Fluctuation Effects in Semiflexible Diblock Copolymers

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Supporting Information

ABSTRACT: We present a simulation study of the equilibrium thermodynamic behavior of semiflexible diblock copolymer melts. Using discretized wormlike chains and field-theoretic Monte Carlo, we find that concentration fluctuations play a critical role in controlling phase transitions of semiflexible diblock copolymers. Polymer flexibility and aspect ratio control the order–disorder transition Flory–Huggins parameter \( \chi_{\text{ODT}} \). For polymers with low aspect ratios, fluctuations strongly elevate the phase transition \( \chi_{\text{ODT}} \) at finite molecular weights. For high aspect-ratio polymers, chain semiflexibility decreases the phase transition \( \chi_{\text{ODT}} \). We find that the simulated phase behavior agrees well with our recently developed fluctuation theory based on wormlike chain configurations and a one-loop treatment of concentration fluctuations.

Copolymers composed of incompatible chemical blocks self-assemble into microstructures with mesoscale domain sizes ranging from a few angstroms to many nanometers.1–4 Such microstructures endow such polymeric materials with ideal mechanical, interfacial, and transport properties.5 Furthermore, copolymer self-assembly can be used as an informative model for the structural organization of biomolecules.9

For several decades, numerous experimental and theoretical works have established our foundational understanding of polymeric self-assembly.10–14 In the theoretical study of the phase behavior of copolymers, polymer field theory has been the primary theoretical framework,1 and the majority of the work implementing polymer field theory uses the Gaussian chain model and mean-field theory. The Gaussian chain model assumes polymer configurations exhibit random walk statistics.15 Mean-field theory assumes that the chemical monomers interact through spatially averaged density fields, neglecting the impact of correlated concentration fluctuations.15–19

A classical example of a copolymer is the diblock copolymer, which consists of two covalently bonded segments with chemically different monomers (i.e., 1-A-A-A-B-B-...). Experiments map out the phase diagram of diblock copolymers at different A-segment fraction \( f_A \) and interaction strength between A and B monomers, controlled by the Flory–Huggins parameter \( \chi \).2,15 The coarse-grained model assuming Gaussian chain configurations and mean-field interactions is able to qualitatively predict the phase diagram of diblock copolymer melts. However, experiments observe an elevated order–disorder transition \( \chi_{\text{ODT}} \) over the mean-field predictions. Such quantitative discrepancy is partially corrected by incorporating finite molecular weight effects with concentration fluctuations.18–20 Molecular simulations and experiments show agreement with the fluctuation-corrected theories at relatively high molecular weights.9 However, nonuniversal phase behavior at low molecular weights is also noted by recent experiments.20

One source of nonuniversality is the finite polymer flexibility at low molecular weights. Recently, we developed a theory that accounts for polymer semiflexibility and fluctuation effects using the wormlike chain model.21 We show that phase transitions of semiflexible diblock copolymers with finite aspect ratios strongly deviate from the Gaussian chain theory at molecular weights lower than \( N \approx 100 \). Such nontrivial strong deviations show that the incorporation of density fluctuations is critical in studying phase transitions of semiflexible copolymers. In this work, we aim to leverage field-theoretic Monte Carlo simulations to study the phase behavior of semiflexible copolymers in the presence of density fluctuations. This work

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provides a concrete assessment of the impact of concentration fluctuations on copolymer phase behavior as the molecular weight is reduced. The technological trend for copolymer materials is to assemble into morphologies with smaller domain sizes (i.e., nanometer length scales), making our predictions crucial for practical applications of copolymer assembly.

We consider a diblock copolymer melt consisting of \( n_p \) polymers. Each polymer has A- and B-type segments, with A-segment fraction \( f_A \). The total energy of the system is the sum of polymer conformation energy and monomer interaction energy

\[
\beta E = \beta E_{\text{poly}} + \beta E_{\text{int}}
\]

(1)

where \( \beta = 1/(k_B T) \) and \( k_B \) is the Boltzmann constant. To capture polymer semiflexibility, we model each chain as a wormlike chain whose conformational energy is proportional to the square of the chain curvature

\[
\beta E_{\text{poly}} = \frac{L_p}{2} \sum_{i=1}^{n_p} \int_0^{L_f} \left( \frac{d \vec{s}^i}{ds} \right)^2 ds
\]

(2)

where \( L_p \) is the persistence length and \( L \) is the chain contour length. For the \( i \)th chain at arclength position \( s, \vec{t}_i(s) \) defines the monomer position, and \( \vec{u}_i(s) = \frac{d \vec{s}^i}{ds} \) is the chain tangent vector. Each Kuhn segment monomer has volume \( 2l_pA \), where \( A \) is the chain cross-sectional area. The chemical incompatibility between the monomers is calculated based on a coarse-grained Flory–Huggins parameter \( \chi \)

\[
\beta E_{\text{int}} = \frac{\chi}{2l_pA} \int d\vec{r} \phi_A(\vec{r}) \phi_B(\vec{r})
\]

(3)

where local monomer densities of each species are given by

\[
\phi_A(\vec{r}) = A \sum_{i=1}^{n_p} \int_{0}^{L_f} ds [\delta(\vec{r} - \vec{t}_i(s))]
\]

(4)

\[
\phi_B(\vec{r}) = A \sum_{i=1}^{n_p} \int_{0}^{L_f} ds [\delta(\vec{r} - \vec{t}_i(s))]
\]

(5)

In addition, the copolymer melt is effectively incompressible, requiring space filling condition of monomers everywhere, that is, \( \phi_A(\vec{r}) + \phi_B(\vec{r}) = 1 \) for all spatial positions \( \vec{r} \).

In our Monte Carlo simulations, we discretize the polymer chains into beads and spatial coordinates \( \vec{r} \) into bins. We use a discrete shearable-stretchable wormlike chain model with each chain represented by \( n_b \) beads spaced an arclength \( l_p \) apart. The discretized wormlike chain consists of quadratic energy penalties associated with stretch, shear, bend, and coupling between the bend and shear degrees of freedom. This model is shown to reproduce the statistical behavior of the continuous inextensible wormlike chain model over the entire range of structural rigidity.

To capture the monomer interactions in eq 3 and effective melt incompressibility, we discretize the spacial coordinates \( \vec{r} \) into \( n_b \) lattice bins. We obtain the monomer density field of chemical species \( A \) in the \( k \)th bin \( \phi_A^{(k)}(\vec{r}) \) from first-order particle-to-mesh interpolations

\[
\phi_A^{(k)}(\vec{r}) = \frac{\nu}{A} \sum_{i=1}^{n_b} \sum_{j=1}^{n_b} \sigma_A^{ij} w(\vec{R}_k - \vec{r}_j)
\]

(6)

where \( \sigma_A^{ij} = 1 \) if the chemical identity of \( j \)th bead on \( i \)th chain is of type \( A \), and \( \sigma_A^{ij} = 0 \) otherwise. The vector \( \vec{R}_k \) is the location of the \( k \)th bin grid vertex, and \( w \) is a weighting factor that gives a linear interpolation of the density in three dimensions. The interaction energy can then be written as

\[
\beta E_{\text{int}} = \frac{\chi}{2l_pA} \sum_{k=1}^{n_b} \phi_A^{(k)} \phi_B^{(k)} + \kappa \Delta^3 \sum_{k=1}^{n_b} (\phi_A^{(k)} + \phi_B^{(k)} - 1)^2
\]

(7)

where \( \Delta \) is the discretization length of each bin, and the bead volume \( v = l_pA \). The compressibility factor \( \kappa \) is chosen to be large to approximately enforce melt incompressibility.

The simulation used to generate Figure 1 has a cube size \( L_{\text{box}} = 20\Delta \) with periodic boundary conditions, filled by \( n_p = L_{\text{box}}^3/(\nu n_b) = 4000 \) polymers each consisting of \( n_b = 20 \) beads. We implement the same type of Monte Carlo moves and parallel tempering method as in our previous work. In each simulation, we use a total of 31 simulations spanning a range of \( \chi \) values that result in an average replica-exchange probability of 12–22% between replicas.

We focus on symmetric diblock copolymers with \( f_A = 0.5 \), with varying number of Kuhn steps per polymer \( N = L/(2l_p) \), and the aspect ratio between a Kuhn segment and cubic root of a Kuhn volume \( \alpha = 2l_p/(\sqrt[3]{2l_pA}) = 2l_p/(\sqrt[3]{2\nu v}) \).

We obtain the desired \( N \) and \( \alpha \) by choosing appropriate persistence length \( l_p \) and discretization length \( l_0 \) simultaneously (see Supporting Information). A Gaussian chain is infinitely flexible, corresponding to chain with \( N \to \infty \), and rigid rod is infinitely stiff with \( N \to 0 \). The chain aspect ratio \( \alpha \) gives the thickness of the Kuhn segments within the chain.

The top panel of Figure 1 shows the morphologies of symmetric, semiflexible diblock copolymers with \( N = 10 \) and \( \alpha = 2 \). Each snapshot of morphology is obtained at the \( \chi N \) values shown in the bottom panel of Figure 1 with corresponding letters A–D. Qualitatively, the diblock copolymer melt transitions from a homogeneous phase to a disordered phase, and then to a lamellar phase.

We quantify the phase transitions of diblock copolymers by looking at the degree of monomer mixing \( \langle \phi_A \phi_B \rangle \). Its response...
to increasing \( \chi N \) is the \( \chi \) component of the heat capacity \( c_v = -\partial (\phi_1 \phi_2) / \partial (\chi N) \). The bottom panel in Figure 1 shows the degree of mixing \( \langle \phi_1 \phi_2 \rangle \) and heat capacity \( c_v \) with increasing \( \chi N \). At \( \chi N = 0 \), the degree of mixing \( \langle \phi_1 \phi_2 \rangle \approx 0.23 \), smaller than the perfectly homogeneous value of 0.25 because of the connectivity of same-type beads along polymers and density fluctuations. With increasing \( \chi N \), chemical incompatibility strengthens the degree of segregation, resulting in a decreasing \( \langle \phi_1 \phi_2 \rangle \). The dashed blue vertical line indicates the mean-field limit of stability of the well-mixed phase at \( \chi_{MF} N = 8.93 \), roughly corresponding to the \( \chi N \) value above which phase segregation starts to take place. The snapshots A and B clearly show a qualitative segregation into local domains. However, these domains remain disordered\(^{26,36-38} \) and no clear lamellar phase emerges at the mean-field theory prediction \( \chi_{MF} N \).

Crossing from \( \chi N = 15.0 \) (C) to \( \chi N = 16.0 \) (D), an abrupt decrease of the degree of mixing is seen with phase transition from a disordered phase (C) to a lamellar phase (D). This phase transition also corresponds to the maximum of the heat capacity \( c_v \). The value of \( \chi N \) at which the phase transition to a lamellar phase occurs is indicated by the vertical solid red line, whereas fluctuation theory predicts the phase transition at \( \chi_{ODT} N = 14.5 \) (dashed red line). Comparing the simulation with theory, we argue that the fluctuation correction to mean-field theory is important.

To quantify the density–density correlations at different length scales, we calculate the correlation function of local monomer density variation \( \psi(\vec{r}) = \phi_A(\vec{r}) - f_A \) which in Fourier space is written as

\[
S(q) = \langle \psi(q) \psi(-q) \rangle = \frac{1}{n_v n_b} \sum_{i=1}^{n_v} \sum_{j=1}^{n_b} (\phi_i^A - f_A) \exp(i \vec{q} \cdot \vec{r}_ij) \tag{8}
\]

where \( \psi(q) \) is the Fourier transform of density variation \( \psi(\vec{r}) \), and the average is taken over all possible \( \vec{q} \) orientations under periodic boundary conditions. We refer to the density–density correlation \( S(q) \) as the structure factor because it is proportional to the scattering intensity in neutron and X-ray scattering experiments.

Next, we compare our simulation results of the structure factor and phase transition \( \chi_{ODT} N \) with our recent theoretical predictions\(^27 \). Figure 2A shows the simulated (symbols) and theoretical (lines) structure factors of semiflexible diblock copolymer melts with chain length \( N = 10 \) and aspect ratio \( \alpha = 2 \) as in Figure 1. When \( \chi N = 0 \) (blue), the simulation and mean-field theory (dashed blue line) agree at all wavevector \( q \). This indicates the approximate validity of the mean-field theory in the absence of monomer interactions. Both simulation and theory exhibit a maximum in the structure factor derived from the correlated monomer densities on connected polymers. At high \( q \), the structure factor has a characteristic \( q^{-1} \) falloff because of the local chain rigidity.

At \( \chi N = 0 \), our fluctuation theory (solid blue line) does not capture the scattering pattern, because the Brazovskii approximation\(^39 \) is only intended to predict the scattering intensity at \( q^* \) and assumes a highly peaked scattering pattern\(^27 \).

With increasing \( \chi N \), mean-field theory (dashed) overpredicts the scattering intensity at all \( q \). In addition, simulations show a left shift of the peak location, indicating an expansion of correlation size during phase transition. This shift is absent in the mean-field theory predictions. Both the suppression of scattering intensity and the peak shift can be attributed to correlated density fluctuation effects. These observations are consistent with previous studies for flexible diblock copolymers\(^19,37,40,41 \). The mean-field structure factors diverge and are not plotted above \( \chi_{MF} N = 8.93 \).

Approaching the phase transition to the lamellar phase (\( \chi N = 15.0 \)), fluctuation theory captures the approximate peak intensity. Our theory does not predict the left shift of the peak, because we assume a stationary peak location. In the scope of fluctuation theory, previous studies use self-consistent equations involving peak location\(^0 \) and fluctuation regularization techniques\(^39 \) to address the peak shift.
We summarize the comparison between the simulation and theory by focusing on the structure factor peak intensities (filled symbols in Figure 2A). Figure 2B shows the inverse peak intensities versus $\chi N$. Mean-field theory (dashed line) predicts a linear decrease of inverse peak intensity versus $\chi N$, with an x-axis intercept (blue dashed line), indicating the mean-field phase transition $\chi_{\text{ODT}}N$ with diverging peak intensity. Fluctuation theory predicts a phase transition to a lamellar phase (solid red line) when the free energy of the fluctuating homogeneous phase matches that of a lamellar phase. The simulated inverse peak intensities (filled symbols) interpolate between the mean-field and fluctuation theories with increasing $\chi N$. This suggests the failure of mean-field theory at strong segregation and increasing validity of the fluctuation theory. The vertical red line at $\chi N = 15.0$ indicates the simulated phase transition $\chi_{\text{ODT}}N$ obtained from the peak in the heat capacity and validated with qualitative morphological transition to a lamellar phase (see Figure 1). The location of the simulated phase transition $\chi_{\text{ODT}}N$ is much more aligned with the fluctuation theory prediction, showing the importance of fluctuations present in semiflexible diblock copolymers. We argue that in studying the phase transitions of semiflexible copolymer melts, the collective phenomena approaching the phase transition becomes more important, rendering fluctuation corrections indispensable.

We now look at diblock copolymers across a range of chain flexibilities and aspect ratios. Figure 3A,B shows inverse peak intensities for number of Kuhn steps per chain $N = 10$ and 100 with common aspect ratio $\alpha = 2$ (Figure 3A is identical to Figure 2B). In both cases, the inverse peak intensities interpolate between the mean-field and fluctuation theories with increasing $\chi N$. Notably, the deviation from the mean-field theory at high $\chi N$ is smaller for polymers with larger lengths (e.g., $N = 100$). For longer polymer (in units of Kuhn steps), each polymer interacts with more neighboring polymers. In this case, concentration fluctuations around each chain is suppressed, and the mean-field theory adequately captures the behavior.

Next, we look at Figure 3C,D displaying inverse peak intensities for chains with number of Kuhn steps per chain $N = 10$ and 100 and aspect ratio $\alpha = 4$. At each $N$ value, the mean-field theory becomes more accurate in comparison with Figure 3A,B. For high aspect ratio polymers (thin polymers), each polymer interacts with more neighbors in a space filling melt, decreasing the impact of correlated fluctuations that render the mean-field theory inaccurate. Finally, across the range of explored $N$ and $\alpha$, fluctuation theory gives better predictions of the simulated phase transition $\chi_{\text{ODT}}N$ than mean-field theory. Especially in the case of low $\chi N$ and low $\alpha$, fluctuations strongly elevate the phase transition $\chi_{\text{ODT}}N$ above the mean-field predictions.

Figure 4 shows the order–disorder transition $\chi_{\text{ODT}}N$ of semiflexible diblock copolymers at different number of Kuhn steps per chain $N$ and aspect ratio $\alpha$. The solid lines show predictions from the fluctuation theory of semiflexible diblock copolymers, and the solid circles are simulation results. The classical mean-field prediction of $\chi_{\text{ODT}}N = 10.5$ (valid for $N \to \infty$, $\alpha \to \infty$) based on the Gaussian-chain theory is shown as the black dashed line. In the infinitely thin chain limit, chain semiflexibility decreases the phase transition $\chi_{\text{ODT}}N$ with decreasing $N$ due to the diminishing impact of elastic chain entropy for shorter chains. The mean-field phase transition of semiflexible diblock copolymers $\chi_{\text{ODT}}N(\alpha \to \infty)$ is recovered, and is shown in blue. The trends of the simulated $\chi_{\text{ODT}}N$ are in agreement with theoretical predictions. For low-aspect-ratio polymers ($\alpha = 2$), the elevation of phase transition $\chi_{\text{ODT}}N$ at low $N$ due to fluctuation effects is very pronounced. When polymers have chain aspect ratios of $\alpha = 4$, fluctuation effects become less important, and chain semiflexibility...
decreases the phase transition $\chi_{ODT} N$ at low $N$. For both low- and high-aspect-ratio polymers, the fluctuation theory predicts a slightly lower $\chi_{ODT} N$ than simulation results. This may be due to the underestimate of the fluctuation correction using the Brazovskii approximation in calculating the divergent one-loop integral.44

The pronounced elevation of the phase transition $\chi_{ODT} N$ at low $N$ and aspect ratio $\alpha$ can be understood in terms of polymer concentration. In the perspective of each chain, there are a total of $C = R^3/(LA)$ polymers in its pervaded volume $R^3$, where $R$ is end-to-end distance (scales with the radius of gyration). In the fluctuation theory, we predict that the elevation of the mean-field phase transition scales as $\Delta(\chi_{ODT} N) = \chi_{ODT} N - \chi_{MF} N \sim C^{-2/3}$. At high $C$, each polymer interacts with many neighbors, and mean-field approximation is valid. In the high-$N$ limit, chain concentration can be related to the invariant degree of polymerization $N = C^3$, that is, $\Delta(\chi_{ODT} N) \sim C^{-2/3} \sim N^{-1/3} \alpha^{-2}$. Generally speaking, the fluctuation correction $\Delta(\chi_{ODT} N)$ becomes important for a combination of low $N$ and low $\alpha$. Depending on $\alpha$, the phase transition $\chi_{ODT} N$ can either increase (low $\alpha$) or decrease (high $\alpha$) with decreasing $N$.

In conclusion, we use a particle-field simulation with wormlike chains to specifically address the role of chain semiflexibility and density fluctuations in the phase behavior of diblock copolymers. We find that symmetric diblock copolymers first segregate into a disordered phase, and then transition to a lamellar phase. This is in agreement with previous theoretical prediction of fluctuation-induced first-order phase transition.7,14 Quantitative comparisons of structure factors show that a mean-field description of density correlation is sufficient at zero $\chi N$, and fluctuation corrections become essential as the system approaches a phase transition. The qualitative dependencies of phase transition $\chi_{ODT} N$ on $N$ and $\alpha$ agree between the simulation and theory.

In the future, a wavelength-cutoff independent theory will be developed. Additionally, such theory will be developed in conjunction with simulations of semiflexible copolymers that address the effect of small-scale spatial cutoff in a field-theoretic simulation. Here, we do not intend to fully address the result of discretization on renormalizing $\chi$ in simulation, due to a lack of a regularized theory for semiflexible diblock copolymers. A resolution to the unregularized fluctuation theory and simulations of semiflexible copolymers will be valuable to our understanding of the cumulative effects of microscopic details in governing the macroscopic properties of polymers.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.7b00638.

A table of the simulation parameters for the results presented in this manuscript and a plot of the structure factors for the simulations presented in Figure 3 (PDF).

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**Notes**

The authors declare no competing financial interest.

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