

Accessing the universal phase behavior of block copolymer melts with complex-Langevin field-theoretic simulations

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The universal phase behavior of block copolymer melts demonstrated previously with particle-based simulations is reproduced using complex-Langevin field-theoretic simulations (CL-FTSs) combined with the Morse calibration. For comparison purposes, the calculations are repeated using conventional Langevin field-theoretic simulations (L-FTSs), where the partial saddle-point approximation (PSPA) is applied to the pressure field. Both FTS methods produce consistent results down to invariant polymerization indices of $\bar{N} \approx 10^5$, implying that the inaccuracies in the PSPA are well compensated for by the Morse calibration. At lower $\bar{N}$, however, the complex fields of the CL-FTSs become prone to the formation of hot spots, causing the simulations to fail. Previous studies have shown that finite-range interactions can help stabilize CL-FTSs. Aided by the L-FTSs, we locate conditions at $\bar{N} = 10^4$, under which the universality is expected to hold and the CL-FTSs are stable. While the L-FTSs continue to obey universality, the CL-FTSs deviate significantly. A number of potential explanations are considered, but only one appears credible. Given the documented problems with CL simulations of nonpolymeric models, it is likely that the inconsistency with universality results from a ‘silent failure’ in the CL-FTSs, preceding the formation of hot spots.

I. INTRODUCTION

It has long been evident from experiments that the general phase behavior of block copolymer melts is largely independent of the specific chemistry of the system.¹ There is now strong evidence from particle-based simulations that block copolymer melts become truly universal in the long-chain regime,^{2–7} at least for models involving pairwise interactions and conformational symmetry. The implication is that all models are essentially equivalent, and thus can be accurately mapped onto the standard Gaussian-chain model (GCM) underpinning most theoretical calculations, which assumes incompressible melts of flexible polymers interacting by contact forces.⁸

For the simplest case of AB diblock copolymer melts, the relevant parameters of the GCM are the number of segments per diblock copolymer, N , the fraction of A-type segments, f , and the Flory-Huggins interaction parameter, χ . We follow the convention where all segments are defined to have a common volume of ρ_0^{-1} , and we limit our attention to conformationally-symmetric systems, where the A and B segments have the same statistical length, a . The self-consistent field theory (SCFT) for the GCM is controlled by f and χN ,⁹ and the fluctuation corrections to it are controlled by the invariant polymerization index, $\bar{N} = a^6 \rho_0^2 N$.¹⁰ If the parameters of any other model satisfying universality were to be mapped onto the parameters of the GCM and adjusted to give

the same values for f , χN , and $\bar{N}$, universality implies that it would exhibit identical behavior on the coarse-grained scale.

To test the universality hypothesis, Morse and coworkers^{3,4} devised a simple procedure for accurately mapping simulation models onto the standard GCM. They then applied it to five distinct models and demonstrated that the order-disorder transitions (ODTs) for symmetric diblock copolymers (i.e., $f = 0.5$) all collapse onto a universal curve,^{3,5}

$$(\chi N)_{\text{ODT}} = 10.495 + 41.0\bar{N}^{-1/3} + 123.0\bar{N}^{-0.56}, \quad (1)$$

when plotted in terms of the GCM parameters. Furthermore, they went on to confirm that the free energy, F , and the equilibrium lamellar period, D_{eq} , were also universal.^{5,7} Remarkably, the universal values of F and D_{eq} coincided with the SCFT predictions of the standard GCM.

In the absence of universality, the behavior of an experimental system will depend on its microscopic details, and thus accurate predictions will generally require a model involving many parameters specially tuned to provide a faithful representation of the system. On the other hand, when the molecular weight is sufficient for universality, it becomes possible to make accurate predictions with simple coarse-grained models. It is unclear what is a sufficient molecular weight, but it is worth noting that lattice simulations have provided accurate predictions for polyisoprene-poly(lactide) (PI-PLA) diblock copolymer melts despite their modest molecular weight.¹¹

The ability to make quantitative predictions with simple models is nothing short of amazing, but unfortunately

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even highly coarse-grained models are challenging to simulate. Indeed, particle-based simulations have yet to produce a complete phase diagram for diblock copolymer melts. Fortunately, there is an alternative, field-theoretic simulations (FTSs).^{12–14} Not only are they much faster,¹⁵ they have actually provided complete phase diagrams for diblock copolymers.^{16–18} Furthermore, they can handle more complicated block copolymer architectures^{19–21} and multi-component blends in various ensembles,^{22–24} without much of an increase in computational cost.

The polymer field theory of a block copolymer system is derived from its particle-based model by a mathematically exact transformation involving Hubbard-Stratonovich identities.^{12–14} For AB-type block copolymer melts, the field-theoretic Hamiltonian, $H_f[W_-, W_+]$, involves a composition field, $W_-(\mathbf{r})$, that couples to the difference in the A and B concentrations and a pressure field, $W_+(\mathbf{r})$, that couples to the total concentration. It is common to approximate the statistical mechanics of $H_f[W_-, W_+]$ by SCFT, where the free energy, $F \approx H_f[w_-, w_+]$, is estimated from the saddle-point fields, $w_-(\mathbf{r})$ and $w_+(\mathbf{r})$, corresponding to $\mathcal{D}H_f/\mathcal{D}W_-(\mathbf{r}) = \mathcal{D}H_f/\mathcal{D}W_+(\mathbf{r}) = 0$. Note that we follow the convention where $W_-(\mathbf{r})$ is real valued and $W_+(\mathbf{r})$ is imaginary valued, which results in real saddle-point fields.¹⁸ The challenge in going beyond SCFT is that the imaginary $W_+(\mathbf{r})$ leads to a complex-valued $H_f[W_-, W_+]$, causing the so-called sign problem.^{25–31}

One way to overcome the sign problem is to apply a partial saddle-point approximation (PSPA),^{32–35} in which $W_+(\mathbf{r})$ is replaced by the solution of $\mathcal{D}H_f/\mathcal{D}W_+(\mathbf{r}) = 0$. As it turns out, the solution, $w_+(\mathbf{r})$, is real and consequently $H_f[W_-, w_+]$ is amenable to conventional Langevin simulations (L-FTSs).³⁶ The justification for the PSPA is that the composition fluctuations in $W_-(\mathbf{r})$ are thought to provide the dominant correction to SCFT. Indeed, L-FTSs have shown impressive agreement with the universality found in particle-based simulations.¹⁸ Not only do their ODTs agree with Eq. (1), the free energy and the domain sizes are well approximated by SCFT, exactly as observed in the particle-based simulations. Although this bodes well for the PSPA, Quah *et al.*³⁷ have reported some serious inaccuracies based on comparisons with complex-Langevin field-theoretic simulations (CL-FTSs).

CL-FTSs provide an exact method of overcoming the sign problem, where $W_-(\mathbf{r})$ and $W_+(\mathbf{r})$ are allowed to explore the entire complex domain.³⁸ Not only do they avoid the PSPA, they are generally faster as there is no need to evaluate $w_+(\mathbf{r})$. The problem, though, is that they are prone to instabilities,^{16,18,39,40} which become serious for strong fluctuations near the ODT at small $\tilde{N}$. The instabilities result from a tendency to form sharp spikes in the field configurations,^{18,39} referred to as hot spots. Delaney and Fredrickson¹⁶ have tamed the instabilities to some degree by incorporating compressibility and finite-range interactions into their model, but the range of their interactions was relatively large. It has

been suggested that this may have caused significant deviations from universality.¹⁸

Kim *et al.*⁴¹ have shown that translational symmetry contributes to the instabilities. It has generally been assumed that $W_-(\mathbf{r})$ and $W_+(\mathbf{r})$ fluctuate about the real saddle-point fields of SCFT.³⁹ However, because the fields are permitted to be complex, the translational invariance (i.e., $\mathbf{r} \rightarrow \mathbf{r} - \mathbf{v}$) extends to complex-valued displacements, $\mathbf{v}$. Consequently, the real saddle point is connected to a continuous family of complex saddle points,⁴² which provides a pathway deep into the complex domain, eventually resulting in the formation of hot spots.¹⁸

This problem is similar to what happens in complex-Langevin (CL) simulations of quantum chromodynamics (QCD), where a gauge symmetry also permits large excursions deep into the complex domain. In QCD, these excursions can be prevented by the continuous application of gauge transformations, a method referred to as gauge cooling.^{43,44} Similarly, Kim *et al.*⁴¹ applied translation cooling to CL-FTSs, whereby imaginary translations were continuously applied to maintain close proximity to the real saddle point. Although this expanded the region of stability, the improvement was limited.

Willis and Matsen⁴⁵ tried another strategy from QCD to stabilize CL simulations, referred to as dynamical stabilization. It involves adding an artificial force to the Langevin dynamics of sufficient strength to prevent the excursions, but not so strong as to significantly bias the statistics.^{28,29,31,47} Unlike the translation cooling, dynamical stabilization expanded the region of stability significantly, producing universal results down to $\tilde{N} \approx 10^5$. Nevertheless, this invariant polymerization is still well above the values typical of experiments.¹ Here, we attempt to push the CL-FTSs to lower $\tilde{N}$ by incorporating finite-range interactions, but with a small enough range not to disrupt the universality. We also compare the results to those of L-FTSs, so as to assess the accuracy of the PSPA.

II. FIELD-THEORETIC SIMULATIONS

In this study, we consider a system of n diblock copolymers each consisting of N monomers, of which the first N_A are of type A and the remaining N_B are of type B. Instead of the standard GCM, we employ a bead-spring model with compressibility and finite-range interactions. The bead (i.e., monomer) coordinates are specified by the set of vectors $\{\mathbf{r}_{\alpha,i}\}$, where $\alpha \in \{1, 2, \dots, n\}$ is the molecule index and $i \in \{1, 2, \dots, N\}$ is the monomer index. In terms of the coordinates, the concentrations of the A and B monomer centers are

$$\hat{\phi}_A(\mathbf{r}) = \frac{1}{\rho_0} \sum_{\alpha=1}^n \sum_{i=1}^{N_A} \delta(\mathbf{r} - \mathbf{r}_{\alpha,i}), \quad (2)$$

$$\hat{\phi}_B(\mathbf{r}) = \frac{1}{\rho_0} \sum_{\alpha=1}^n \sum_{i=N_A+1}^N \delta(\mathbf{r} - \mathbf{r}_{\alpha,i}), \quad (3)$$

respectively. As usual, we divide by the bulk monomer density, $\rho_0 \equiv nN/V$, to make the concentrations dimensionless.

The Hamiltonian,

$$H_p[\{\mathbf{r}_{\alpha,i}\}] = U_b[\{\mathbf{r}_{\alpha,i}\}] + U_{\text{int}}[\{\mathbf{r}_{\alpha,i}\}], \quad (4)$$

of our generalized model is expressed as a sum of bonded and nonbonded interactions. The bonds are modeled as harmonic springs,

$$\frac{U_b}{k_B T} = \frac{3}{2a_b^2} \sum_{\alpha=1}^n \sum_{i=1}^{N-1} |\mathbf{r}_{\alpha,i+1} - \mathbf{r}_{\alpha,i}|^2, \quad (5)$$

where a_b is the bare statistical segment length for noninteracting polymers. The nonbonded interactions,

$$\frac{U_{\text{int}}}{k_B T} = \rho_0 \int [\chi_b \hat{\phi}_{\Gamma,A} \hat{\phi}_{\Gamma,B} + \frac{\zeta}{2} (\hat{\phi}_{\Gamma,A} + \hat{\phi}_{\Gamma,B} - 1)^2] d\mathbf{r}, \quad (6)$$

involve the usual Flory-Huggins term with a bare interaction strength of χ_b and a Helfand-type compressibility controlled by a dimensionless compression modulus, ζ .⁴⁶ Following Delaney and Fredrickson,¹⁶ the interactions are evaluated using smeared concentrations, $\hat{\phi}_{\Gamma,A}(\mathbf{r})$ and $\hat{\phi}_{\Gamma,B}(\mathbf{r})$, obtained by convolutions,

$$f_{\Gamma}(\mathbf{r}) \equiv \int f(\mathbf{r} - \mathbf{r}') \Gamma(r') d\mathbf{r}', \quad (7)$$

with a spherically-symmetric ‘smearing’ function, $\Gamma(r)$, of $r \equiv |\mathbf{r}|$ that satisfies $\int \Gamma(r) d\mathbf{r} = 1$. The convolutions are mathematically equivalent to using finite-range interactions, where the interaction profile is given by

$$u_{\text{int}}(r) = \int \Gamma(|\mathbf{r} - \mathbf{r}'|) \Gamma(r') d\mathbf{r}'. \quad (8)$$

The equivalence follows from the fact that the Flory-Huggins interaction can be re-expressed using

$$\int \hat{\phi}_{\Gamma,A}(\mathbf{r}) \hat{\phi}_{\Gamma,B}(\mathbf{r}) d\mathbf{r} = \int \hat{\phi}_A(\mathbf{r}) u_{\text{int}}(|\mathbf{r} - \mathbf{r}'|) \hat{\phi}_B(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (9)$$

An analogous identity also exists for the Helfand compressibility term. Delaney and Fredrickson chose a Gaussian smearing function,

$$\Gamma(r) = \frac{1}{(2\pi a_{\text{int}}^2)^{3/2}} \exp(-r^2/2a_{\text{int}}^2). \quad (10)$$

which also results in a Gaussian interaction profile,

$$u_{\text{int}}(r) = \frac{1}{(4\pi a_{\text{int}}^2)^{3/2}} \exp(-r^2/4a_{\text{int}}^2). \quad (11)$$

In polymer field theory,^{12–14,18} Hubbard-Stratonovich identities are used to transform this particle-based Hamiltonian into an equivalent field-based Hamiltonian,

$$\frac{H_f}{nk_B T} = -\ln Q + \frac{\chi_b N}{4} + \frac{N}{V} \int \left(\frac{W_-^2}{\chi_b} - \frac{W_+^2}{\chi_b + 2\zeta} - W_+ \right) d\mathbf{r}. \quad (12)$$

Here, $Q[W_-, W_+]$ is the partition function for a single molecule in a system of noninteracting polymers (i.e., $\chi_b = \zeta = 0$) acted upon by the fields. See the supplementary material for details of the transformation.

Simulations of $H_f[W_-, W_+]$ are typically performed in $L_x \times L_y \times L_z$ orthorhombic boxes with periodic boundary conditions. To represent the fields on a computer, the boxes are overlaid with $m_x \times m_y \times m_z$ grids of uniform spacing, $\Delta_\nu = L_\nu/m_\nu$, in the $\nu = x, y$, and z directions. As such, the total volume of the box is $V = L_x L_y L_z$, the total number of grid points is $M = m_x m_y m_z$, and the volume of each cell is $V_{\text{cell}} = V/M$. Our simulations will focus on the lamellar-disorder transition, for which cubic boxes with $L_\nu \equiv L$, $m_\nu \equiv m$, and $\Delta_\nu \equiv \Delta$ will suffice. We generally choose $m = 32$ and $L = 3D_{\text{eq}}$, where the equilibrium lamellar period, D_{eq} , is determined by balancing the normal and transverse stresses of the lamellae.

In CL-FTSs, both fields sample the entire complex domain according to

$$W_-(\mathbf{r}; \tau + \delta\tau) = W_-(\mathbf{r}; \tau) - \Lambda_-(\mathbf{r})\delta\tau + \mathcal{N}(0, \sigma), \quad (13)$$

$$W_+(\mathbf{r}; \tau + \delta\tau) = W_+(\mathbf{r}; \tau) + \Lambda_+(\mathbf{r})\delta\tau + i\mathcal{N}(0, \sigma). \quad (14)$$

The stochastic function, $\mathcal{N}(0, \sigma)$, provides real-valued Gaussian noise with a mean of zero and a variance of $\sigma^2 = 2\delta\tau/V_{\text{cell}}\rho_0$. The deterministic forces are given by

$$\Lambda_-(\mathbf{r}) = \phi_{\Gamma,-}(\mathbf{r}) + \frac{2}{\chi_b} W_-(\mathbf{r}) + i\alpha_{\text{ds}} N \text{Im}[W_-(\mathbf{r})], \quad (15)$$

$$\Lambda_+(\mathbf{r}) = \phi_{\Gamma,+}(\mathbf{r}) - 1 - \frac{2}{\chi_b + 2\zeta} W_+(\mathbf{r}), \quad (16)$$

where $\phi_{\Gamma,\pm}(\mathbf{r})$ are ensemble averages of

$$\hat{\phi}_{\Gamma,\pm}(\mathbf{r}) \equiv \hat{\phi}_{\Gamma,A}(\mathbf{r}) \pm \hat{\phi}_{\Gamma,B}(\mathbf{r}), \quad (17)$$

in the system of noninteracting polymers. Note that $\Lambda_-(\mathbf{r})$ includes the usual contributions from the functional derivative of the Hamiltonian, $\mathcal{D}H_f/\mathcal{D}W_-(\mathbf{r})$,^{16,18} plus an additional contribution of strength α_{ds} for the dynamical stabilization.⁴⁵ See the supplementary material for more details.

In practice, we modify the simple Euler-Maruyama algorithm in Eqs. (13) and (14) to facilitate larger time steps, $\delta\tau$. For conditions prone to the formation of hot spots, we evolve $W_-(\mathbf{r})$ and $W_+(\mathbf{r})$ using the predictor-corrector algorithm with an adaptive time step, $\delta\tau$.³⁹ Although we are able to target a time step of $\delta\tau N = 0.1$, it nevertheless drops by orders of magnitude when hot spots occur, causing the simulations to run extremely

slow. However, when the CL-FTSs are sufficiently stable with respect to hot spot formation, the Leimkuhler-Matthews algorithm⁴⁸ can be applied with a large time step of $\delta\tau N = 2$. Source code for the CL-FTSs is provided in the supplementary material.

For comparison purposes, we also perform L-FTSs, where $W_-(\mathbf{r})$ evolves according to Eq. (13) with $\alpha_{ds} = 0$, while $W_+(\mathbf{r})$ is replaced by its PSPA. The partial saddle point, $w_+(\mathbf{r})$, is evaluated iteratively at each Langevin step using the linear-response Anderson-mixing algorithm introduced by Chen and Morse.⁴⁹ Although this extra calculation slows the L-FTSs, that is largely compensated for by the fact the Leimkuhler-Matthews algorithm can operate with a remarkably large time step of $\delta\tau N = 8$. Source code for the L-FTSs is also available in the supplementary material.

In this study, we will need to evaluate several observables. The first is the structure function used to measure the level of segregation in the disordered phase, of which there are two natural choices,

$$S_\Gamma(k) \equiv \frac{\rho_0^2}{4V} \langle \delta\hat{\phi}_{\Gamma,-}(\mathbf{k}) \delta\hat{\phi}_{\Gamma,-}(-\mathbf{k}) \rangle, \quad (18)$$

$$S(k) \equiv \frac{\rho_0^2}{4V} \langle \delta\hat{\phi}_-(\mathbf{k}) \delta\hat{\phi}_-(-\mathbf{k}) \rangle, \quad (19)$$

corresponding to fluctuations of $\hat{\phi}_{\Gamma,-}(\mathbf{k})$ and $\hat{\phi}_-(\mathbf{k})$, respectively, where the Fourier transforms are defined by

$$f(\mathbf{k}) = \int f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}. \quad (20)$$

The structure functions are evaluated using^{51,52}

$$S_\Gamma(k) = \frac{\rho_0^2}{V\chi_b^2} \langle W_-(\mathbf{k}) W_-(-\mathbf{k}) \rangle - \frac{\rho_0}{2\chi_b}, \quad (21)$$

$$S(k) = S_\Gamma(k)/\Gamma^2(k), \quad (22)$$

where

$$\Gamma(k) = \exp(-a_{\text{int}}^2 k^2/2), \quad (23)$$

for the case of Gaussian smearing. In particle-based simulations, correlations are generally specified in terms of the relative positions of the monomer centers. Thus, the relevant structure function is $S(k)$, and so that is the definition we generally use. Nevertheless, the choice becomes immaterial once $a_{\text{int}} \ll R_0$.

We also need to determine the equilibrium period, D_{eq} , of the lamellar phase. This is done by simulating a lamellar morphology with the layers oriented normal to the z direction, and evaluating ensemble averages of $\partial \ln Q / \partial L_\nu$. Fredrickson and Delaney⁵⁰ have worked out analytical expressions for these derivatives, but we conclude that it is better to just evaluate them using finite differences. The value of D_{eq} is obtained by adjusting the box size such that^{53,54}

$$L_x \left\langle \frac{\partial \ln Q}{\partial L_x} \right\rangle + L_y \left\langle \frac{\partial \ln Q}{\partial L_y} \right\rangle = 2L_z \left\langle \frac{\partial \ln Q}{\partial L_z} \right\rangle. \quad (24)$$

Note that this condition assumes the grid spacing, Δ_ν , is the same in all three directions, $\nu = x, y$, and z . If not, differences in $\partial z_\infty / \partial L_\nu$ may need to be accounted for as explained in Ref. 53 and 54.

Lastly, we need to distinguish the lamellar phase from the disordered phase. For this, we evaluate the order parameter

$$\Psi = \frac{1}{R_0^3} \left(\frac{V}{(2\pi)^3} \int f(k) |W_-(\mathbf{k}) W_-(-\mathbf{k})|^2 d\mathbf{k} \right)^{1/4}, \quad (25)$$

where $f(k)$ is a Heaviside-like function that screens out the large wavevectors beyond the principle peak, k^* , in the structure function. Past studies⁵⁵ have shown that Ψ is distinctly larger for lamellar configurations than for disordered ones.

III. MORSE CALIBRATION

The Morse calibration^{3,4} is used to map our generalized model with discrete chains, compressibility, and finite-range interactions onto the standard GCM. The first step is to determine the bare segment length, a_b , such that the average end-to-end length of the polymers satisfies $R_0 = aN^{1/2}$ in the $\chi_b \rightarrow 0$ and $N \rightarrow \infty$ limits.⁵⁶ In the CL-FTSs,

$$a_b = a \left(1 + \frac{a^2}{72(2\pi)^3 \rho_0} \int \frac{k^2 d\mathbf{k}}{s^2(k)[1+t(k)/\zeta]} \right)^{-1}, \quad (26)$$

where the integration is over the interval $-\pi/\Delta_\nu \leq k_\nu \leq \pi/\Delta_\nu$ and

$$s(k) \equiv \sinh(k^2 a^2/12), \quad (27)$$

$$t(k) \equiv \tanh(k^2 a^2/12)/\Gamma^2(k). \quad (28)$$

In the L-FTSs, just as in SCFT, $R_0 = a_b N^{1/2}$ and thus $a_b = a$. The second step of the calibration is to determine a linear approximation for the Flory-Huggins parameter $\chi \approx z_\infty \chi_b$, such that the free energy of a disordered melt reduces to the Flory-Huggins expression, $F/nk_B T \rightarrow \chi N f(1-f)$ in the same $\chi_b \rightarrow 0$ and $N \rightarrow \infty$ limits.⁵⁷ In this case,

$$z_\infty = 1 - \frac{1}{(2\pi)^3 \rho_0} \int \frac{d\mathbf{k}}{t(k)[1+t(k)/\zeta]}, \quad (29)$$

for both simulation methods. Derivations of Eqs. (26) and (29) are provided in the supplementary material.

Accurate numerical calculations generally require the grid spacing, Δ_ν , to be fine relative to the smallest length scale of the model. This is a potential problem for short-range interactions. To illustrate the issue, Fig. 1 shows $S(k)$ for symmetric diblock copolymer melts in the disordered phase at $\chi_b N = 9.5$, using cubic simulation boxes with $L = 4.5R_0$ and $m = 32, 40$, and 48 . The solid and dashed curves correspond to CL-FTSs and L-FTSs, respectively. In both cases, the grid dependence is

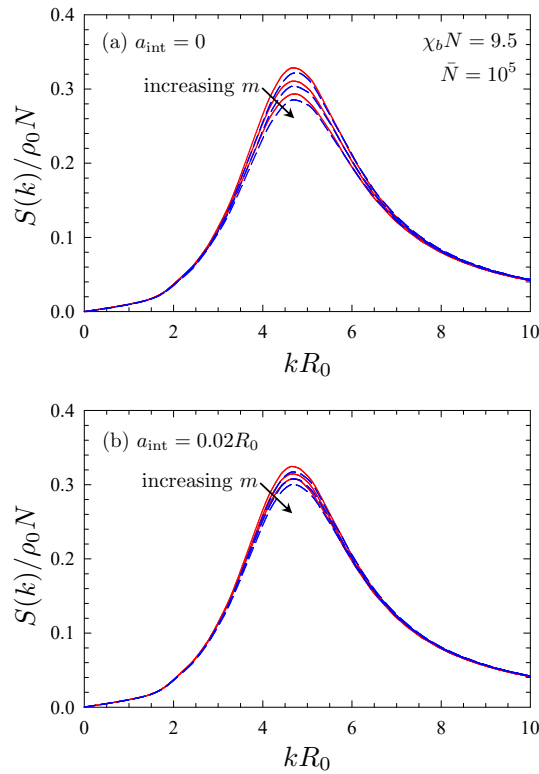


FIG. 1. Structure functions, $S(k)$, evaluated with a bare segregation of $\chi_b N = 9.5$ and an invariant polymerization of $\bar{N} = 10^5$ for (a) contact interactions and (b) short-range interactions of $a_{\text{int}} = 0.02R_0$. The CL-FTSs (solid curves) and L-FTSs (dashed curves) are performed in cubic simulation boxes of $L = 4.5R_0$ with $m = 32, 40$, and 48 grid points along each direction. Notice that the peaks, $S(k^*)$, decrease with increasing resolution (i.e., increasing m).

strongest for the contact interactions of Fig. 1(a), but it also remains significant for the short-range interactions of Fig. 1(b). The requirement for convergence can be seen in Fig. 2, where we compare z_∞ and a_b/a calculated for the finite values of m to the converged results corresponding to $m \rightarrow \infty$. This shows that the grid spacing for $m = 32$ only becomes sufficient once $a_{\text{int}} \gtrsim 0.08R_0$. For the smearing range of $a_{\text{int}} = 0.02R_0$, corresponding to Fig. 1(b), convergence requires $m \gtrsim 200$, which is simply impractical. For the $a_{\text{int}} = 0$ of Fig. 1(a), z_∞ actually exhibits an ultraviolet (UV) divergence,^{60,61} and thus no value of m will suffice. Note that the usual UV divergence of a_b/a is avoided because our model involves discrete rather than continuous Gaussian chains.⁵⁸ To resolve these convergence problems, Fig. 3 reevaluates $S(k)$, this time, holding $z_\infty \chi_b N = 9$ constant for $m = 32, 40$, and 48 . This accelerates the convergence for $a_{\text{int}} = 0.02R_0$ such that $m = 32$ is now sufficient, and furthermore it removes the UV divergence for $a_{\text{int}} = 0$.

The insets in Fig. 3 compare the peak heights, $S(k^*)$, to the prediction from renormalized one-loop (ROL) theory^{58,59} evaluated at $\chi N = 9$. To correct for the dis-

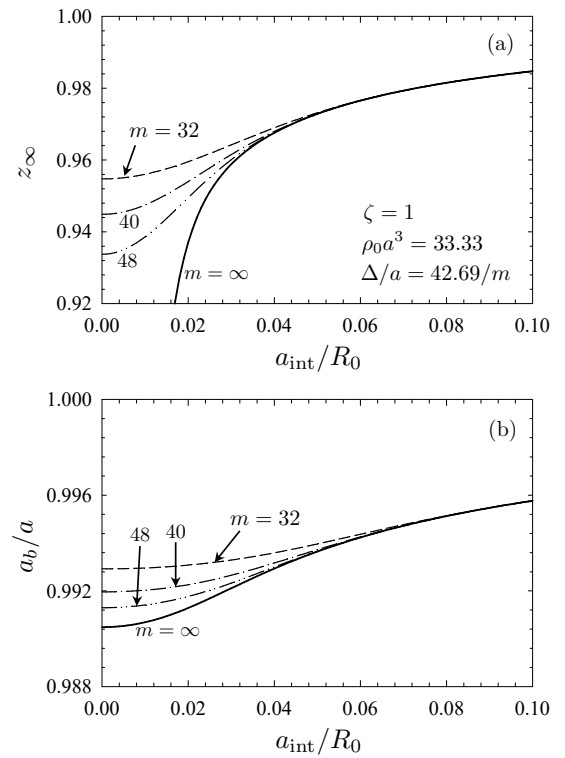


FIG. 2. Calibration of (a) the linear $\chi \approx z_\infty \chi_b$ and (b) the bare segment length, a_b , as a function of the interaction range, a_{int} , for simulations with $N = 90$, $\zeta = 1$, and $\bar{N} = 10^5$ in cubic simulation boxes of size $L = 4.5R_0$ with $m = 32, 40$, and 48 grid points along each dimension. Solid curves denote converged results corresponding to $m \rightarrow \infty$.

crepancy, the Morse calibration defines a nonlinear

$$\chi = z_\infty \chi_b + c_2 (z_\infty \chi_b)^2 + c_3 (z_\infty \chi_b)^3 + \dots, \quad (30)$$

where the coefficients, c_i , are adjusted to bring the $S(k^*)$ values at different χ_b into agreement with ROL theory. Given the large $\bar{N}$ values of our study, we can generally truncate the $i \geq 3$ terms from Eq. (30).

It is important to note that the nonlinear calibration of χ is only possible in the universal regime. In the absence of universality, the homopolymer (i.e., $\chi_b \rightarrow 0$) limit of $S(k^*)$ will differ from the ROL prediction, and no choice of fitting parameters can bring them into agreement. This is also a potential problem for the L-FTSs, because their structure functions converge to the random-phase approximation (RPA),⁶² which gradually deviates from ROL at small $\bar{N}$. Fortunately, the difference between ROL and RPA is not significant for the values of $\bar{N} \geq 10^4$ examined in our study.⁵⁹

It may appear that the nonlinear χ is dependent on which particular structure function is used, but that is not the case. Universality implies that the coarse-grained behavior of the model is independent of its microscopic details. As such, the smearing should not affect the structure function at the large length scales corresponding to $k \lesssim k^*$. This, in turn, implies that universality can only

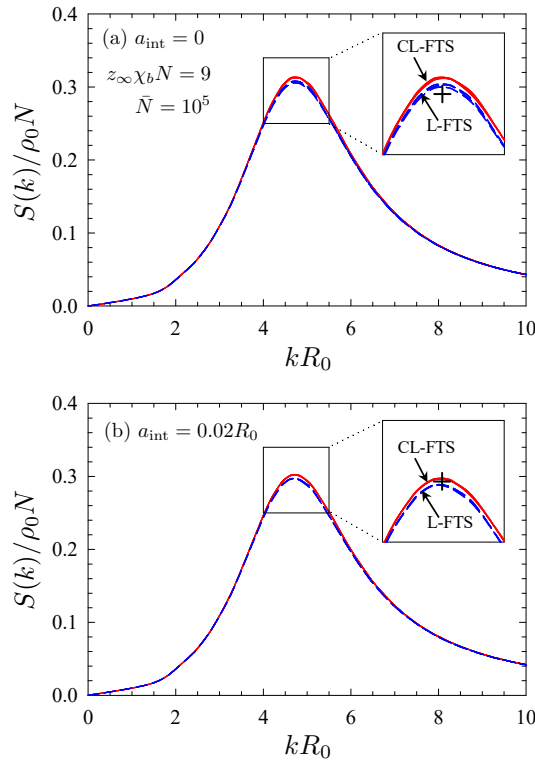


FIG. 3. Analogous plots to those of Fig. 1 for (a) contact interactions and (b) short-range interactions of $a_{\text{int}} = 0.02R_0$, this time evaluated at an effective segregation of $z_\infty \chi_b N = 9$. In both cases, the curves for $m = 32, 40$, and 48 collapse. The insets compare the peaks, $S(k^*)$, to the ROL prediction denoted by crosses.

occur if $\Gamma(k^*) \approx 1$. Indeed, for the Gaussian smearing, we will find that universal behavior emerges once $a_{\text{int}} \lesssim 0.02R_0$, which coincides with where the difference between $S(k^*)$ and $S_\Gamma(k^*)$ drops below 1%.

The coefficients, c_i , of the nonlinear χ are dependent on the dimensionless monomer density, $\rho_0 a^3$, the compression modulus, ζ , and the smearing function, $\Gamma(r)$. In Eq. (30), we intentionally expressed χ as a function of $z_\infty \chi_b$. As a result, the c_i values are, to a good approximation, independent of the grid resolution.⁵⁴ Although there remains a weak dependence that needs to be considered when performing precise free energy comparisons between different ordered phases,^{17,21} it is of no concern here because we compare the lamellar and disordered phases using identical grids.

IV. RESULTS

The previous study by Willis and Matsen,⁴⁵ comparing the ODTs from CL-FTSs and L-FTSs to the universal prediction in Eq. (1), assumed the lamellar period, D_{eq} , as predicted by the SCFT of the standard GCM. It also neglected the renormalization of the segment length, Eq. (26), for the CL-FTSs. Here, we begin by repeating their

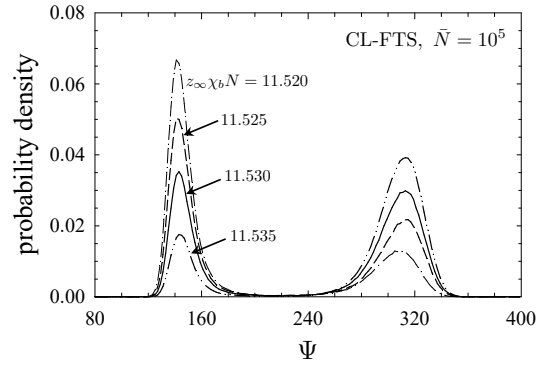


FIG. 4. Histograms of the order parameter, Ψ , calculated from CL-FTSs for a series of $z_\infty \chi_b N$ values at $\bar{N} = 10^5$. The ODT occurs at $(z_\infty \chi_b N)_{\text{ODT}} = 11.526$, where the disorder and order peaks are of equal area (i.e., equal probability).

calculations, this time evaluating the actual periods and using the proper segment lengths. As before, we include a modest compressibility of $\zeta = 1$, but still retain the usual contact interactions of the standard model [i.e., $\Gamma(r) = \delta(r)$].

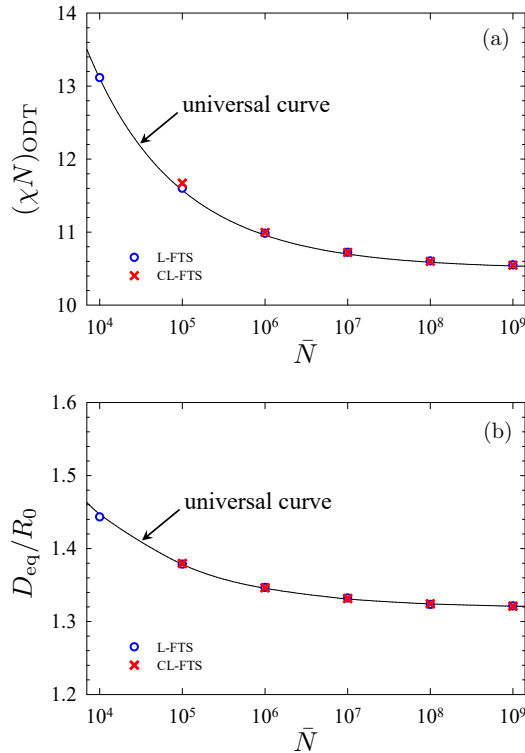
We locate the ODTs using the order parameter, Ψ , defined in Eq. (25). Histograms of Ψ generated from CL-FTSs at $\bar{N} = 10^5$ are shown in Fig. 4 for a series of $z_\infty \chi_b N$ values. As we can see, the system readily transitions between the lamellar and disordered phases, producing well-defined peaks at $\Psi \approx 145$ and 315 , respectively. Because the system never remains in the lamellar phase for long near the ODT, we evaluate D_{eq} at $\Delta(z_\infty \chi_b N) \approx 0.1$ and 0.2 above the transition, and then linearly extrapolate back to the ODT. The histograms are generally collected over long durations of $\tau N = 10^7$, which is sufficient time for $\sim 10^2$ transitions. This large number of transitions results in accurate histograms as evident by the smooth progression observed in Fig. 4. Matching the areas (i.e., probabilities) of the two peaks locates the ODTs with remarkable precision. In this case, the ODT occurs at $(z_\infty \chi_b N)_{\text{ODT}} = 11.526$.

The L-FTSs do not transition as frequently as the CL-FTSs, but nevertheless we can obtain equally precise ODTs using well-tempered metadynamics (WTMD), where a potential, $U(\Psi)$, is added to the Hamiltonian to reduce the energy barrier.⁵⁵ The WTMD has the advantage that the χ_b -dependence of the histogram is obtained from a single simulation. For $\bar{N} = 10^5$, the L-FTSs predict the ODT at $(z_\infty \chi_b N)_{\text{ODT}} = 11.501$. Note that the WTMD method cannot be applied to the CL-FTSs, because it requires $U(\Psi)$ to be an analytic function of $W_-(\mathbf{r})$,⁴¹ which is impossible given that Ψ is real valued.

The last step is to evaluate the coefficient, c_2 , for the effective χ in Eq. (30). We repeat the calculations from before, but this time accounting for the renormalization of the segment length when evaluating $\bar{N} = a^6 \rho_0^2 N$ for the CL-FTSs. This has the effect of reducing c_2 . We also improved our procedure for fitting the FTS results to the ROL predictions. The new calibrations are listed

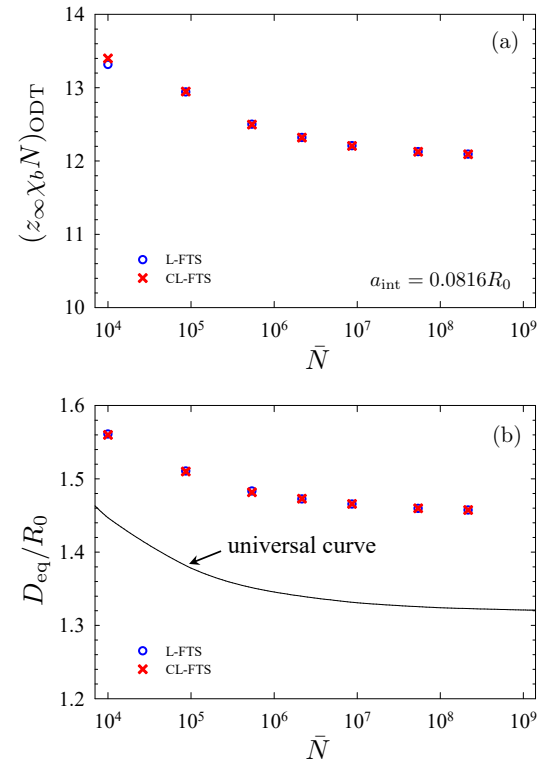
TABLE I. Coefficients of the nonlinear χ in Eq. (30) for $\zeta = 1$.

$\rho_0 a^3$	$\bar{N}$ (for $N = 90$)	c_2 (CL-FTS)	c_2 (L-FTS)
10.5	10^4		0.23
33.3	10^5	0.099	0.067
105	10^6	0.033	0.023
333	10^7	0.015	0.012
1054	10^8	0.009	0.009
3333	10^9	0.008	0.008


 FIG. 5. (a) Position of the ODT plotted in terms of nonlinear χ as a function of the invariant polymerization index, $\bar{N}$, obtained from CL-FTSs (crosses) and L-FTSs (circles) with contact forces. (b) Equilibrium lamellar periods at the ODT. The universal predictions are denoted by solid curves.

in Table I. Note that we are able to turn off the dynamical stabilization when calculating $S(k)$ in the disordered phase.

Using the nonlinear calibration, we obtain ODTs of $(\chi N)_{\text{ODT}} = 11.68$ and 11.60 for the CL-FTSs and L-FTSs, respectively, which agree reasonably well with the universal value of 11.57 . Figure 5(a) compares the ODTs for a range of other $\bar{N}$ values to the universal result in Eq. (1). Similarly, Fig. 5(b) compares the equilibrium lamellar periods, D_{eq} , at the ODT to the SCFT prediction for the standard GCM evaluated at the $(\chi N)_{\text{ODT}}$ given by Eq. (1). As we can see, both FTSs conform to the expected universal behavior. The agreement implies that the inaccuracies in the PSPA are well compensated for by the Morse calibration.


 FIG. 6. (a) Position of the ODT plotted in terms of linear $\chi \approx z_{\infty} \chi_b$ as a function of the invariant polymerization index, $\bar{N}$, obtained from CL-FTSs (crosses) and L-FTSs (circles) with a Gaussian smearing of $a_{\text{int}} = 0.2 R_g$. (b) Equilibrium lamellar periods at the ODT compared to the universal prediction (solid curve). Note that the significant deviation from universality prevents the nonlinear calibration of χ .

We were unable to obtain reliable CL-FTS results below $\bar{N} \approx 10^5$, because the large dynamical stabilization required to control the hot spots creates a significant bias for the lamellar phase. However, Fredrickson and coworkers^{16,37} were able to perform CL-FTSs at $\bar{N} \approx 10^4$ without dynamical stabilization by instead smearing the concentrations. Therefore, we repeat the comparison using the same Gaussian smearing of $a_{\text{int}} = 0.2 R_g = 0.0816 R_0$ from Quah *et al.*³⁷ The ODTs and corresponding lamellar periods are plotted in Fig. 6. This time, both FTSs can be extended down to $\bar{N} = 10^4$, and the agreement is remarkably good, contrary to claims by Quah *et al.* As we will explain later, their results are likely inaccurate due to the computational challenges involved in locating ODTs using free energy, as opposed to our more direct method of using an order parameter.

Although the smearing permits CL-FTSs at lower $\bar{N}$, the results no longer conform to universality. This is evident in Fig. 6(b), where the lamellar periods significantly exceed the universal prediction (solid curve). As a result of the nonuniversal behavior, it is impossible to fit $S(k^*)$ to the ROL prediction, which is why the ODTs in Fig. 6(a) are plotted in terms of the linear $\chi \approx z_{\infty} \chi_b$. The universality is, undoubtedly, lost due to the long range,

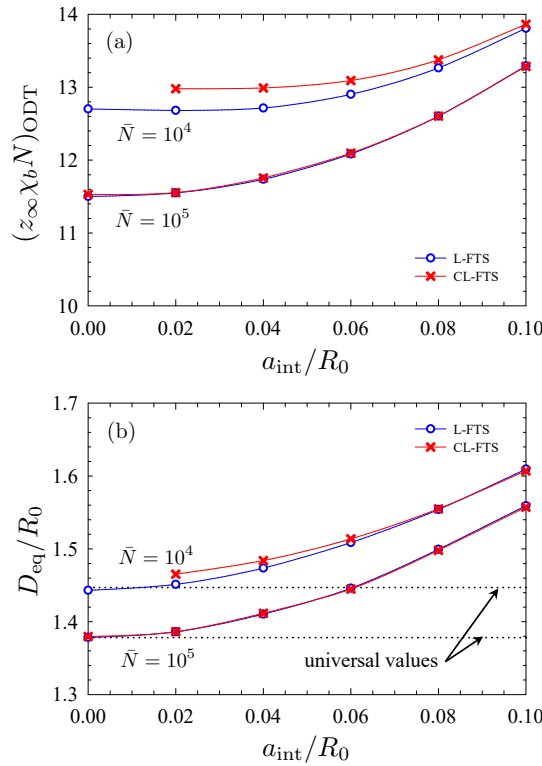


FIG. 7. (a) Position of the ODT plotted in terms of linear $\chi \approx z_\infty \chi_b$ for $\bar{N} = 10^5$ and 10^4 , obtained from CL-FTSs (crosses) and L-FTSs (circles) with Gaussian smearing. (b) Equilibrium lamellar periods at the ODT. Based on the universal values of D_{eq} (dotted lines), universality requires $a_{\text{int}} \lesssim 0.02R_0$.

$a_{\text{int}} \approx 0.08R_0$, of the interactions, $u_{\text{int}}(r)$.

To gauge the amount of smearing the universality can tolerate, we evaluate $(z_\infty \chi_b N)_{\text{ODT}}$ and D_{eq} as a function of the smearing length, a_{int} . As before, the CL-FTS and L-FTS results, shown in Fig. 7, are virtually identical at $\bar{N} = 10^5$. In both cases, the lamellar period becomes consistent with the universal value of $D_{\text{eq}} = 1.378R_0$ once $a_{\text{int}} \lesssim 0.02R_0$. Indeed, when we perform the nonlinear calibration of χ at $a_{\text{int}} = 0.02R_0$, we obtain values of $(\chi N)_{\text{ODT}} = 11.59$ and 11.55 for the CL-FTSs and L-FTSs, respectively, which match the universal value of 11.57 reasonably well. However, at $\bar{N} = 10^4$, only the L-FTS prediction of D_{eq} remains consistent with universality for $a_{\text{int}} = 0.02R_0$. Furthermore, if we attempt a nonlinear calibration of χ for the CL-FTSs, we obtain an ODT of $(\chi N)_{\text{ODT}} \approx 14$, which is well above the universal value of 13.11 . In any case, the CL-FTSs become sensitive to the grid resolution at $a_{\text{int}} = 0.02R_0$ and are thus unreliable. The failure of the renormalization is undoubtedly due to the sporadic occurrence of hot spots, which requires adaptive time steps to prevent the simulations from crashing.

To obtain reliable results at $\bar{N} = 10^4$, we considered different functional forms for the smearing function, $\Gamma(r)$. Our first choice was a Heaviside function with a sharp

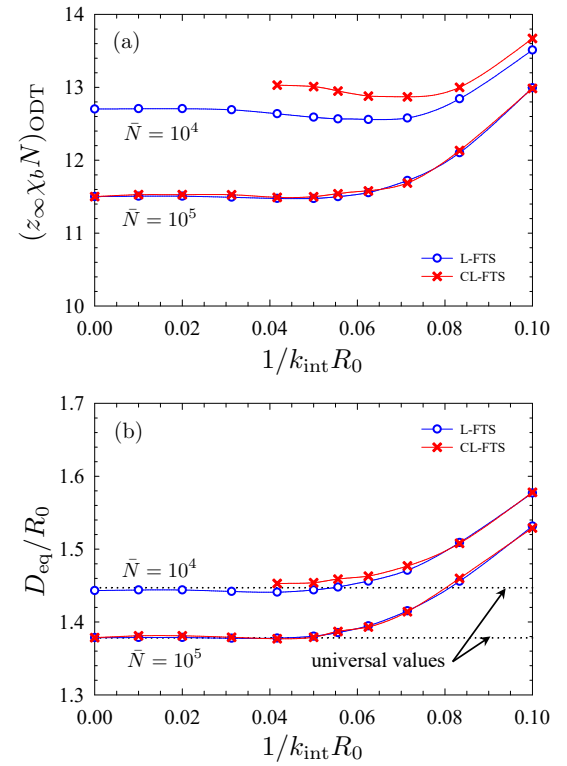


FIG. 8. (a) Position of the ODT plotted in terms of linear $\chi \approx z_\infty \chi_b$ for $\bar{N} = 10^5$ and 10^4 , obtained from CL-FTSs (crosses) and L-FTSs (circles) with sigmoidal smearing. (b) Equilibrium lamellar periods at the ODT. Based on the universal values of D_{eq} (dotted lines), universality requires $k_{\text{int}} \gtrsim 20/R_0$.

cutoff at $r = r_{\text{int}}$. However, it produces analogous results without any notable improvement; see the supplementary material for more details. Rather than focusing on the real-space form of $\Gamma(r)$, we contemplate the shape of its Fourier transform, $\Gamma(k)$. As discussed previously, universality requires that $\Gamma(k) \approx 1$ for $k \lesssim k^*$. Furthermore, from experience, damping the large- k fluctuations helps suppress the formation of hot spots. Based on that reasoning, we select the sigmoidal function,

$$\Gamma(k) = C_0 \left[1 - \tanh \left(\frac{k - k_{\text{int}}}{\Delta k_{\text{int}}} \right) \right], \quad (31)$$

where the constant C_0 is chosen such that $\Gamma(k) = 1$ at $k = 0$. Here, the important parameter is k_{int} , and so we fix $\Delta k_{\text{int}} = 5/R_0$.

Figure 8 shows results for the sigmoidal smearing, analogous to those of Fig. 7 for the Gaussian smearing. In this case, the range of the interaction is inversely proportional to k_{int} , and therefore we plot the results in terms of k_{int}^{-1} . As before, the CL-FTS and L-FTS results are more or less indistinguishable for $\bar{N} = 10^5$, whereas again significant differences emerge for $\bar{N} = 10^4$. The plot of D_{int} in Fig. 8(b) implies that universality sets in once $k_{\text{int}} \gtrsim 20/R_0$. Fortunately, this is within the range where the hot spots are well controlled by the dynamical

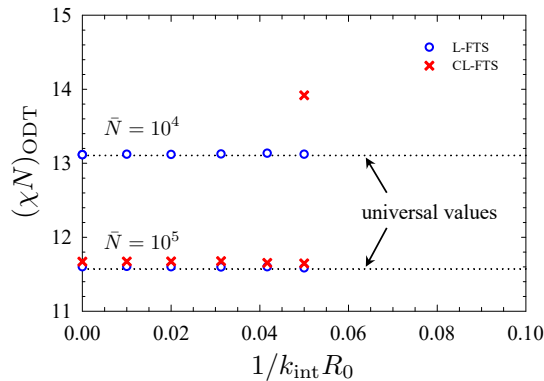


FIG. 9. Position of the ODT plotted in terms of nonlinear χ for $\bar{N} = 10^5$ and 10^4 , obtained from CL-FTSs (crosses) and L-FTSs (circles) with sigmoidal smearing. The dotted lines denote the universal values from Eq. (1). The general agreement confirms the universality for $k_{\text{int}} \gtrsim 20/R_0$.

stabilization and the renormalization continues to function properly. It is not until $k_{\text{int}} \gtrsim 24/R_0$ that we are forced to use adaptive time steps.

In Fig. 9, we perform the nonlinear χ calibration for $k_{\text{int}} \geq 20/R_0$ and compare $(\chi N)_{\text{ODT}}$ to the universal predictions (dotted lines). At $\bar{N} = 10^5$, the CL-FTSs and L-FTSs are both consistent with the universal value of $(\chi N)_{\text{ODT}} = 11.57$, while at $\bar{N} = 10^4$, only the L-FTSs agree with universality. The one reliable result we have from the CL-FTSs for $k_{\text{int}} = 20/R_0$ predicts an ODT of $(\chi N)_{\text{ODT}} = 13.9$, which is similar to what we found for Gaussian smearing but again inconsistent with the universal value of $(\chi N)_{\text{ODT}} = 13.11$. For some reason, the CL-FTSs are no longer exhibiting universal behavior at $\bar{N} = 10^4$.

V. DISCUSSION

Although the CL-FTSs are generally free of approximations, the dynamical stabilization does introduce a degree of inaccuracy. In our experience, it enhances the segregation, causing a small decrease in $(z_\infty \chi_b N)_{\text{ODT}}$ and a slight increase in $S(k^*)$. Nevertheless, we can assess the inaccuracy to ensure that it remains small.⁴⁵ The strongest stabilization, used in some of our $\bar{N} = 10^4$ simulations, was $\alpha_{\text{ds}} = 0.03$. Even then, the effect on $(z_\infty \chi_b N)_{\text{ODT}}$ was less than 0.01. For the larger $\bar{N} = 10^5$, 10^6 , 10^7 , 10^8 , and 10^9 , we used even smaller values of $\alpha_{\text{ds}} = 0.01, 0.003, 0.001, 0.0003$, and 0.0001 , respectively, for which the effect on $(z_\infty \chi_b N)_{\text{ODT}}$ was less than that of the statistical noise. The simulations for $S(k)$, used to calibrate c_2 , were more sensitive to α_{ds} , but fortunately they did not require any stabilization because of the distance from the ODT.

Most previous CL-FTSs have neglected the renormalization of the segment length,⁵⁶ which occurs when the polymers are subjected to a fluctuating pressure field,

$W_+(\mathbf{r})$. By doing so, they underestimate the natural end-to-end length, R_0 , and the radius of gyration, R_g , corresponding to the homopolymer melt (i.e., $\chi_b = 0$). Since one or the other of these is generally used as a reference length, the CL-FTSs would have overestimated the other lengths, including D_{eq} and $1/k^*$. Likewise, the invariant polymerization, $\bar{N}$, would appear larger than it actually was, causing the CL-FTSs to underestimate the level of fluctuations. Although these effects are generally minor, they are nevertheless significant.

In the L-FTSs, the partial saddle-point approximation (PSPA) of the pressure field, $w_+(\mathbf{r})$, fluctuates in response to the composition field, $W_-(\mathbf{r})$, but those fluctuations vanish in the homopolymer limit. Consequently, $w_+(\mathbf{r})$ becomes uniform as $\chi_b \rightarrow 0$, and thus the R_0 and R_g of noninteracting chains no longer expand when immersed in a homopolymer melt. Nevertheless, this effect of the PSPA is readily accounted for by simply setting $a_b = a$, as is done in SCFT. Indeed, this one adjustment generally brings the L-FTSs into good agreement with the CL-FTSs.

Contrary to the comparison in Fig. 6, Quah *et al.*³⁷ reported significant discrepancies between the CL-FTSs and L-FTSs for Gaussian smearing with $a_{\text{int}} = 0.2R_g$. The differences in the ODT were particularly large, which prompted us to repeat a number of their simulations. When we compare the two FTSSs in terms of the bare parameters, χ_b and a_b , as they did, we find good agreement as illustrated in the supplementary material. If we compare using the renormalized segment length, a , then the agreement is even better. Notably, Quah *et al.* did not have the benefit of dynamical stabilization, and furthermore they tried to locate the ODT using free energy, F . Although it is possible to locate order-order transitions (OOTs) accurately,^{16,17,21} it is difficult to do so for ODTs because of how similar the derivatives $\partial F/\partial \chi_b$ are for the competing phases. To obtain the necessary accuracy, it is imperative that the phases remain in their respective energy basins for long durations. However, as we have illustrated, the system readily transitions between order and disorder, especially in the CL-FTSs.

As expected,¹⁸ the smearing levels used by Fredrickson and coworkers^{16,37} do not produce the universal behavior corresponding to high molecular weights. To obtain universality, the range of the interactions needs to be small relative to R_0 . How small is small enough will depend on the form of the smearing function. For Gaussian smearing, we saw that universality emerges once $a_{\text{int}} \lesssim 0.02R_0$, while for the sigmoidal smearing it requires $k_{\text{int}} \gtrsim 20/R_0$. Figure 10(a) compares the Fourier transform of the smearing functions, $\Gamma(k)$, at the point where universality began to occur. Interestingly, the functions are very similar at the small wavevectors most relevant to the coarse-grained behavior (i.e., $k \lesssim 2\pi/D_{\text{eq}}$). The real difference occurs at large wavevectors. The sigmoidal function has a much stronger damping effect on the large-wavevector fluctuations, which presumably suppresses the formation of hot spots.

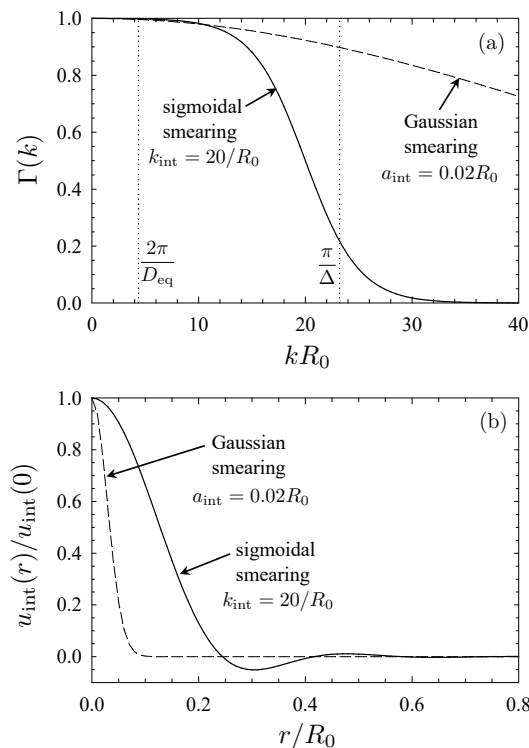


FIG. 10. (a) Fourier transforms of the Gaussian (solid curve) and sigmoidal (dashed curve) smearing functions, $\Gamma(k)$, and (b) the pairwise interaction profile, $u_{\text{int}}(r)$, evaluated at the approximate smearing levels, $a_{\text{int}} = 0.02R_0$ and $k_{\text{int}} = 20/R_0$, where universality emerges. The dotted lines in plot (a) denote the principle vector, $2\pi/D_{\text{eq}}$, and edges of reciprocal space, π/Δ .

Figure 10(b) compares the profiles of the pairwise interactions, $u_{\text{int}}(r)$, resulting from the smearing functions in Fig. 10(a). Evidently, the universality can tolerate a much longer range of interaction with the sigmoidal smearing. Interestingly, its $u_{\text{int}}(r)$ becomes slightly negative at large r , because $\Gamma(r)$ is no longer strictly positive. Although this will result in negative values of the smeared concentrations, $\phi_{\Gamma,\pm}(\mathbf{r})$, which may seem unphysical, there is no problem if we interpret the smearing in terms of finite-range interactions. The physically relevant quantity is the gradient of $u_{\text{int}}(r)$, which provides the force between pairs of monomers. Thus, sigmoidal smearing produces a force that oscillates between repulsive and attractive, whereas Gaussian smearing results in a strictly repulsive force. It is conceivable that this distinction has something to do with why the sigmoidal smearing has a milder effect on the universality.

Although we generally obtained good agreement between the CL-FTSs and L-FTSs when the segment lengths were properly calibrated, large differences emerged for short-range interactions at $\bar{N} = 10^4$. One would naturally suspect that this is a result of the PSPA. However, it is hard to accept that the PSPA could produce such a large inaccuracy, and that it could appear so

abruptly after the nearly perfect agreement for $\bar{N} \gtrsim 10^5$. Furthermore, it is the L-FTSs that continue to agree with universality. If the CL-FTSs are indeed correct, they would represent a counterexample to the universality hypothesis. The implication, of even one counterexample, is that the hypothesis is false, despite all the evidence to the contrary.^{2-7,11} Likewise, it would imply that the impressive agreement of the current and previous L-FTSs⁵⁴ with the universal predictions for the ODTs, domain sizes, and free energies were merely accidental.

Alternatively, one might suspect a problem with the calibration of the segment length in Eq. (26), which relies on $\bar{N}$ being sufficiently large. An inaccuracy here would affect the CL-FTSs but not the L-FTSs, and thus could potentially explain how the L-FTSs conform to universality while the CL-FTSs do not. However, this explanation does not survive careful scrutiny. The fact that D_{eq}/R_0 exceeds the universal prediction would imply that the calculated values of a_b/a were too large. This, in turn, would imply that the CL-FTSs were performed at larger values of $\bar{N}$ than intended. However, reducing $\bar{N}$ to the correct values would amplify the fluctuations, shifting $(\chi N)_{\text{ODT}}$ even further from the universal prediction. Not only would the correction have the wrong sign, it would also be far too small in magnitude. We note that there could, likewise, be an inaccuracy in Eq. (29) for z_∞ . However, if it was large, then we would not have been able to perform the nonlinear calibration of χ , and if it was small, then it would be largely compensated for by the c_2 parameter in the fit of $S(k^*)$ to ROL theory.

In the absence of other credible explanations, it appears that there might be a problem with the CL-FTSs. Despite the theoretical justification that CL simulations provide exact results, there is no rigorous proof.¹⁴ In fact, no general proof can possibly exist as there are now numerous documented examples where CL simulations of complex-valued Hamiltonians fail, either catastrophically or where higher-order moments of their distributions become undefined.^{26,27,31,47} Indeed, these failures are present in the CL-FTSs.¹⁸ More concerning, however, are the ‘silent failures’ that have been identified in the XY model for magnetic systems^{47,63} and various toy models,^{26,30,64-68} for which either the exact solution can be calculated or can be obtained by other simulation techniques. Even though the CL simulations of those models appear to perform flawlessly, their ensemble averages deviate from the correct values. If it was not for the *a priori* knowledge of the exact solutions, there would be no way of knowing anything was wrong.

Realistically, the inaccuracies in the CL-FTSs should emerge gradually,^{30,66} and hence they must be present even before their effect is visibly evident in the simulations. This is consistent with the fact that the departure from universality occurs just prior to where hot spots are encountered. Thus, it would be prudent to keep well away from this region of parameter space. The question, though, is how far is far enough? Presumably, in

the parameter space where we observed good agreement with the L-FTSs, we can safely assume that the CL-FTSs were performing properly and that the small differences with the L-FTSs are attributable to the PSPA. As such, we can be reasonably confident that the previous CL-FTSs by Fredrickson and coworkers^{16,37} were unaffected by these silent failures.

Our study adds to previous tests^{33,45,69} of the PSPA that have shown it to be accurate. One could reasonably expect this level of accuracy to hold for AB-type block copolymer melts in general. Thus, it may make sense to avoid the possibility of silent failures, and just apply L-FTSs rather than CL-FTSs. However, there will be systems, perhaps those involving solvent,⁷⁰ where the PSPA will lose its quantitative accuracy, and even others, such as those involving electrostatic charges,⁷¹ where the PSPA will actually become qualitatively inaccurate. In such cases, where the fully-fluctuating fields of CL-FTSs are necessary, researchers will just have to precede with caution.

VI. SUMMARY

Our study began by considering the generalized model with $N = 90$, $\zeta = 1$, and $\Gamma(r) = \delta(\mathbf{r})$, which was mapped onto the standard Gaussian-chain model (GCM) using the Morse calibration.^{3,4} With the help of dynamical stabilization,⁴⁵ we were able to conduct CL-FTSs down to invariant polymerizations of $\tilde{N} = 10^5$. The position of the ODT, $(\chi N)_{\text{ODT}}$, and the corresponding lamellar period, D_{eq} , plotted in Fig. 6, were both consistent with universality.^{3,5,7} For comparison, we also conducted L-FTSs, where the effect of the PSPA was compensated for by increasing the bare segment length to $a_b = a$. With this one adjustment, the L-FTSs also produced universal results in agreement with the CL-FTSs. Previous comparisons have supported the validity of PSPA,^{33,45,69} but this is certainly the most compelling.

To help stabilize the CL-FTSs, we then included finite-range interactions by smearing the concentrations with the Gaussian function, $\Gamma(r)$, in Eq. (10).¹⁶ Using the same smearing range $a_{\text{int}} = 0.2R_g \approx 0.08R_0$ as Quah *et al.*,³⁷ we were able to extend the CL-FTSs down to $\tilde{N} = 10^4$. However, contrary to the claims by Quah *et al.*, the L-FTSs agreed well with the CL-FTSs, particularly if the segment lengths were calibrated appropriately. However, neither of the FTSs exhibited universal results, as evident by the fact that D_{eq} at the ODT greatly exceeded the universal prediction and that it was impossible to perform the nonlinear calibration of χ .

For universality to hold, the range of the Gaussian smearing had to be reduced to $a_{\text{int}} \lesssim 0.02R_0$. Unfortunately, this reduction in a_{int} caused the hot spots to reappear at $\tilde{N} = 10^4$. We then considered the sigmoidal smearing function in Eq. (31), for which $k_{\text{int}} \gtrsim 20/R_0$ appears sufficient for universality. This time, the CL-FTSs were exceptionally stable at $\tilde{N} = 10^4$, but nev-

ertheless they disagreed with universality. In particular, the lamellar period was 1% too large and the fluctuation correction to the ODT was 30% too large. In contrast, the L-FTSs remained consistent with universality.

Normally, a difference between the CL-FTSs and L-FTSs would point to an inaccuracy in the PSPA, except that it is the CL-FTSs, not the L-FTSs, that deviated from universality. It is also difficult to believe that the PSPA could be responsible for the large differences we observed. After ruling out inaccuracies in the Morse calibration as a possible explanation, we concluded that the deviation from universality at $\tilde{N} = 10^4$ likely results from a silent failure of the CL-FTSs, preceding the appearance of hot spots. This tentative conclusion is supported by the fact that there are numerous documented examples of silent failures in other CL simulations.^{26,30,47,63–68} Nevertheless, given the general agreement with the L-FTSs, we can be confident that the CL-FTSs do provide exact results when performed sufficiently far from the parameter region where hot spots are observed.

SUPPLEMENTARY MATERIAL

Derivations of Eqs. (12), (15), (16), (26), and (29), results for the Heaviside smearing function, and calculations repeated from Quah *et al.*³⁷ are provided in the supplementary material. Also included are computer source codes for the L-FTSs and CL-FTSs.

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DATA AVAILABILITY

The data that support the findings of this study can be reproduced using the computer source codes provided in the supplementary material.

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