U_i$  and  $\Omega_i = \Omega(U_i)$  are discrete states of the energy and density of states obtained from the WLMC simulation. It is also useful to define a dimensionless heat capacity,

$$\tilde{C}_V = \frac{\langle C_V \rangle}{k_B N_c (N_b - 2)}.$$
(19)

At a phase transition temperature  $T_m$ ,  $\tilde{C}_V(T_m)$  exhibits a large narrow peak.

Order parameter "melting curves" can be obtained using

$$\langle M(T) \rangle = \frac{\sum_{i} \langle M_i \rangle \exp(\ln \Omega_i - U_i / k_B T)}{\sum_{i} \exp(\ln \Omega_i - U_i / k_B T)}$$
(20)

where M is an order parameter such as  $P_2$  or  $f_{\text{cryst}}$  and  $M_i = M(U_i)$ . The order parameter curves  $\langle M \rangle$  exhibit discontinuities at a phase transition temperature.

The parameter  $P_2$  characterizes the average local nematic alignment of the polymer chain contours. The chain orientation is determined by computing the angle between the bond vectors of a polymer chain with those of its neighbors. More precisely, each of the  $N_c$  chains contains  $N_b - 1$  bond vectors,

$$\boldsymbol{l}_i = \boldsymbol{r}_i - \boldsymbol{r}_{i-1} \tag{21}$$

and a local order parameter for each bond vector is given by

$$p_2(i) = \frac{3}{2} \langle \cos^2 \theta_{ij} \rangle_{\text{neigh}} - \frac{1}{2}$$
(22)

where  $\theta_{ij}$  is the angle between bond vectors  $l_i$  and  $l_j$ , and the average  $\langle \rangle_{\text{neigh}}$  is over all j neighbors (regardless of which chain) that lie within a distance of  $1.3\sigma$  from  $r_i$ . The global order parameter is calculated as an average over all bond vectors in the system using

$$P_2 = \langle p_2(i) \rangle. \tag{23}$$

 $P_2$  varies from zero when the system is isotropic, to one when all bond vectors are perfectly aligned along a single direction.

The parameter  $f_{\text{cryst}}$  is the fraction of monomers in the system that are crystalline. Following Reinhardt et al. [66], we define a monomer to be crystalline if it resides in a cluster with a minimum number of neighbors with solid-like ordering. Solid ordering is determined by the pairwise local order parameter

$$d_l(i,j) = \boldsymbol{q}_l(i) \cdot \boldsymbol{q}_l^*(j) \tag{24}$$

between beads i and j that are within a pairwise distance of  $1.3\sigma$ . The vectors

$$\boldsymbol{q}_l(i) = [q_{l,m}(i)]^T \tag{25}$$

in Eq. 24 have 2l + 1 components that are the Steinhardt order parameters of bead *i* [65],

$$q_{l,m}(i) = \langle Y_{l,m}(\boldsymbol{r}_{ij}) \rangle_{\text{neigh}}$$
(26)

with  $m \in [-l, l]$ . In the above,  $q_l^*$  is the complex conjugate of  $q_l$ ,  $Y_{l,m}$  is the spherical harmonic function of degree l and order m,  $r_{ij} = r_j - r_i$  is the vector between bead i and its neighbor j, and  $\langle \rangle_{\text{neigh}}$  is again the average over all neighbors within a distance of  $1.3\sigma$  of  $r_i$ . The symmetries of the hexagonal crystals formed by these molecules are well distinguished by sixth order (l = 6) Steinhardt parameters, and so we use  $q_6$ .

Using these definitions, we can more precisely define a monomer to be crystalline when there are at least  $n_c$ neighbors within a distance of  $1.3\sigma$  where  $d_6(i, j) > d_c$ . In this work, we set the critical solid ordering parameter to be  $d_c = 0.6$  and the minimum number of neighbors to be  $n_c = 6$ . Mathematically, the number of crystalline neighbors of bead *i* can be expressed as

$$n_{\rm cryst}(i) = \sum_{j=1}^{N_n(i)} H(d_6(i,j) - d_c)$$
(27)

where H(x) is the Heaviside function

$$H(x) = \begin{cases} 1 & x > 0\\ 0 & x \le 0 \end{cases},$$
 (28)

and  $N_n(i)$  is the number of neighbors of bead *i* within a radius of  $r_{ij} < 1.3a$ . Finally, the total fraction of crystalline monomers  $f_{\text{cryst}}$  is determined via

$$f_{\rm cryst} = \langle H(n_{\rm cryst}(i) - n_c) \rangle \tag{29}$$

As is the case with  $P_2$ , the value of  $f_{\text{cryst}}$  is zero when the system has no crystalline order and approaches one when the chains fully crystallize.

## III. RESULTS AND DISCUSSION

### A. Order Parameter Thermal Profiles for Model A and Model B

Our goal is to construct phase diagrams in the  $\phi$ - $T_r$  plane for various models to probe the universality of phase behavior. In this section, we provide details of the calculations that are necessary to determine phase diagrams for models A and B. As outlined in Section II B, WLMC simulations permit the direct calculation of  $\Omega$  as a function of energy at a fixed volume fraction  $\phi$ . One can then use  $\Omega$  and simulation configurations to compute the order parameter as a function of temperature. The values and discontinuities in the order parameter thermal profiles enable one to identify the phases and the location of the phase transitions.

Figure 3 shows  $\Omega$  for a representative system of Model A at  $\phi = 0.463$ . The relevant energy range

$$U \in \left[-N_c \left(N_b - 2\right) \epsilon_{\theta}, 0\right] \tag{30}$$

is subdivided into 32 overlapping WLMC windows (with eight replicates for each window). To accelerate convergence, we used a replica-exchange scheme where configurations are exchanged between windows and an entropyexchange method where global histograms and entropies are aggregated from replicates. After all windows converge, shown in Fig. 3a, the areas of overlap between windows are used to stitch together a global  $\Omega$ , shown in Fig. 3b. This latter step is necessary because  $\Omega$  is only known to within an arbitrary constant. The inset of Fig. 3b shows the least-squares stitching procedure for the last two windows ( $R^2 = 0.998$ ).

In addition to  $\Omega$ , configurations generated from the last WLMC iteration (n = 27) can be used to compute the nematic and crystal order parameters. Figure 3c shows curves of  $P_2$  and  $f_{\text{cryst}}$  obtained from WLMC (averaged over the eight replicates) as a function of U. At high U, both order parameters are small indicating that the high energy state is a disordered melt. By contrast, both order parameters rise significantly above zero at the ground



FIG. 3. Direct result of WLMC simulations for Model A at  $\phi = 0.463$ . (a) Density of states  $\Omega$  for 32 overlapping windows, averaged over 8 replicates, versus potential energy U. (b) The "stitched" global  $\Omega$  with inset showing the stitching protocol for the rightmost pair of windows.  $\Omega'$  in the inset corresponds to the value before stitching. (c) Average order parameters  $P_2$  and  $f_{\rm cryst}$  as a function of U. The apparent level of noise is a consequence of the small bin size of U.

state  $(U = -1000\epsilon_{\theta})$ , indicating the occurrence of a crystal phase.

We desire phase diagrams in the  $\phi$ - $T_r$  plane, so we use the equations in Section II B to transform the data to be a function of T rather than U. Accordingly, Fig. 4 shows thermal profiles of the nematic order parameter  $P_2$ , the fraction of crystalline beads  $f_{cryst}$ , and the dimensionless heat capacity  $\tilde{C}_V$  for Model A and Model B at both low and high values of the volume fraction  $\phi$ .

Figure 4a shows thermal profiles for the order parameters and heat capacity for Model A at the relatively low volume fraction  $\phi = 0.407$ . At high  $T_r$  the system has small values of nematic and crystalline order, characteristic of an isotropic melt. At low  $T_r$ ,  $P_2$  rises significantly but  $f_{\text{cryst}}$  does not, indicating a transition to a phase with orientational (but not crystalline) order. This isotropic (I) to nematic (N) transition happens at  $T_r = T_{IN} \approx 0.246$ , where  $P_2$  sharply increases and the heat capacity  $\tilde{C}_V$  shows a distinct peak. The step discontinuity in the order parameter and divergence in the heat capacity at  $T_{IN}$  (tempered by finite-size effects) are classical indicators of a first-order phase transition.

Figure 4b shows corresponding thermal profiles for  $P_2$ ,  $f_{\rm cryst}$ , and  $C_V$  for model A at a larger volume fraction,  $\phi = 0.463$ . Once again,  $P_2$  and  $f_{cryst}$  are small at high  $T_r$ —evidence that the system is an isotropic melt. At low  $T_r$ , both  $P_2$  and  $f_{cryst}$  show a pronounced increase, indicating the simultaneous development of both orientational and crystalline order. In other words, there is an isotropic (I) to crystalline (C) transition that happens at  $T_r = T_{IC} \approx 0.302$ , and again, the appearance of step discontinuities and a narrow peak in the heat capacity at the same temperature provide evidence that this is a firstorder transition. Notably, at this higher volume fraction, the IC transition temperature is at a larger  $T_r$  than the IN transition, showing the impact of system density on the transition temperature as well as the nature of the transition.

The behavior of Model B differs qualitatively from that of Model A at both low and high volume fraction. Figure 4c shows  $P_2$ ,  $f_{cryst}$ , and  $\tilde{C}_V$  for Model B at the relatively low volume fraction of  $\phi = 0.407$ . As before, the values of  $P_2$  and  $f_{cryst}$  are small at large  $T_r$  indicating an isotropic melt. Unlike the previous results, in this case there are *two* phase transitions. At  $T_r = T_{IN} \approx 0.117$ there is a jump in the nematic order parameter  $P_2$  and a peak in  $\tilde{C}_V$ , indicative of an isotropic–nematic transition. In addition, at  $T_r = T_{NC} \approx 0.025$  there is a rapid rise in the crystalline order parameter  $f_{cryst}$ , marking a transition from a nematic to a crystalline phase.

Notably,  $\tilde{C}_V$  shows no distinguishable peak at this transition. We explain the lack of a second peak to a low "signal-to-noise" ratio, i.e., this transition has a small heat of fusion (see the Supplemental Material [70] for curves of the internal energy) making the peak small, and there is statistical sampling error in the heat capacity (a second order derivative of  $\Omega$ ) that makes the peak indistinguishable from noise. Physically, we reason that the heat of fusion for the crystallization transition is small, because the chains are already nematically aligned, and positional ordering is a relatively small collective movement from aligned chains. Regardless, the order parameter profiles make it clear that crystallization in this system requires a transition from an isotropic melt to a nematic phase, and a transition from a nematic to a crystal phase.

The evidence for two transitions is further reinforced by simulations at higher volume fraction. Figure 4d shows plots of the thermal profiles of  $P_2$ ,  $f_{cryst}$ , and



FIG. 4. Thermal profiles of  $P_2$  in blue,  $f_{cryst}$  in green, and  $\tilde{C}_V$  in red. (a) WLMC simulation of Model A at a low volume fraction ( $\phi = 0.407$ ) showing a discontinuity at  $T_r = 0.246$ . (b) WLMC simulation of Model A at a high volume fraction ( $\phi = 0.463$ ) showing a discontinuity at  $T_r = 0.302$ . (c) WLMC simulation of Model B at a low volume fraction ( $\phi = 0.407$ ) showing two discontinuities at  $T_r = 0.025 T_r = 0.117$ . (d) WLMC simulation of Model B at a high volume fraction ( $\phi = 0.463$ ) showing two discontinuities at  $T_r = 0.131$  and  $T_r = 0.164$ .

 $\tilde{C}_V$  for Model B at  $\phi = 0.463$ . Here the results are qualitatively similar to the lower density case, with an IN transition at  $T_{IN} \approx 0.164$  and an NC transition at  $T_{NC} \approx 0.131$ . Again in this case, because of a small heat of fusion, one cannot distinguish the peak in the heat capacity for the crystallization transition from statistical sampling error, which give rise to spurious fluctuations in  $\tilde{C}_V$  that are on the order of  $k_B$  per bead.

From the above, we conclude that there are three equilibrium phases in Model A and Model B: an isotropic melt (I), a nematic phase (N), and a crystal phase (C). Additionally, we find evidence that isochoric crystallization in Model A proceeds via a single step, but takes place in two steps in Model B. The data for Model A agrees with our previous study that also included images of real-space configurations, 2D structure factors, and other order parameters [17].

## B. Comparison of the Phase Behavior of Model A and Model B

In this section, we explore in greater detail the surprising result that Model A has a single-step melt to crystalline transition, whereas Model B has a two-step transition with an intermediate nematic phase. Recall that the only difference between these models is the form of the bending potential: Model A has a discontinuous squarewell potential, and Model B has a continuous wormlike potential. We first compile the results from numerous WLMC simulations of Model A and Model B at different volume fractions into phase diagrams in the  $\phi$ - $T_r$  plane in Figure 5. The order parameter profiles for both models at all values of  $\phi$  that are used to create these phase diagrams are provided in the SM [70].

The phase diagram for Model A is shown in Fig. 5a, and it contains two types of transitions along isochores. At low  $\phi$ , there is a transition  $T'_{IN}$  from an isotropic melt to a nematic phase. At high  $\phi$ , there is a transition  $T'_{IC}$  from an isotropic to a crystalline phase. Separating these two transitions, there is an isochoric critical volume fraction  $\phi'_{IN}^* = 0.440$ .

The phase diagram for Model B is shown in Fig. 5b, and it displays qualitatively different behavior. For nearly all of the volume fractions we computed, there is an isotropic to nematic transition  $T_{IN}$  along an isochore, and a nematic to crystal transition that follows at  $T_{NC} < T_{IN}$ . At very low  $\phi$ , the NC transition occurs at or very close to  $T_r = 0$  or it disappears entirely. As we discuss below, we suspect that this behavior is due to the



FIG. 5. Phase diagrams for (a) Model A and (b) Model B in the  $\phi$ - $T_r$  plane containing crystalline (C), nematic (N), and isotropic melt (I) phases. Solid curves are least-square fits to the data provided as a guide to the eye.

temperature-dependent stiffness of the chains at low  $T_r$ . At high  $\phi$ , the IN and NC curves appear to converge, and we speculate that there is a single-step IC transition  $T_{IC}$ beyond a critical point  $(T_{IN}^*, \phi_{IN}^*) \approx (0.164, 0.473)$ . Unfortunately, we were unable to directly observe a singlestep IC transition in Model B due to large computational costs for very dense systems.

It is useful to compare both of these models to a system of freely-jointed chains (FJC) of hard spheres, which crystallizes at a critical volume fraction of  $\phi^* \approx 0.57$  independent of temperature [61, 92]. We hypothesize that the presence of temperature-dependent chain stiffness in the present models promotes alignment that reduces the volume fraction where crystallization can occur compared to the FJC.

The difference between the phase diagrams for the two models is relevant for the debate in the literature on the mechanism of polymer crystal nucleation. The crystallization transition for Model A when  $\phi > \phi'_{IN}^*$  is a singlestep transition consistent with CNT. By contrast, the crystallization transition for Model B when  $\phi < \phi_{IN}^*$  is a two-step transition with a nematic intermediate, consistent with the theories of Strobl et al. [14] and Milner [15]. The change in equilibrium behavior will also significantly impact the free energy barriers and the relative free energy of metastable intermediates, the latter of which has been shown to be important in flow-induced crystallization [27]. Computing such barriers requires a complete temperature-dependent free energy surface [17], which we leave for future investigation.



FIG. 6. Dimensionless persistence length  $l_p/l_0$  versus reduced temperature  $T_r = k_B T/\epsilon_{\theta}$  for phantom Model A (magenta) and phantom Model B (blue). For both models, lines are theoretical predictions (detailed in the SM [70]). The standard errors of data points are smaller than the size of the symbols.

It remains to understand why there is such a dramatic qualitative difference in the phase behavior of the two models. Because the only difference is the bending potential, we reason that chain stiffness must be a key factor. To better understand how chain stiffness differs between the two models, we computed the temperature dependence of the persistence length  $l_p$  for both types of chains. The persistence length is defined as the length scale that characterizes the decorrelation of segments along the chain backbone and is a measure of chain stiffness [81],

$$\langle \cos \theta(s) \rangle = \exp\left(-sl_0/l_p\right)$$
 (31)

where  $\theta(s)$  is the angle between two bonds along the chain separated by s bonds. To eliminate excluded volume and density effects, we calculated  $l_p$  using "phantom chain" (i.e., models neglecting nonbonded interactions) NVTensemble Monte Carlo (MC) simulations. Further details of these calculations are given in the SM [70].

In addition, as both models are types of freely rotating chains, it is possible to compute closed form expressions for the persistence length of both models as a function of temperature. The persistence length of a freely rotating chain is given by [81]

$$\frac{l_p}{l_0} = \frac{1}{2} \left[ \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} \right]. \tag{32}$$

For phantom Model A, the ensemble-averaged bond angle is given by,

$$\langle \cos \theta \rangle = \frac{19}{20} \frac{\exp(1/T_r) - 1}{\exp(1/T_r) + 19}.$$
 (33)

For phantom Model B, the average bond angle is given by,

$$\langle \cos \theta \rangle = 1 - T_r - \frac{2}{1 - \exp\left(2/T_r\right)}.$$
 (34)

Further details on the derivation of the relationship between the ensemble-averaged angle  $\langle \cos \theta \rangle$  and temperature are available in the SM [70].

Fig. 6 shows the dimensionless persistence length  $l_p/l_0$ for phantom Model A and phantom model B versus the reduced temperature  $T_r$  alongside the theoretical expressions defined by Equations 32, 33, and 34. The data for the phantom chains agrees very well with the theoretical results. Intuitively, both models have a smaller  $l_p$  (indicating more flexible chains) at higher temperatures when thermal fluctuations are strong and a larger  $l_p$  (indicating stiffer chains) at lower temperatures when thermal fluctuations are weak. Additionally, both models become flexible as  $T_r \to \infty$ , approaching  $l_p/l_0 = 0.5$ (the value for a freely jointed chain). Finally, we show in the Supplemental Material [70] that data for phantom simulations with additional models (DSH, CSH) collapse to the same curves, indicating that the reduced temperature that has been normalized by the bending elasticity is the proper dimensionless parameter.

The differences in the persistence length curves between the models is more interesting. For Model A, the stiffness sharply increases around  $T_r \approx 0.25$ , and the persistence length converges to  $l_p/l_0 = 19.5$  as  $T_r \to 0$ . By contrast, the chains in phantom Model B smoothly proceed from flexible to stiff and the persistence length diverges as  $l_p \sim T_r^{-1}$  as  $T_r \to 0$ . Upon reflection, both behaviors are consistent with their respective bending potentials. The discontinuous stiffness in Model A has a finite reward per bond for remaining below  $\theta_s$ , meaning increasingly low temperatures cannot induce further stiffening. On the other hand, the harmonic penalty for wormlike chains in Model B penalizes even minute deviations of bond angles from 180°, and this penalty increasingly dominates as  $T_r$  approaches 0.

Because the persistence length of the chains in Model B diverges and those in Model A do not, the most drastic difference between the models is at low  $T_r$ , precisely where crystallization occurs. We hypothesize that this difference in persistence length at low  $T_r$  is the cause of the differences in phase behavior, and therefore accounts for the one-step or two-step crystallization transition. In order for entropy to favor chain crystallization, the chain must either be (i) very stiff locally to prefer a lattice to conformational fluctuations (stiffness-driven crystallization) or (ii) it must be in a very dense environment to prefer the relative freedom of a lattice to liquid-like packing (density-driven crystallization). Chains in Model A align nematically as temperature decreases, but because  $l_p$  reaches a plateau, they apparently cannot become stiff enough to crystallize via mechanism (i). Thus, Model A must be above a critical density in order to crystallize, limiting them to a one-step crystallization transition at constant  $\phi$ . By contrast, the chains in Model B have no such plateau, so a stiffness-driven crystallization is possible as temperature decreases even for moderate densities. Thus, Model B can exhibit an isochoric two-step crystallization transition.

## C. Effect of Excluded Volume on the Phase Behavior of Model C

While useful for Monte Carlo studies, models with hard sphere repulsion and rigid bonds are rarely useful in molecular dynamics and are not compatible with simulations in a constant pressure ensemble. As such, in this section we investigate a model with a continuous bending potential, spring-like bonds, and nonbonded interactions modeled by a WCA potential (i.e., the CSW model or Model C). The softness of nonbonded interactions are also important for the debate on polyethyleene crystallization, because models with different levels of coarsegraining are largely distinguished by their nonbonded interaction parameters. Accordingly, we investigate here if the relative strength of excluded volume interactions significantly alter the phase behavior [93, 94].

The addition of spring-like bonds and soft-sphere repulsive interactions introduces new degrees of freedom to the dimensional analysis. The spring bonding potential (Eq. 12) contains a length scale  $l_0$  and an energy scale  $\epsilon_l$ , and the WCA nonbonded potential (Eq. 16) contains an energy scale  $\epsilon_{ij}$ . As discussed in Section II A,  $l_0$  is constrained to be equal to the bead diameter  $\sigma$  in order to ensure crystallization is possible. Additionally, very flexible bonds are only appropriate for capturing the "entropic spring" behavior of highly coarse-grained models, rather than the more detailed models we examine here that are appropriate for studying crystallization. As such, we are restricted to the case where  $\epsilon_l \gg 1k_BT/a^2$ . Our preliminary tests with this parameter did not result in meaningful effects on low-temperature phase behavior.

By contrast, the strength of nonbonded interactions are very impactful for crystallization. We define a dimensionless parameter  $\epsilon_{\theta}^* = \epsilon_{\theta}/\epsilon_{ij}$  as the ratio of the bending modulus to the excluded volume parameter. When  $\epsilon_{\theta}^* \gg 1$ , bending dominates over excluded volume interactions, and when  $\epsilon_{\theta}^* \ll 1$ , excluded volume interactions dominate over bending.

Fig. 7 shows a phase diagram for Model C with  $\epsilon_{\theta}^* \in \{0.1, 1, 10\}$  alongside the data for Model B from above.



FIG. 7. Phase diagram for Model C (soft bead) where the parameter characterizing excluded volume interactions  $(\epsilon_{\theta}^{*})$  varies over two orders of magnitude. Data for Model B (hard bead) is also shown for comparison. (a) The IN transition line in the  $\phi$ - $T_r$  plane for various values of  $\epsilon_{\theta}^{*}$ . Curves are drawn on the data to guide the eye. (b) The NC transition line in the  $\phi$ - $T_r$  plane for various values of  $\epsilon_{\theta}^{*}$ . Curves are drawn on the data to guide the eye. (c) All data in a rescaled phase diagram in the  $\phi_{\text{eff}}$ - $T_r$  plane. Lines and shading are unchanged from Fig. 5b above.

The thermal profiles for Model C used to create this diagram are given in the SM [70]. Similar to Model B, the phase diagram for Model C contains a IN transition at higher  $T_r$  and a NC transition at lower  $T_r$  along an isochore. While the phase diagram for Model C appears qualitatively similar to the behavior of Model B, there are apparent quantitative differences in the  $\phi$ - $T_r$  plane based on the relative strength of the excluded volume interactions  $\epsilon_{\theta}^*$ .

The isotropic to nematic (IN) transition line for Model C with  $\epsilon_{\theta}^* \in \{0.1, 1, 10\}$  and for Model B is shown in Fig. 7a. The line for hard bead interactions (Model B) appears to be the limiting behavior, and the IN line shifts to the left as excluded volume interactions weaken. In other words, for an equal value of  $\phi$ , chains with softer nonbonded interactions order at a lower  $T_{IN}$ .

The nematic to crystallization transition line (NC) from the same simulations is shown in Fig. 7b. Similarly, the hard bead interactions are to the right of all of the soft bead curves, with the NC line shifting to the left as the nonbonded interactions soften.

Apparently, for both types of transitions, softness reduces the drive to order. Given that both alignment and crystallization are driven by entropy, softer excluded volume interactions mean the effective bead size is smaller, giving the system relatively more degrees of freedom for individual bead motion. Finally, recall that  $T_r$  is normalized by the bending modulus, so the effect of bending is scaled out.

The importance of excluded volume reinforces the notion that the system volume fraction is of primary importance. However, the volume fraction  $\phi$  defined in Eq. 1 does not account for the bead overlap that is permitted when using the softer WCA potential. As such, we compute an effective hard sphere diameter [71]

$$a_{\rm eff} = \int_0^\infty \left( 1 - e^{-U_{\rm pair}(r_{ij})/k_B T} \right) dr_{ij} \tag{35}$$

and use it to define an effective volume fraction

$$\phi_{\text{eff}}(T) = \frac{\pi a_{\text{eff}}^3 N_c N_b}{6V}.$$
(36)

Figure 7c shows the phase diagram for Model C using the newly defined  $\phi_{\text{eff}}$ . Remarkably, both the IN and NC curves for all values of  $\epsilon_{\theta}^*$  collapse to the hard sphere data from Model B. From this, we infer that the dimensionless parameters  $\phi_{\text{eff}}$  and  $T_r$  are sufficient to explain the phase behavior, and that Model C exhibits the same qualitative and quantitative phase behavior as Model B when propertly scaled.

### IV. CONCLUSION

We have shown that the crystallization behavior of simple polymer models critically depends on the character of its local stiffness. Using an equilibrium approach based on WLMC simulations, we simulated two families of relatively simple polymer models: polymers with a discontinuous local bending potential (Model A) and those with continuous local bending potential (Models B and C). Polymers in Model A exhibit only a one-step isochoric crystallization transition due to excluded volume interactions. By contrast, polymers in Models B and C can show a two-step isochoric crystallization transition that is mediated by nematic ordering. Importantly, the persistence length behavior of the chain is only a function of the reduced temperature, and its low temperature trend predicts the crystallization behavior.

Comparing simulations of hard beads (Model B) and purely repulsive soft beads (Model C) reveals that the strength of the excluded volume interactions also plays an important role in the crystallization behavior. Remarkably, these interactions are fully accounted for using an effective hard sphere diameter. Thus, the type of bending potential appears to determine the "universality class" of crystallization phase behavior for these models.

The hypothesis that local polymer stiffness controls the mechanism of polymer crystallization mechanism is intriguing but it has yet to be tested with chemistryspecific models or experimental data. Certainly, an immediate area of interest are models that include attraction and models with stiffness created by torsional degrees of freedom rather than bending. Notably, the role of attractive interactions has already generated attention, with recent research suggesting that attraction "shifts" phase boundaries but does not qualitatively change behavior [37–40, 59, 60, 69].

Additionally, more study is needed related to the ef-

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12

fects of a finite simulation box and chain length. Studies on finite-size scaling of first-order phase transitions [95– 97] and our own preliminary data [70] suggest that the precise values of the transition temperatures (but not the relative location) may depend on the box size, but additional data is needed to perform a more careful study. The effects of polymer chain length are also very interesting and potentially have implications for the origin of folded-chain crystals [37, 38, 98]. Studies of both effects will require methodological refinements to be able to access larger simulation domains.

Regardless, the approach and results demonstrated here have the potential to reframe the ongoing debate about primary nucleation in polymer crystallization. For example, one can imagine reframing simulation parameters of existing models in terms of dimensionless groups with respect to universal phase diagrams. Doing so could help researchers rigorously compare their models and to better understand the effects of thermodynamics versus kinetics in determining the crystal nucleation mechanism.

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## For Table of Contents Only



FIG. 8. Schematic showing that the form of chain bending stiffness potential determines dominant crystal nucleation mechanism.

# Supplemental Material for "The effect of local chain stiffness on oligomer crystallization from a melt"

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## CONTENTS

S1.	Parameterization of Soft Pair Potential Model	2
S2.	Effective Hard Bead Sizes at Finite Temperatures	3
S3.	Details of Persistence Length Calculations	3
S4.	Wang-Landau Monte Carlo (WLMC) Simulations	6
	A. Multiple Walker Scheme for WLMC Simulations	8
S5.	Thermal Profiles and Phase Diagrams of Model A	9
	A. Finite-Size Effects for Model A	11
S6.	Thermal Profiles and Phase Diagrams for Model B	13
S7.	Thermal Profiles for Model C	16
S8.	Effect of Softness of Beads on Phase Behavior	25
	References	26

## S1. PARAMETERIZATION OF SOFT PAIR POTENTIAL MODEL

To study crystallization of polymers using the WCA potential model, we choose a value of  $\sigma = 2^{-1/6}a \sim 0.891a$  that promotes crystallization at low temperatures. This choice of  $\sigma = 2^{-1/6}a$  sets the cutoff radius equal to the bond length,  $r_c = 2^{1/6}\sigma = l_0 = a$ , a necessary choice resulting in commensurate bead diameter and bond length and is therefore a choice that does not preclude crystallization. This can be seen in Fig. S1 where both the WCA potential with  $\sigma = 2^{-1/6}a$  and harmonic stretching potential are graphed versus the interbead distance. As  $T \to 0$ , the chains will be in their ground state, i.e., U = 0, when both energies reach their minima. With  $\sigma = 2^{-1/6}a$ ,  $r_{ij}(T \to 0) = l_i(T \to 0) = a$ , which allows for bead spacings of a within the crystalline lattice. Other choices result in glassy states as  $T \to 0$ , compared to the desired crystal phase in this paper's investigation [1, 2]. Additionally, this choice adjusts the softness of beads to result in effective diameters  $a_{\text{eff}} = a$ at  $T \to 0$  (c.f., Section S2), improving comparisons to chains using the hard sphere potential.

Unlike hard spheres, using soft WCA beads adds a pair potential energy scale,  $\epsilon_{ij}$ . When used in tandem with a bending stiffness potential, WCA chains are classified via their dimensionless stiffness energy scale,  $\epsilon_{\theta}^* = \epsilon_{\theta}/\epsilon_{ij}$ . Higher  $\epsilon_{\theta}^*$  result in high bending stiffness whereas lower values result in strong excluded volume interactions.



FIG. S1. Potentials from the WCA potential and harmonic stretching potential versus interbead distance shows that  $\sigma = 2^{-1/6}a$  results in commensurate bead spacing at  $U \to 0$ .

### **S2. EFFECTIVE HARD BEAD SIZES AT FINITE TEMPERATURES**

With soft beads, the effective (hard sphere) bead diameter  $a_{\text{eff}}$  is a function of T. Setting  $\sigma = 2^{-1/6}a$  for the WCA potential results in  $a_{\text{eff}}(T \to 0) = a$  (c.f., Section S1). The WCA potential allows beads to overlap, thereby changing the effective volume fraction of beads within the box at a given  $\epsilon^*_{\theta}$  and  $T_r$ . Our chains of course experience ordering at non zero temperatures and therefore when comparing simulation results from soft and hard potentials, we correct the soft bead system's  $\phi$  to  $\phi_{\text{eff}}(T)$  using Eq. 36 where  $a_{\text{eff}}(T)$  is given by Eq. 35 [3].

Plotting Eq. 35 for  $\epsilon_{ij} = 1$  and  $\sigma = 2^{-1/6}a$  against temperature results in Fig. S2. As expected, WCA beads only result in unit diameters as  $T \to 0$ . At finite non-zero temperatures, beads are soft and therefore result in non-unit diameters,  $a_{\text{eff}} < a$ .



FIG. S2. Effective bead diameter  $a_{\text{eff}}$ , computed from Eq. 35 for  $k_B T/\epsilon \in (0, 1]$ .

## S3. DETAILS OF PERSISTENCE LENGTH CALCULATIONS

To quantify the  $T_r$  response of the chains, we conducted "ideal" chain NVT MC simulations, i.e., simulations with no excluded volume interactions. In NVT MC, the stiffness potential effect manifests in the persistence length,  $l_p$ , which quantifies alignment of chains, given by Eq. 31. These NVT MC simulations featured 720 independent phantom chains, initialized with random configurations, the configurations were equilibrated for  $3 \times 10^{10}$  MC move attempts, and data was produced for  $2 \times 10^{10}$  MC move attempts. Practically,  $l_p$  is obtained from a fit of NVT MC data to Eq. 31. Low  $l_p/l_0$  indicates a chain's bonds are not

oriented with each other beyond short distances along its backbone, and vice versa.

 $l_p/l_0$  data obtained from ideal chain NVT MC for  $T \in [0, 1]$  using the various bonded potential models used here are shown in Fig. 6 and in Fig. S3. At high temperatures, all models exhibit  $l_p/l_0 \sim 1$  indicating that bond vectors are not correlated/aligned at all and that chains resemble flexible coils. As the temperature decreases, the energy cost of extension increases and therefore bonds become extended and  $l_p$  increases as in Fig. 6. This increase in  $l_p$  manifests in real chains into the first order nematic alignment at some  $T_r$  at all  $\phi$ . Figure S3 depicts the lack of significant effect of the bonding potential and its strength, mediated by  $\epsilon_l^*$ , on the value of  $l_p$  or its dependence on  $T_r$ .



FIG. S3. Dimensionless persistence length  $l_p/l_0$  versus reduced temperature  $T_r = k_B T/\epsilon_{\theta}$  for phantom Model A (magenta) and phantom Model B (blue). For both models, lines are theoretical predictions (detailed in the SI) and data is shown for three different kinds of bonded interactions: rods (triangles), very stiff springs with  $\epsilon_l a^2/\epsilon_{\theta} = 600$  (circles), and moderately stiff springs with  $\epsilon_l a^2/\epsilon_{\theta} = 30$  (squares). The standard errors of data points are smaller than the size of the symbols.

To verify our simulation results, we plot analytical expressions for  $l_p/l_0$  of both models as a function of temperature. The persistence length of a freely rotating chain is given by [4]

$$\frac{l_p}{l_0} = \frac{1}{2} \left[ \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} \right].$$
(S1)

For discrete stiffness chains (i.e., Model A), the ensemble-averaged bond angle is given by [5]

$$\langle \cos \theta \rangle = \frac{1}{2} \frac{\exp\left(1/T_r\right) \sin^2 \theta_s + \cos^2 \theta_s - \cos^2 \theta_m}{\exp\left(1/T_r\right) \left(1 - \cos \theta_s\right) + \cos \theta_s - \cos \theta_m}$$

$$= \frac{19}{20} \frac{\exp\left(1/T_r\right) - 1}{\exp\left(1/T_r\right) + 19}$$
(S2)

where the second equation substituted the values of  $\theta_s = \cos^{-1}(0.9)$  and  $\theta_m = \pi$ , the latter of which is the maximum possible bond angle.

For continuous stiffness chains (i.e., Model B), the average bond angle is computed analytically via,

$$\left\langle \cos \theta \right\rangle = \frac{\int_{U_{\min}}^{U_{\max}} \cos \theta P_U dU}{\int_{U_{\min}}^{U_{\max}} P_U dU}$$
(S3)

where  $U_{\min}$  and  $U_{\max}$  are the minimum and maximum bending energies, respectively, while  $P_U$  is the probability of an energy state U using the bond angle potential  $U_{\text{bend}}^{\text{cont}}$  from Eq. 3.  $P_U dU$ , the differential probability of an energy state, is given by Eq. S4.

$$P_U dU = \exp\left(-U/k_B T\right) dU$$
  
=  $\exp\left(\frac{\cos\theta - 1}{T_r}\right) d\left[\epsilon_\theta \left(1 - \cos\theta\right)\right]$   
=  $\epsilon_\theta \sin\theta \exp\left(\frac{\cos\theta - 1}{T_r}\right) d\theta$  (S4)

Substituting  $P_U dU$  into Eq. S3 gives,

$$\begin{aligned} \langle \cos \theta \rangle &= \frac{\int_{0}^{\theta_{m}} \oint \cos \theta \sin \theta \exp\left(\frac{\cos \theta - 1}{T_{r}}\right) d\theta}{\int_{0}^{\theta_{m}} \oint \sin \theta \exp\left(\frac{\cos \theta - 1}{T_{r}}\right) d\theta} \\ &= \frac{\exp\left(\cos \theta_{m}/T_{r}\right) \cos \theta_{m} - \exp\left(1/T_{r}\right)}{\exp\left(\cos \theta_{m}/T_{r}\right) - \exp\left(1/T_{r}\right)} - T_{r} \\ &= 1 - T_{r} - \frac{2}{1 - \exp\left(2/T_{r}\right)} \end{aligned}$$
(S5)

where the second equation is an algebraic simplification with a substituted value of  $\theta_m = \pi$ .

Substituting Eq. S2 and Eq. S5 into Eq. S1 gives the values of  $l_p/l_0$  versus  $T_r$  shown in Fig. S3 and Fig. 6 for Models A and B, respectively. At low  $T_r$ , Eq. S2 (discrete stiffness chain) reduces to

$$\lim_{T_r \to 0} \langle \cos \theta \rangle = \frac{19}{20} \tag{S6}$$

and using Eq. S1 gives

$$\lim_{T_r \to 0} \frac{l_p}{l_0} = \frac{39}{2}.$$
 (S7)

At low  $T_r$ , Eq. S5 (continuous stiffness chain) reduces to

$$\lim_{T_r \to 0} \langle \cos \theta \rangle = 1 - T_r \tag{S8}$$

and substituting into Eq. S1 gives

$$\lim_{T_r \to 0} \frac{l_p}{l_0} = \frac{1}{T_r} - \frac{1}{2}.$$
(S9)

Importantly, the collapse of this figure regardless of the value of  $\epsilon_{\theta}$  indicates the 1:1 pairing of stiffness and temperature in  $T_r$ ; temperature and stiffness are coupled here in the lack of thermal (soft) excluded volume interactions. In ideal MC, there is a single energy scale,  $\epsilon_{\theta}$ , that also defines the energy range as  $E = [-N_c(N_b - 2)\epsilon_{\theta}, 0]$  for discrete stiffness polymers and  $E = [0, 2N_c(N_b - 2)\epsilon_{\theta}]$  for continuous stiffness polymers. The minimum in energy is encountered when all chains are perfectly aligned in a close-packed configuration. Additionally, the plot also shows results for experiments from continuous stiffness and discrete stiffness springs with  $\epsilon_l^* = 600$ . Clearly, comparison of plots from harmonic stretching (spring chains) and rod-like chains shows that there is no effective difference between simulations of springs and rods, at least in the lack of excluded volume interactions. Our findings suggest that this is true even in the presence of a pairwise potential.

## S4. WANG-LANDAU MONTE CARLO (WLMC) SIMULATIONS

We utilize (constant number and volume) WLMC simulations [6] to determine the phase behavior of an oligomer melt in the vicinity of the crystallization transition [7, 8]. WLMC proceeds by iteratively building the density of states,  $\Omega$ , simultaneously using this quantity to bias sampling towards rarely-visited states. This biasing property leads to efficient sampling of rare events such as crystallization. The density of states provides a direct calculation of the system entropy S through Boltzmann's famous equation,

$$S = k_B \ln \Omega \tag{S10}$$

where  $k_B$  is Boltzmann's constant. The entropy contains all of the thermodynamic information necessary for determining phase behavior of the system.

As in other Monte Carlo (MC) methods, WLMC proceeds by generating a candidate "move", calculating the energy of the system before and after the move, and using a stochastic acceptance criteria that results in either acceptance or rejection of the move. We utilize a variety of standard moves for polymers including: bead displacement, kink [9, 10], end-kink [10], reptation [9, 11], and configurational-bias versions of these moves [12–15]. With short chains, we did not find it necessary to use bond-breaking and bridging moves. [16–19]

The acceptance criteria for WLMC differs from other MC methods, leading to its unique features. In WLMC, the acceptance criteria is given by

$$P_{\rm acc} = \min\left[1, \frac{\Omega(U_{\rm old})}{\Omega(U_{\rm new})}\right] \tag{S11}$$

where  $\Omega(U_i)$  is the value of the density of states for a configuration with potential energy  $U_i$ . The use of the density of states in the acceptance criteria ensures that all states of the system are visited with equal frequency. Practically, this is tracked in a WLMC simulation by monitoring a histogram of the number of visits to an energy state, and the algorithm proceeds until it has visited all accessible states of the system with nearly uniform frequency. Our criterion for the latter condition is that the deviation between the minimum and average number of visits is less than 20%.

The density of states used in the acceptance criteria is also the principal product of the WLMC simulation.  $\Omega(U_i)$  is initially assumed to be unity for all  $U_i$  and when the simulation visits  $U_{\text{new}}$ ,  $\Omega(U_{\text{new}})$  is increased by multiplying it with a modification factor, f. Execution of the above procedure generates only a rough estimate of  $\Omega$ , whose accuracy is limited by the value of f. Consequently, multiple iterations are necessary to obtain an accurate value. By convention,  $f_1 = e$  and  $f_n = \sqrt{f_{n-1}}$  where the subscript n denotes the number of iterations of the WLMC algorithm [7]. We use n = 27 WLMC iterations in our calculations, giving a modification factor (and error estimate) of  $f_{27} = e^{0.5^{27}} < 1 + 10^{-8}$  on the final iteration.

In principle, one could use a single WLMC simulation to determine  $\Omega$  for the entire accessible range of system energies, effectively providing information spanning all relevant temperatures. In practice, this would require prohibitively large computational times and memory. To remedy this, WLMC simulations are subdivided into multiple overlapping energy windows that are then combined by least-squares fitting of overlapping bins. To speed convergence, we employ a multiple window scheme with multiple walkers (replicates) that can move between energy windows (replica exchange) [20–23]. Additionally, these walkers accumulate global  $\Omega$  and histograms for each window in parallel [24, 25]. This scheme (replica- and entropy-exchange) improves sampling, accelerates convergence, and, ultimately, improves  $\Omega$  accuracy. Additional details for implementing this scheme are provided in Section S4 A.

## A. Multiple Walker Scheme for WLMC Simulations

The simulation space is divided into overlapping windows and each window is given multiple "walkers", i.e. replicate WLMC simulations that run in parallel in the same window. In WLMC,  $\Omega$  is only determined to within an additive constant, so linear regression is used to "stitch" overlapping windows together to obtain a master curve. The internal energy space is subdivided into 15-20 windows with 8-16 walkers in each window, depending on the difficulty of simulation (high  $\phi$ ), each simulation converged to O(10<sup>-9</sup>) error in its  $\Omega$  estimate. Note that each of the walkers must be seeded with an independent initial configuration that obeys the energy constraints of the window, generated via biased umbrella-sampling MC simulations.

Then, these overlapping windows are allowed to exchange configurations via the following scheme. Consider two walkers,  $\alpha$  and  $\beta$ , with respective configurations A and B that reside in neighboring windows. If the energies of these configurations  $U_A = U(A)$  and  $U_B = U(B)$  are within the overlap region between the two windows, they may swap configurations according the acceptance criteria [23]

$$P_{\rm acc} = \min\left[1, \frac{\Omega_{\alpha}(U_A)\Omega_{\beta}(U_B)}{\Omega_{\alpha}(U_B)\Omega_{\beta}(U_A)}\right]$$
(S12)

In such simulations, each walker maintains a separate, local estimate of  $\Omega$  and a separate histogram. These are averaged, and when the global histogram is flat, the global  $\Omega$  is re-distributed among all walkers and a new WLMC iteration starts.

We implemented multiple walker replica-exchange Wang Landau simulations, and in our experience they speed convergence via parallelization and through improved sampling efficiency. A well-known problem in the WLMC algorithm is that single walkers get "stuck" due to hidden barriers and can oversample certain regions of phase space. Multiple independent walkers partially solve this problem, because each independent replica begins in a different initial state and is unlikely to be trapped by the same hidden barriers. The configuration exchange in these simulations samples a wider range of phase space creating walkers that are even more efficient at overcoming these hidden barriers. Exchange between windows also improves the ergodicity of the simulation, allowing walkers to explore an energy range that is larger than a single window.

## **S5. THERMAL PROFILES AND PHASE DIAGRAMS OF MODEL A**

To compliment the analysis in the main text of the thermal profiles of discrete stiffness chains, we present thermal profiles for various densities explored in this Section. Figure S4 shows thermal profiles of ensemble-averaged U,  $f_{cryst}$ ,  $P_2$ ,  $\tilde{C}_V$ ,  $S_{MS}$ , and  $Q_6$ .  $Q_6$  is the "global" Steinhardt bond orientational order parameter of the sixth order and is given by,

$$Q_6 = \frac{1}{N} \sum_{i=1}^{N} q_6(i) \tag{S13}$$

where the sum is over all beads and  $q_6(i)$  is given by,

$$q_6(i) = \left[\frac{4\pi}{13} \sum_{m=-6}^{6} |q_{6,m}(i)|^2\right]^{0.5}$$
(S14)

and  $q_{6,m}$  is given by Eq. 26.  $S_{MS}$  is the largest eigenvalue of the Maier-Saupe Q-tensor Q. It quantifies the degree chain orientational order with a nematic alignment direction. Q is a symmetric and traceless tensor computed via bond lengths along the chain backbone,

$$\boldsymbol{Q} = \frac{3}{2N_c(N_b - 1)} \sum_{i=1}^{N_b - 1} \left[ \frac{\boldsymbol{l}_i}{|\boldsymbol{l}_i|} \otimes \frac{\boldsymbol{l}_i}{|\boldsymbol{l}_i|} - \frac{\boldsymbol{I}}{3} \right]$$
(S15)

where I is an 3 × 3 identity matrix. The larger the value of  $S_{MS}$ , the more nematically aligned the melt is.

Much like in Fig. 4, the single first order transition shifts to lower temperatures as the density decreases. Potential energy in Fig. S4a encounters a sharp discontinuity at some T at the largest volume fraction  $\phi = 0.492$ . At high T, the behavior is nearly  $\phi$  agnostic. As T decreases, the effect of  $\phi$  increases. As  $\phi$  decreases, the discontinuity T shifts to lower T and  $\Delta U$  becomes smaller. Finally, at the lowest volume fraction  $\phi = 0.298$ , no transition occurs and U changes smoothly to its ground state value.

Although U informs the position of the transition, it does not reveal the nature of the transition. However, Fig. S4b and Fig. S4c show  $f_{cryst}$  and  $P_2$ , respectively, which carry structural information. Trends in  $P_2$  on panel c show that this transition includes a nematic alignment;  $P_2$  and U both decrease at the same T and at the last T,  $P_2$  also lacks a first order transition. However,  $f_{cryst}$  only has a discontinuity for the four largest  $\phi$ , which indicates that the transition is crystallization at higher than some critical  $\phi$  and  $T_m = T_{IC}$ , whereas  $T_m = T_{IN}$  below this critical  $\phi$ .  $C_V$  identifies transitions well via a peak. The crystallization



FIG. S4. Thermal profiles of a) potential energy per bond  $U/(\epsilon_{\theta}N_{\text{bonds}})$ , b) fraction of crystal beads  $f_{\text{cryst}}$ , c) nematic order parameter  $P_2$ , d) dimensionless heat capacity  $\tilde{C}_V = C_V/(k_B N_c(N_b - 2))$ , e) largest eigenvalue of Maier-Saupe Q-tensor Q,  $S_{MS}$ , and f) global crystalline OP  $Q_6$  obtained from the WLMC density of states at constant volume for hard rods with a discrete bending stiffness potential (Model A). All values are ensemble-averaged and averaged over 16 replicates.

peak starts off narrow and large at high  $\phi$  but broadens and decreases in height as the density decreases and, finally, the peak disappears altogether at the lowest investigated  $\phi = 0.298$ .

The remaining two panels in Fig. S4 show alternate order parameters that quantify nematic alignment along the chain backbone ( $S_{MS}$  in panel e) and global crystalline structure ( $Q_6$  in panel f).  $S_{MS}$  shows similar trends as  $P_2$ .  $Q_6$  is the "global" version of  $f_{cryst}$  and encodes similar information. However, it's range of values shifts with density and it's changes at transitions are more difficult to distinguish. This is precisely the reason that local metrics of structure, such as  $f_{cryst}$ , are more precise discriminators of structure, especially when studying nucleation.

Our equilibrium WLMC simulations for various  $\phi \in [0.3, 0.5]$  allow construction of a phase diagram. Much like in the preceding analysis in the main text of Fig. 4,  $C_V$  peaks pinpoint transition locations ( $T_{IN}$  or  $T_{IC}$ ) at each  $\phi$  and changes in  $f_{cryst}$  determine whether the transition is IC or IN. Those  $T_{IN}(\phi)$  (green cicles) and  $T_{IC}(\phi)$  (red squares) values are overlayed over the phase diagram, as shown in Fig. S5. By fitting a straight line to each transition temperature, we plot the two best fit lines to divide the phase diagram into three domains: the (isotropic) melt (off-white), nematic (yellow) and crystal (light blue) phase domains.

Once again, at high  $T_r$  and all  $\phi$ , the polymer is an isotropic melt. As  $T_r$  decreases, the polymers either only nematically align at  $\phi < \phi_c \approx 0.441$ , or they simultaneously align and densify into crystals at higher  $\phi$ . Seemingly, at no single  $\phi$  is there a cascade of transitions with an IN transition followed by a nematic–crystal transition (NC). Rather, the phase boundary between the nematic and crystal phase is horizontal at the critical density,  $\phi_c$ , which we estimate to be 0.441.

### A. Finite-Size Effects for Model A

To quantify the degree of finite-size effects in the semiflexible oligomers, we also conduct WLMC simulations of 90 chains, keeping all else constant. Results from these simulations at  $N_c = 90$  for  $T_{IN}$  and  $T_{IC}$  at  $\phi \in [0.379, 0.407, 0.428, 0.438, 0.471]$  are shown in Fig. S5 using blue circles and blue squares, respectively. The smaller system will have a smaller box size and should have more pronounced finite-size effects than when  $N_c = 125$ . If this effect is small, e.g. equal  $T_{IN}$  and  $T_{IC}$  at equal  $\phi$  from the two systems, then chains do



FIG. S5. Phase diagram for hard discrete stiffness rods (Model A) in the  $\phi$ - $T_r$  plane. Three regions with different phases are colored: disordered melt at high  $T_r$  in off white, nematic phase at low  $T_r$  and  $\phi$  in yellow, and crystal phase at low  $T_r$  and high  $\phi$  in light blue. Transition temperatures estimated via  $C_V$  peaks from WLMC simulations at two system sizes are shown via scatter points: red squares for  $T_{IC}$  at  $N_c = 125$ , green circles for  $T_{IN}$  at  $N_c = 125$ , and blue squares and circles at  $N_c = 90$  for  $T_{IC}$  and  $T_{IN}$ , respectively. Dashed dark blue line labels an *estimate* of the critical volume fraction,  $\phi_c = 0.441$ , beyond which IC (simultaneous nematic and crystal ordering) transitions occur, ending at the triple point at  $T_r = 0.276$ .

not experience quantifiable finite-size effects. The agreement in  $T_{IN}$  from  $N_c = 90$  and  $N_c = 125$  is promising.  $T_{IN}(N_c = 90)$  values fall on top of the fit for the 125 chain  $T_{IN}$  data for  $\phi \in [0.379, 0.407]$ . This suggests that despite the small size of our system, the isotropic-nematic transition is not severely affected by finite-sized effects.

The shift of  $\phi_c$  in the smaller system to a lower value suggests that the smaller system has an increased motivation to crystallize. The  $N_c = 90$  critical density,  $\phi_c(N_c = 90) = 0.428$ , is where the dark blue dashed line is for 90 chains. As is apparent,  $\phi_c(N_c = 90) = 0.428 < \phi_c(N_c = 125) = 0.44$ . Despite the agreement between the two transition temperatures, one involves a transition to the crystal and the other to the nematic. In other words, the 90 chain box has an added drive to crystallize. This added drive towards the crystal is apparent by the increased  $T_{IC}$  at the two largest  $\phi \in [0.438, 0.471]$ . Unlike at  $\phi = 0.428$ ,  $T_{IC}(N_c = 90) > T_{IC}(N_c = 125)$  at the same  $\phi$ . Apparently, the 90 chain  $\phi$ - $T_{IC}$  line is shifted to the right with a smaller slope.

These results suggest that the  $N_c = 90$  box is subject to finite-size effects for crystalline conditions and the same could be true at  $N_c = 125$ , but the effect is not pronounced. However, because it is well known that hard sphere chains crystallize at a large enough  $\phi$ , we are confident that the crystalline transition is not an artifact of the box size for  $N_c = 125$ .

We suppose that these effects are similar for the other systems explored in this study. For Model B, the drive to crystallize could also decrease as the box size increases. This will likely shift  $\phi_{IN}^*$  to higher temperatures and shift the crystallization temperature  $T_{NC}$  to a lower value at constant volume fraction (see Fig. 5b). However, for similar reasons to model A, we believe that neither the drive to crystallize nor to nematically align will disappear. Given the collapse of behavior for models B and C (see Fig. 7c), we argue that Model C will behave similarly.

## S6. THERMAL PROFILES AND PHASE DIAGRAMS FOR MODEL B

Figure S6 shows thermal profiles of average potential energy,  $f_{\text{cryst}}$ ,  $P_2$ , the heat capacity,  $S_{MS}$ , and  $Q_6$ . Like Fig. S4 for discrete stiffness chains, the heat capacity peaks in panel d shift to the left as  $\phi$  decreases due to a reduced drive to order yielding a smaller  $T_{IN}$ and  $T_{NC}$ . Unlike Fig. S4, there is an apparent separation of the crystal transition from the nematic one, occuring at  $T_{NC} < T_{IN}$ . Importantly, continuous stiffness chains encounter alignment and crystallization at far lower densities than discrete stiffness chains. In fact, Fig. S6b suggests that  $f_{\text{cryst}}$  increases for all studied densities as  $T_r \rightarrow 0$ . In other words, the crystal is the stable zero temperature phase, although the low temperatures preclude nucleation with a large barrier in our simulations.



FIG. S6. Thermal profiles of a) potential energy per bond  $U/(\epsilon_{\theta}N_{\text{bonds}})$ , b) fraction of crystal beads  $f_{\text{cryst}}$ , c) nematic order parameter  $P_2$ , d) dimensionless heat capacity  $\tilde{C}_V = C_V/(k_B N_c(N_b - 2))$ , e) largest eigenvalue of Maier-Saupe Q-tensor Q,  $S_{MS}$ , and f) global crystalline OP  $Q_6$  obtained from the WLMC density of states at constant volume for hard rods with a continuous bending stiffness potential (Model B). All values are ensemble-averaged and averaged over 16 replicates.

To illustrate more of the phase behavior, we constructed a phase diagram for Model B in the  $\phi - T_r$  plane, shown in Fig. S7. At high  $T_r$ , the rods are in a melted liquid state. Additionally, the melt nematically aligns at some  $T_{IN}(\phi)$  as T decreases for all the  $\phi$  values investigated, as indicated by green cicles in Fig. S7. Then, the behavior is separated into two regimes. Below some  $\phi \sim 0.310$ , rods remain in the nematic phase as  $T_r \rightarrow 0$ . However, for  $\phi > 0.310$ , the rods encounter another transition between the nematic phase and a crystal at a  $T_{NC} < T_{IC}$  depicted by red triangles in Fig. S7. In this system, the nematic phase always mediates the isotropic melt to crystal transition acting as a precursor.

To guide the eyes and segregate the phase diagrams,  $T_{IN}$  and  $T_{NC}$  data was fitted to two curves. First,  $T_{IN}$  data collapsed onto a linear line, suggesting that a higher  $\phi$  increases the drive to nematically align linearly; there is no compounding effect. However, this behavior is very much different for the crystal transition temperature. First, the crystal transition does not occur at low  $\phi$ . Then, it occurs as a second transition after nematic alignment. Finally, at  $\phi > \phi_{IN}^*$ , we predict that a single  $T_{IC}$  exists with the isotropic phase transitioning directly to the crystal phase. This is unconfirmed and we believe that finite sized effects



FIG. S7. Phase diagram for hard continuous stiffness rods (Model B) in the  $\phi$ - $T_r$  plane. Three regions with different phases are colored: disordered melt at high  $T_r$  in off white, nematic phase at low  $T_r$  and  $\phi$  in yellow, and crystal phase at low  $T_r$  and high  $\phi$  in light blue. Red and green scatter points show  $T_{NC}$  and  $T_{IN}$  estimates, respectively, from  $C_V$  peaks from WLMC simulations.

may preclude investigations of this with the current model and system size.

Much like the system preceding it, nematic alignment is motivated by a stiffening as temperature decreases. This manifests in  $l_p$  increasing as the temperature decreases (c.f., Fig. 6). However, regardless of how dense the rods were, IN transitions were not accompanied by a simultaneous crystallization. Rather, crystallization always occurred at  $T_{NC} < T_{IN}$ . This is probably due to the not-so-pronounced jumps at the nematic transitions. These small differences across the transition may not lead to a big enough entropy decrease to inspire a crystal transition. As the chains get colder, the surface entropy further decreases and motivates the NC transition.

## S7. THERMAL PROFILES FOR MODEL C

To quantify the impact of hard versus soft repulsive interactions, we constructed WLMC thermal profiles for soft continuous stiffness chains, i.e., Model C. Phase behavior is affected by the parameter  $\epsilon_{\theta}^* = \epsilon_{\theta}/\epsilon_{ij}$ . Chains with  $\epsilon_{\theta}^* \gg 1$  have minimal excluded volume interactions, and we would expect such chains to crystallize only via a nematic intermediate (two-step process). Chains with  $\epsilon_{\theta}^* \ll 1$  have strong excluded volume interactions, and like the hard bead data in Fig. 5, should also be able to crystallize at high  $\phi$  via a single-step process.

First, we present data at various densities at constant  $\epsilon_{\theta}^* = \epsilon_{\theta}/\epsilon_{ij}$  in Fig. S8, Fig. S9 and Fig. S10 for chains with  $\epsilon_{\theta}^* = 0.1$ , 1.0 and 10.0, respectively. Insights from these figures mirror those from hard continuous stiffness chains in Section S6. At high  $\phi$  values, there exists an IN transition followed by NC transition. As  $\phi$  decreases, transitions shift to lower temperatures until the crystallization transition disappears. At the lowest investigated volume fraction ( $\phi = 0.194$ ), no recognizable nematic transition remains with no first order jump in  $P_2$  nor a peak in  $C_V$ .



FIG. S8. Thermal profiles for soft continuous stiffness chains at dimensionless stiffness strength  $\epsilon_{\theta} = 0.1$ .



FIG. S9. Thermal profiles for soft continuous stiffness chains at  $\epsilon_{\theta} = 1.0$ .



FIG. S10. Thermal profiles for soft continuous stiffness chains at  $\epsilon_{\theta} = 10.0$ .

To explore the effect of the value of  $\epsilon_{\theta}^*$  at various densities, we present thermal profiles from simulations with  $\epsilon_{\theta}^* \in [0.1, 1.0, 10.0]$  for  $\phi = 0.194$ , 0.298, 0.438 and 0.492 in Fig.s S11, S12, S13 and S14, respectively. First, Fig. S11 shows no transitions, as expected; the chains are too dilute and therefore encounter a negligible driving force to align. The second smallest density in Fig. S12 displays a nematic transition at low temperatures with a small peak in  $\tilde{C}_V$ . Importantly, the transition occurs at larger  $T_r$  for lower values of  $\epsilon_{\theta}^*$ . This is due to the larger excluded volume interactions at lower  $\epsilon_{\theta}^*$  that should increase the drive to both align and crystallize; the more crowded the beads are (lower  $\epsilon_{\theta}^*$ ), the larger their driving forces become. Similar conclusions can be drawn from Fig. S13 and Fig. S14 at  $\phi = 0.438$ and  $\phi = 0.492$ , respectively. Notably, measurements with  $\epsilon_{\theta}^* = 0.1$  are at very low absolute values of temperature and therefore feature large uncertainties.



FIG. S11. Thermal profiles for soft continuous stiffness chains at  $\phi=0.194.$ 



FIG. S12. Thermal profiles for soft continuous stiffness chains at  $\phi=0.298.$ 



FIG. S13. Thermal profiles for soft continuous stiffness chains at  $\phi=0.438.$ 



FIG. S14. Thermal profiles for soft continuous stiffness chains at  $\phi=0.492.$ 

## **S8. EFFECT OF SOFTNESS OF BEADS ON PHASE BEHAVIOR**

Figure S15a and b show phase boundaries of both the hard and soft continuous stiffness chains in the  $\phi$ - $T_r$  and  $\phi_{\text{eff}}$ - $T_r$  plane. The blue phase boundaries in Fig. S15 are the same boundaries from Fig. S7 for Model B. After switching out the hardness with soft beads, the phase boundaries (IN and NC) are shifted to the left in Fig. S15a; at commensurate  $\phi$ , soft chains order at lower  $T_{IN}$  and  $T_{IC}$ . For example, soft chains at  $\phi = 0.438$  have  $T_{IN} = 0.111$ and  $T_{IC} = 0.030$ , while hard chains at the same (nominal) density have  $T_{IN} = 0.136$  and  $T_{IC} = 0.048$ . In this way, softness can be interpreted as a reduced drive to order. At the same  $\phi$ , soft beads can reduce their surface free energy by reducing their volume. By having an effective size,  $a_{\text{eff}}$ , lower than a, soft chains postpone  $T_{IN}$  and  $T_{IC}$  to lower  $T_r$ . Further evidence to this hypothesis can be seen by observing that the  $T_{IC}$  from hard and soft chains are equal at low  $T_r$ , where Eq. 35 predicts that  $a_{\text{eff}}(T = 0) = a$ .

Correcting for  $T_r \neq 0$ , changes the size, and therefore the volume fraction, occupied by soft beads. Accordingly, we can use Eq. 35 to calculate  $a_{\text{eff}}(T)$  and correct  $\phi$  to  $\phi_{\text{eff}} = \phi \times a_{\text{eff}}^3/a^3$ for a more accurate measure at the temperature of interest. Taking  $\phi = 0.438$  as an example



FIG. S15. Phase barriers for hard continuous stiffness rods (Model B) and soft continuous stiffness springs (Model C) in the a)  $\phi$ - $T_r$  and b)  $\phi_{\text{eff}}$ - $T_r$  plane. Scattered circles and triangles show  $T_{IN}$ and  $T_{NC}$ , respectively, in blue for Model B and magenta for Model C. Lines are best fits to the data.

again, correcting  $T_{IN}$  to the  $\phi_{\text{eff}}(T_{IN} = 0.111) = 0.438 \times a_{\text{eff}}(0.111)$  results in  $a_{\text{eff}} = 0.959$ and  $\phi_{\text{eff}} = 0.386$ . Similarly, for  $T_{IC} = 0.030$  at  $\phi = 0.438$ ,  $a_{\text{eff}} = 0.977$  and  $\phi_{\text{eff}} = 0.408$ . Repeating this procedure for each result provides the data points in Fig. S15b.

Comparison of the two figures shows the importance of shifting  $\phi$  to the  $\phi_{\text{eff}}(T_m)$  for the soft system for any transition temperature,  $T_m$ . Figure S15a suggests that softness shifts the phase diagram to the left whereas the figure collapses after the correction to  $\phi_{\text{eff}}$ . At a constant  $\phi$ , soft beads are able to reduce their effective repulsive size, thereby reducing the effective volume fraction of chains,  $\phi$ . After correcting for  $a_{\text{eff}}$ , the impact of this reduced drive to crystallize is accounted for and no significant deviations from the hard bead phase diagram are observed.

Unlike the impact of the stiffness potential, soft bead and hard bead potentials do not result in qualitatively different results. The nucleation mechanism is the same. A quench in both the hard and soft spheres results in an initial IN at  $T_{IN}$  and an IC at a lower  $T = T_{IC}$ . Additionally, Fig. S15 suggests that the results from both models are quantitatively similar, provided one corrects for the effective instantaneous  $\phi_{\text{eff}}$  at each T.

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