

Stabilizing complex-Langevin field-theoretic simulations for block copolymer melts

J. D. Willis^{1, a)} and M. W. Matsen^{1, 2, b)}

¹⁾Department of Physics & Astronomy, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

²⁾Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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Complex-Langevin field-theoretic simulations (CL-FTSs) provide an approximation-free method of calculating fluctuation corrections to the self-consistent field theory (SCFT) of block copolymer melts. However, the complex fields are prone to the formation of hot spots, which cause the method to fail. This problem has been attributed to an invariance under complex translations, which allows the system to drift away from the real-valued saddle-point of SCFT. Here, we apply dynamical stabilization to CL-FTSs of diblock copolymer melts, whereby the drift is suppressed by a small imaginary force on the composition field. The force needs to be sufficient to hold the system near the real saddle-point, but also small enough not to significantly bias the statistics. Although larger forces are required as the fluctuations become more intense, we are able to lower the invariant polymerization indices of the CL-FTSs by several orders of magnitude, before this becomes a problem. The new CL-FTS results are then used to test conventional Langevin simulations (L-FTSs), in which the instability is removed by a partial saddle-point approximation (PSPA) to the pressure field. As found previously, the L-FTSs agree accurately with the CL-FTSs, provided that the comparison is performed using a Morse calibration.

I. INTRODUCTION

Quantitatively accurate predictions for complicated block copolymer materials are becoming feasible on account of field-theoretic simulations^{1–3} coupled with universality.^{4–8} The universality allows accurate predictions with the use of simple coarse-grained models, once the polymers are large relative to their atomistic-level details. Although universality foregoes the need for atomistic details, coarse-grained models are still challenging to simulate. Indeed, particle-based simulations have yet to produce a complete phase diagram even for the simple AB diblock copolymer melt. However, complete phase diagrams can be, and have been,^{9–11} generated with field-theoretic simulations (FTSs). Furthermore, FTSs are able to readily handle complicated block copolymer architectures^{12–14} and multi-component blends in a range of ensembles.^{15–17}

As a result of the universality, simulations and experiments can be accurately mapped onto the standard Gaussian chain model (GCM),¹⁸ which treats block copolymer systems as incompressible melts of elastic threads with pairwise contact forces controlled by Flory-Huggins interaction χ parameters. For monodisperse AB diblock copolymers, the behavior of the GCM depends on just four quantities: the molecular composition f , the degree of segregation χN , the ratio of segment lengths a_A/a_B , and the invariant polymerization index $\bar{N} \equiv a^6 \rho_0^2 N$, where a is an average segment length, ρ_0 is an average segment density, and N is the number of segments

per molecule. Morse and coworkers^{5,6} have introduced a simple procedure for mapping simulations onto the standard GCM. Once expressed in terms of the GCM parameters, the results from different simulations collapse onto universal curves. For instance, they^{5,7} showed that the order-disorder transitions (ODTs) of symmetric diblock copolymers (i.e., $f = 0.5$ and $a_A = a_B$) from five different simulation models collapse onto the universal curve

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

They likewise demonstrated that the free energy, F , and the lamellar period, D , are universal. We note that the universality has been further corroborated by subsequent particle-based simulations^{8,19,20} as well as an experimental system.²¹

In polymer field theory, Hubbard-Stratonovich identities are used to transform a particle-based model into a field-theoretic model.^{1–3} 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 self-consistent field theory (SCFT),²² 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 whereby $W_-(\mathbf{r})$ is real-valued and $W_+(\mathbf{r})$ is imaginary-valued, which results in real-valued saddle-point fields.¹¹ 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.^{23–29}

One way to overcome the sign problem is to ap-

^{a)}Electronic mail: jdwillis@uwaterloo.ca

^{b)}Electronic mail: mwmatsen@uwaterloo.ca

ply a partial saddle-point approximation (PSPA),^{30–33} whereby $W_+(\mathbf{r})$ is replaced by the solution, $w_+(\mathbf{r})$, of $\mathcal{D}H_f/\mathcal{D}W_+(\mathbf{r}) = 0$. The partial saddle-point, $w_+(\mathbf{r})$, is real valued and consequently $H_f[W_-, w_+]$ is amenable to conventional Langevin simulations (L-FTSs).³⁴ The justification for the PSPA is that the composition fluctuations in $W_-(\mathbf{r})$ are thought to provide the dominant correction to SCFT. Although the PSPA has a noticeable impact as documented by Quah *et al.*,³⁵ it appears that the effect can be largely removed by applying the Morse calibration.¹¹

An alternative solution to the sign problem is to apply complex-Langevin simulations (CL-FTSs), where $W_-(\mathbf{r})$ and $W_+(\mathbf{r})$ are allowed to explore the entire complex domain.³⁶ When they work, CL-FTSs provide exact results. Unfortunately, they suffer from a serious instability,^{9,11,37,38} which becomes increasingly problematic for strong fluctuations near the order-disorder transition (ODT) at small $\bar{N}$. The instability results from a tendency to form hot spots, where the fields acquire extreme values.^{11,37} Delaney and Fredrickson⁹ managed to tame this instability to some degree by incorporating compressibility and finite-range interactions into their model, but the range of the interactions was unrealistically large causing significant deviations from universality.¹¹

Kim *et al.*³⁹ have shown that translational symmetry contributes to the instability. It has generally been assumed that $W_-(\mathbf{r})$ and $W_+(\mathbf{r})$ fluctuate about the real saddle-point fields of SCFT.³⁷ 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,⁴⁰ which provides a pathway deep into the complex domain, eventually resulting in the formation of hot spots.¹¹

This problem is similar to what happens in complex-Langevin simulations of quantum chromodynamics (QCD), where a gauge symmetry likewise 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 a gauge cooling.^{41,42} Similarly, Kim *et al.*³⁹ applied translation cooling to CL-FTSs, whereby imaginary translations are continuously applied to keep the fields in close proximity to the real saddle-point. Although this expands the region of stability, the improvement is limited. Here, we attempt another strategy used in QCD to stabilize complex-Langevin simulations, called dynamical stabilization.^{26,27,29,43} It involves adding an artificial force to the Langevin dynamics of sufficient strength to prevent the large excursions, but not so strong as to significantly bias the statistics.

II. THEORY AND SIMULATION

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. The system is modeled as a compressible melt of bead-spring chains interacting by simple contact forces. 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. The Hamiltonian,

$$H_p[\{\mathbf{r}_{\alpha,i}\}] = U_b[\{\mathbf{r}_{\alpha,i}\}] + U_{\text{int}}[\{\mathbf{r}_{\alpha,i}\}], \quad (2)$$

is expressed as a sum of bonded interactions

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

where a_b is the bare statistical segment length, and non-bonded interactions,²²

$$\frac{U_{\text{int}}}{k_B T} = \rho_0 \int [\chi_b \hat{\phi}_A \hat{\phi}_B + \frac{\zeta}{2} (\hat{\phi}_A + \hat{\phi}_B - 1)^2] d\mathbf{r}, \quad (4)$$

where χ_b is the bare Flory-Huggins interaction parameter, ζ is a dimensionless compression modulus, and

$$\hat{\phi}_A(\mathbf{r}) = \frac{1}{\rho_0} \sum_{\alpha=1}^n \sum_{i=1}^{N_A} \delta(\mathbf{r} - \mathbf{r}_{\alpha,i}) \quad (5)$$

$$\hat{\phi}_B(\mathbf{r}) = \frac{1}{\rho_0} \sum_{\alpha=1}^n \sum_{i=N_A+1}^N \delta(\mathbf{r} - \mathbf{r}_{\alpha,i}) \quad (6)$$

are dimensionless concentrations of the A and B monomers, respectively. In polymer field theory,^{1–3,11} Hubbard-Stratonovich transformations are used to transform this particle-based Hamiltonian into an equivalent field-based Hamiltonian,

$$\frac{H_f}{nk_B T} = -\ln Q + \frac{\chi_b N}{4} + \frac{N}{V} \int \left(\frac{W_-^2}{\chi_b} - \frac{W_+^2}{\chi_b + 2\zeta} - W_+ \right) d\mathbf{r}, \quad (7)$$

where $Q[W_-, W_+]$ 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.

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 accurately estimated from SCFT using an effective χ .⁴⁴

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

$$W_-(\mathbf{r}; \tau + \delta\tau) = W_-(\mathbf{r}; \tau) - \Lambda_-(\mathbf{r})\delta\tau + \mathcal{N}(0, \sigma), \quad (8)$$

$$W_+(\mathbf{r}; \tau + \delta\tau) = W_+(\mathbf{r}; \tau) + \Lambda_+(\mathbf{r})\delta\tau + i\mathcal{N}(0, \sigma). \quad (9)$$

The stochastic functions, $\mathcal{N}(0, \sigma)$, provide 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

$$\Lambda_-(\mathbf{r}) = \phi_-(\mathbf{r}) + \frac{2}{\chi_b}W_-(\mathbf{r}) + i\alpha_{\text{ds}}N \text{Im}[W_-(\mathbf{r})], \quad (10)$$

$$\Lambda_+(\mathbf{r}) = \phi_+(\mathbf{r}) - 1 - \frac{2}{\chi_b + 2\zeta}W_+(\mathbf{r}), \quad (11)$$

where $\phi_\pm(\mathbf{r})$ are ensemble averages of $\hat{\phi}_\pm(\mathbf{r}) \equiv \hat{\phi}_A(\mathbf{r}) \pm \hat{\phi}_B(\mathbf{r})$ in the system of noninteracting polymers. Note that $\Lambda_-(\mathbf{r})$ includes the usual contributions from the functional derivative, $DH_f/DW_-(\mathbf{r})$,^{9,11} plus an addition contribution of strength α_{ds} for the dynamical stabilization.

For conditions prone to the formation of hot spots, we evolve Eqs. (8) and (9) using the predictor-corrector algorithm with an adaptive time step, $\delta\tau$.³⁷ Although we target a time step of $\delta\tau N = 0.1$, it nevertheless drops by orders of magnitude when a hot spot forms, causing the simulation to run extremely slow. However, when the CL-FTSs are performing well, the Leimkuhler-Matthews algorithm⁴⁵ can be used with a large time step of $\delta\tau N = 2$. Source code for CL-FTSs is available from Ref. 11.

We use the Morse calibration to map our compressible model with discrete bead-spring chains onto the standard GCM. The calibration has the added benefit of removing an ultraviolet (UV) divergence that occurs as $\Delta_\nu \rightarrow 0$.^{44,46–48} The effective statistical length, defined such that the natural end-to-end length of the polymers satisfies $R_0 = aN^{1/2}$ in the large- N limit, is given by¹¹

$$a = \left(1 + \frac{a_b^2}{72(2\pi)^3\rho_0} \int \frac{k^2 d\mathbf{k}}{s^2(k)[1 + t(k)/\zeta]}\right) a_b, \quad (12)$$

where $s(k) \equiv \sinh(k^2 a_b^2/12)$, $t(k) \equiv \tanh(k^2 a_b^2/12)$, and the integration interval is $-\pi/\Delta_\nu \leq k_\nu \leq \pi/\Delta_\nu$. For the large $\bar{N}$ considered in our study, the effective χ corresponding to the GCM is a weakly-nonlinear function of χ_b , and therefore we approximate it as

$$\chi = z_\infty \chi_b + c_2 (z_\infty \chi_b)^2. \quad (13)$$

The linear coefficient is given by¹¹

$$z_\infty = 1 - \frac{1}{(2\pi)^3\rho_0} \int \frac{d\mathbf{k}}{t(k)[1 + t(k)/\zeta]}, \quad (14)$$

and c_2 is obtained by fitting the disordered-state structure function, $S(k)$, of symmetric diblocks to ROL theory.^{49,50}

TABLE I. Coefficients of the nonlinear χ in Eq. (13) for $\zeta = 1$.

$\rho_0 a^3$	$\bar{N}$ (for $N = 90$)	c_2 (CL-FTS)	c_2 (L-FTS)
10.5	10^4	0.46	0.23
33.3	10^5	0.11	0.065
105	10^6	0.038	0.026
333	10^7	0.021	0.019
1054	10^8	0.012	0.011
3333	10^9	0.011	0.010

The nonlinear coefficient, c_2 , is a function of ζ and ρ_0 . Here, our simulations are performed with a compression modulus of $\zeta = 1$, which increases the stability of the CL-FTSs without compromising the universality. We will need to vary $\bar{N} = a^6 \rho_0^2 N$ by orders of magnitude, for which is impractical to simply adjust N . Therefore, we fix the polymerization at $N = 90$, which again is generally sufficient for universal behavior, and instead we adjust ρ_0 . Table I lists calibrations from Ref. 11 for $\bar{N} = 10^4$, 10^5 , and 10^6 as well as new ones for 10^7 , 10^8 , and 10^9 .

For comparison purposes, we perform L-FTSs where $W_-(\mathbf{r})$ evolves according to Eq. (8) and $W_+(\mathbf{r})$ is approximated by $w_+(\mathbf{r})$. The saddle-point $w_+(\mathbf{r})$ is reevaluated iteratively at each time step using Anderson mixing,³³ which typically slows the L-FTSs by more than an order of magnitude. However, this is partially compensated for by the fact that the Leimkuhler-Matthews algorithm can operate with a remarkably large time step of $\delta\tau N = 8$. Source code for the L-FTSs is available from Ref. 11.

As mentioned previously, the PSPA affects the UV divergence.¹¹ The main effect is to eliminate the divergence in the segment length, such that $a = a_b$. Although the linear coefficient, z_∞ , for the effective χ in Eq. (13) does not change, the nonlinear coefficient, c_2 , does. Therefore, separate calibrations are required for the L-FTSs, the results of which are included in Table I.

III. RESULTS

We begin by considering a previous CL-FTS from Ref. 39 for the lamellar phase at $f = 0.5$, $z_\infty \chi_b N = 12$, and $\bar{N} = 10^6$. At this relatively weak segregation, the pressure field, $W_+(z)$, is nearly zero and the small composition field can be approximated by the first harmonic

$$W_-(\mathbf{r}) \approx A_R \cos(k^*(z - z_R)) + iA_I \cos(k^*(z - z_I)), \quad (15)$$

where A_R , A_I , z_R , and z_I are real-valued. Without loss of generality, we choose $A_R > 0$ and $0 \leq \theta < \pi$, where $\theta \equiv k^*(z_I - z_R)$.

Figure 1(a) plots the amplitudes, A_R and A_I , from a CL-FTS of duration $\tau N = 10^6$, which was initialized with an equilibrated configuration from a L-FTS³³ (i.e., $A_I = 0$ at $\tau = 0$). Without the dynamical stabilization, the system diffuses along the line of complex saddle-points emerging from the real saddle-point of SCFT, as

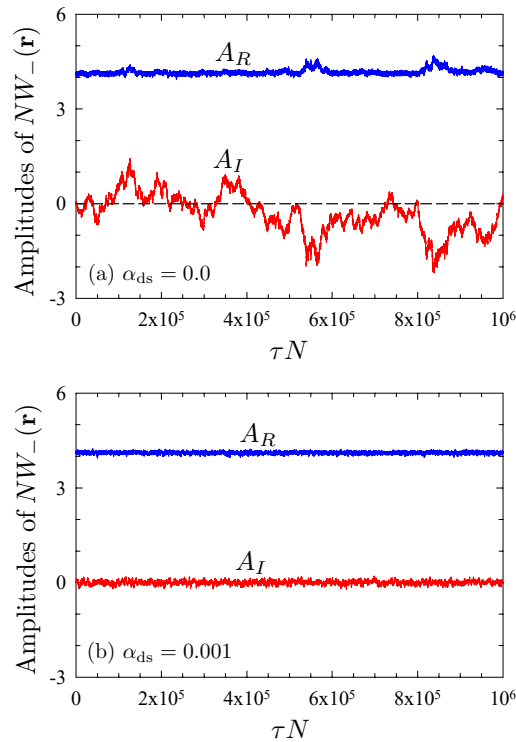


FIG. 1. Amplitudes of the first harmonic of $W_-(\mathbf{r})$ for the lamellar phase at $f = 0.5$, $z_\infty \chi_b N = 12$, and $\bar{N} = 10^6$ plotted as a function of simulation time, τ , during a CL-FTS (a) without and (b) with dynamical stabilization.

evident by the large deviations from $A_I = 0$.^{11,39} Figure 1(b) shows results of a second CL-FTS, this time with a restoring force of $\alpha_{ds} = 0.001$. The value of A_I is now tightly constrained to small values, confirming that dynamical stabilization successfully holds the system close to the real saddle-point.

Having confirmed that the dynamical stabilization is performing as expected, we move to the order-disorder transition (ODT) where fluctuation effects are strongest and the tendency to form hot spots is most severe. For $\bar{N} \gtrsim 10^9$, the CL-FTSs are generally free of hot spots, and for $\bar{N} \approx 10^8$, the adaptive time step allows the system to cope with their occasional occurrence. It is not until $\bar{N} \lesssim 10^7$ that hot spots become a serious issue.

Figure 2 plots the real and imaginary parts of the Hamiltonian during a CL-FTS without dynamical stabilization near the ODT at $f = 0.5$, $z_\infty \chi_b N = 10.7$, and $\bar{N} = 10^7$. As before, the CL-FTS was initialized with an equilibrated configuration from a L-FTS. The simulation behaves well up until $\tau N \approx 1.7 \times 10^5$, at which point we begin to observe spikes resulting from the formation of hot spots. The system manages to recover from the initial hot spots, until abnormal behavior sets in at $\tau N \approx 6.1 \times 10^5$ beyond which $\text{Im}[H_f]$ starts fluctuating about nonzero values.

Faulty behavior in complex-Langevin simulations can be diagnosed by examining histograms of observables on

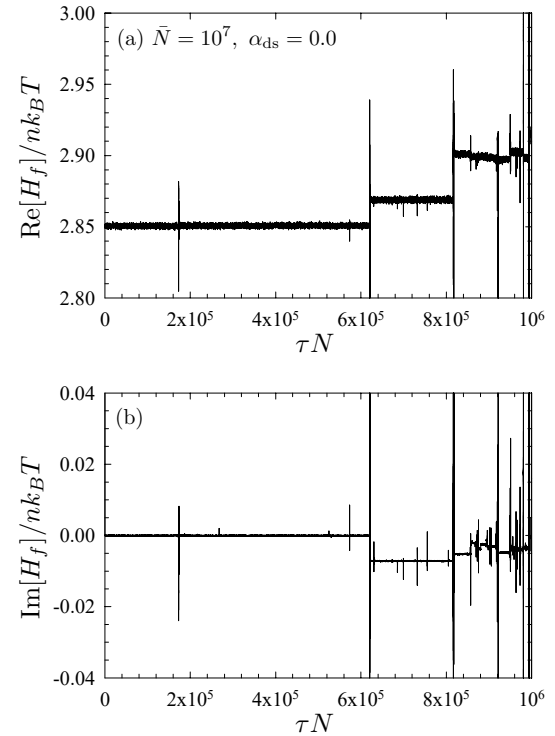


FIG. 2. (a) Real and (b) imaginary parts of the Hamiltonian, $H_f[W_-, W_+]$, at $f = 0.5$, $z_\infty \chi_b N = 10.7$, and $\bar{N} = 10^7$ sampled from a CL-FTS without dynamical stabilization.

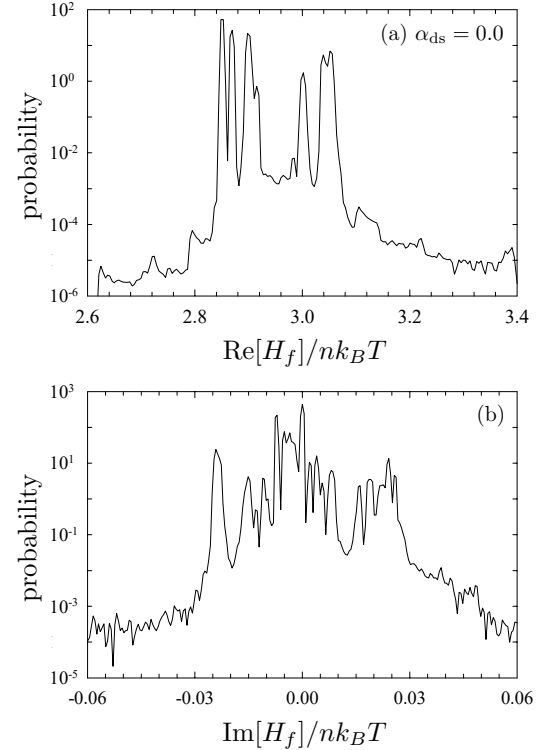


FIG. 3. Histograms of the (a) real and (b) imaginary parts of $H_f[W_-, W_+]$ from the CL-FTS of Fig. 2.

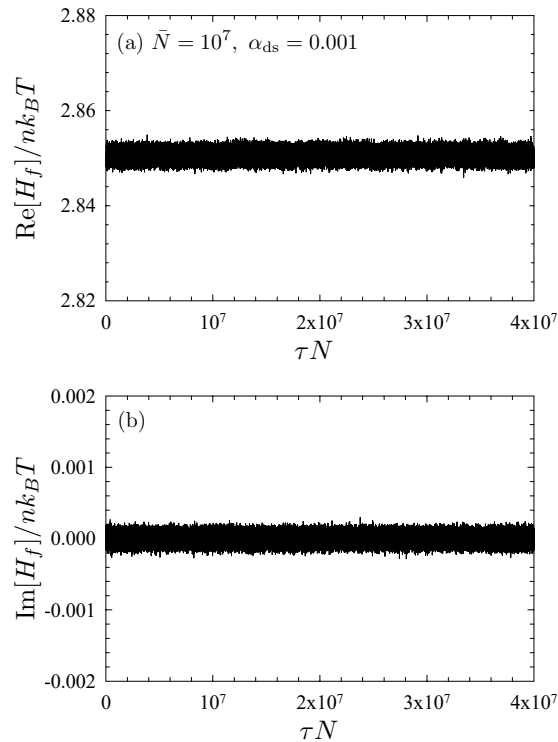


FIG. 4. (a) Real and (b) imaginary parts of $H_f[W_-, W_+]$ from an analogous CL-FTS to that of Fig. 2, but this time with dynamical stabilization.

a semi-logarithmic scale. Indeed, Fig. 3 displays the histograms of the real and imaginary parts of $H_f[W_-, W_+]$, which not only reveal irregular distributions indicative of poor sampling, but also sub-exponentially decaying tails that lead to divergent moments. This is the tell-tale sign that a complex-Langevin simulation is failing.^{24,25,29,43}

We now turn on the dynamical stabilization and repeat the CL-FTS using $\alpha_{ds} = 0.001$. From Fig. 4, we can see that the spikes in the Hamiltonian are completely gone, even for a run that is $40\times$ longer than before. Furthermore, the histograms shown in Fig. 5 exhibit unimodal distributions with rapidly decaying tails. Not only that, the semi-logarithmic plot of the distributions are accurately fit by parabolas (dashed curves), corresponding to Gaussian distributions characteristic of proper behavior. Note that in the absence of hot spots, we were able to switch to the Leimkuhler-Matthews algorithm.

Although it is not apparent in Fig. 4, the system is alternating between the lamellar and disordered phases. To observe this, we need to sample an appropriate order parameter that can distinguish the two phases. From past experience,⁵¹ a good choice is

$$\Psi = \frac{1}{R_0^3} \left(\frac{V}{(2\pi)^3} \int f(k) |W_-(\mathbf{k}) W_-(-\mathbf{k})|^2 d\mathbf{k} \right)^{1/4}, \quad (16)$$

where $f(k)$ is a Heaviside-like function that screens out the large wavevectors beyond the principal peak in $S(k)$. In Fig. 6, we can see that the order parameter switches

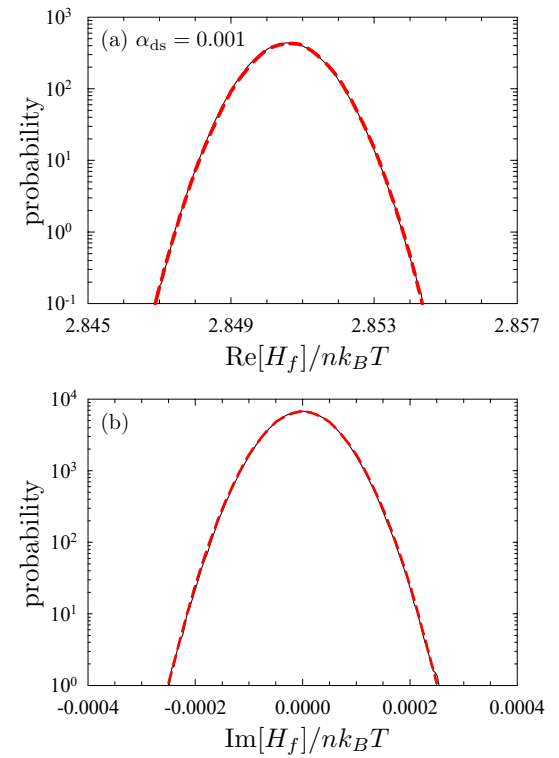


FIG. 5. Histograms of the (a) real and (b) imaginary parts of $H_f[W_-, W_+]$ from the CL-FTS of Fig. 4. The dashed curves are fits to Gaussian distributions.

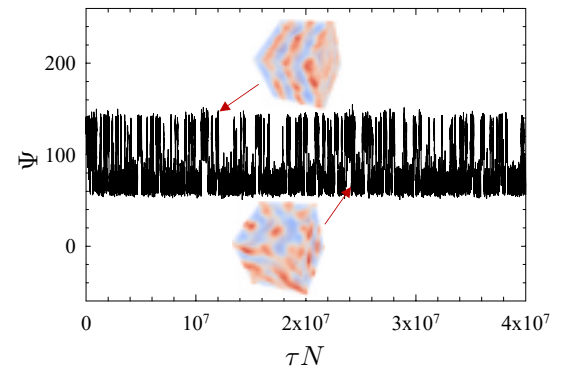


FIG. 6. Order parameter, Ψ , during the same CL-FTS of Fig. 4. The two images show typical snapshots of $\text{Re}[\phi_-(\mathbf{r})]$ at small and large values of Ψ .

between values of $\Psi \approx 70$ and 140 . From visual inspection of the field configurations, the two values correspond to the disordered phase and lamellar phase, respectively (see the images in Fig. 6). It appears that the system spends more time in the disordered phase than the lamellar phase, but that is more easily assessed from a histogram.

Figure 7(a) plots a histogram of the data in Fig. 6, as well as those of analogous CL-FTSs performed with different strengths, α_{ds} , of the dynamical stabilization. Note that statistically accurate histograms require suffi-

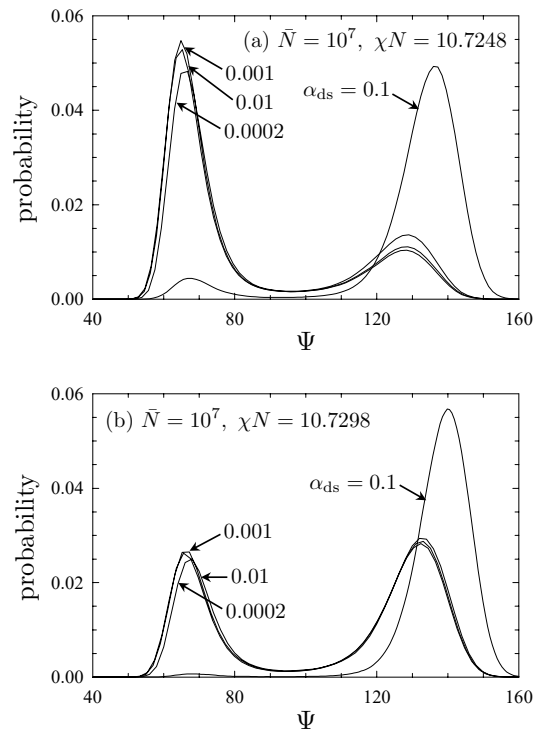


FIG. 7. Histograms of the order parameter, Ψ , for $\bar{N} = 10^7$ at (a) $z_\infty \chi_b N = 10.7$ and (b) $z_\infty \chi_b N = 10.705$ from CL-FTS runs with dynamical stabilization of different strengths, α_{ds} .

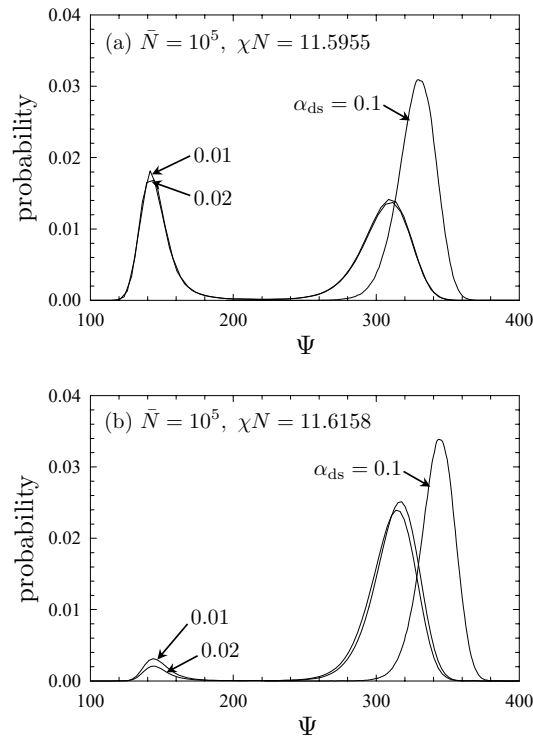


FIG. 8. Histograms of the order parameter, Ψ , for $\bar{N} = 10^5$ at (a) $z_\infty \chi_b N = 11.43$ and (b) $z_\infty \chi_b N = 11.45$ from CL-FTS runs with dynamical stabilization of different strengths, α_{ds} .

ciently long simulations such that the system transitions many times between the lamellar and disordered phases, as is the case in Fig. 6. Provided $\alpha_{ds} \ll 0.1$, the distribution is not significantly biased by the force of the dynamical stabilization. In the absence of a significant bias, the probability (i.e., area under the peak) of the disordered phase is larger than that of the ordered phase, implying that $z_\infty \chi_b N = 10.7$ is below the ODT. Therefore, we repeat the CL-FTS at a higher $z_\infty \chi_b N = 10.705$ in Fig. 7(b), again with a range of different α_{ds} values. As before, the smaller values of α_{ds} produce consistent results. This time, the probability of the lamellar phase is slightly larger, and thus the two runs have bracketed the ODT. In terms of the nonlinear χ in Eq. (13), we estimate the position of the ODT for $\bar{N} = 10^7$ to be $(\chi N)_{ODT} = 10.73$, which is close to the value of 10.70 given by Eq. (1).

We now repeat the simulations for $\bar{N} = 10^5$, where the hot spots are more problematic. Figure 8 shows histograms of the order parameter for $z_\infty \chi_b N = 11.43$ and 11.45 with different strengths, α_{ds} , of the dynamical stabilization. At this lower $\bar{N}$, a larger $\alpha_{ds} \gtrsim 0.01$ is required to suppress the hot spots. Nevertheless, this remains small enough that the restoring force does not significantly perturb the histogram, as evident by the fact that values of $\alpha_{ds} = 0.01$ and 0.02 produce equivalent results to within the statistical inaccuracy. Again, $\alpha_{ds} = 0.1$ is found to be too large, causing a noticeable preference for the ordered phase. Based on the small- α_{ds} results, the two histograms in Fig. 8 bracket the ODT. A linear interpolation of the relative probabilities estimates the ODT at $(\chi N)_{ODT} = 11.60$, which as before compares favorably with the value 11.57 from Eq. (1).

We attempted to locate the ODT for an experimentally relevant value of $\bar{N} = 10^4$,⁵² but unfortunately a much stronger restoring force is required to suppress the hot spots. Figure 9 shows the results of a CL-FTS with $\alpha_{ds} = 1.0$. Even with this relatively strong force, the Hamiltonian exhibits a series of spikes indicative of hot-spot formation. Although the dynamical stabilization is not strong enough to completely suppress hot spots, they only survive for a short duration. Thus, it is potentially feasible to calculate meaningful histograms from the intervals exhibiting proper behavior. However, there is no doubt that the results would be significantly biased by the dynamical stabilization.

For comparison purposes, we repeat the ODT calculations using L-FTSs. In this case, we apply the well-tempered metadynamics (WTMD) described in Ref. 51, where a potential, $U(\Psi)$, is added to $H_f[W_-, W_+]$ so as to reduce the energy barrier between the disordered and ordered phases. Not only does this allow better statistics for the larger energy barriers at small $\bar{N}$, the resulting histograms can be extrapolated in terms of χ reducing the number of required simulations. The WTMD could not be used with the CL-FTSs, because Ψ is not an analytic functional of $W_-(\mathbf{r})$.³⁹

Figure 10 compares the $(\chi N)_{ODT}$ values obtained from

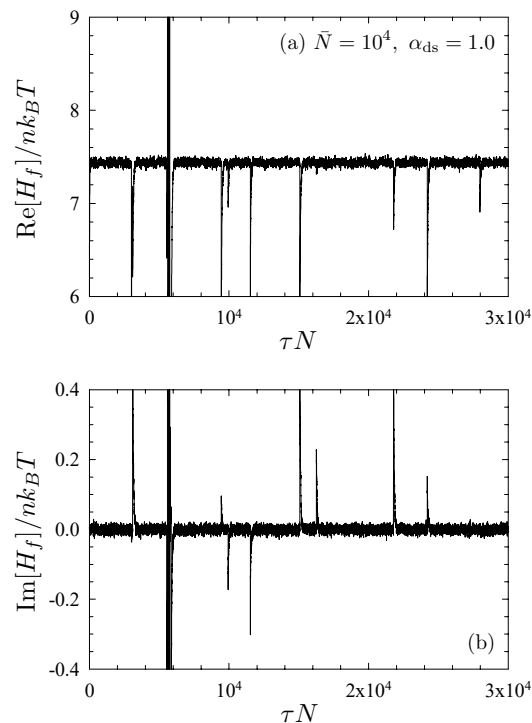


FIG. 9. (a) Real and (b) imaginary parts of the Hamiltonian, H_f , for $\bar{N} = 10^4$ at $z_\infty \chi_b N = 12.7$ from a CL-FTS with a strong dynamical stabilization ($\alpha_{ds} = 1.0$).

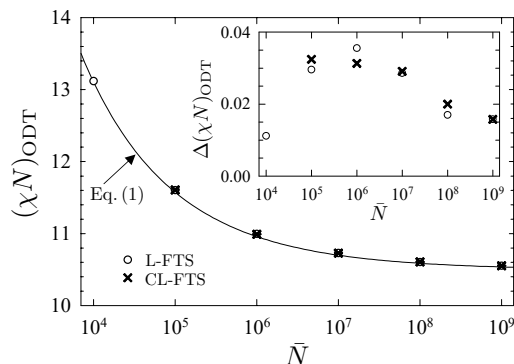


FIG. 10. Order-disorder transitions, $(\chi N)_{ODT}$, from CL-FTSs (crosses) and L-FTSs (circles) for different invariant polymerizations, $\bar{N}$. The solid curve denotes the fit to particle-based simulations in Eq. (1).⁶ The inset shows the differences, $\Delta(\chi N)_{ODT}$, between the FTS results and Eq. (1). Note that the CL-FTS and L-FTS results are indistinguishable on the scale of the main plot.

CL-FTSs and L-FTSs over a wide range of $\bar{N}$ values to the universal curve in Eq. (1). The agreement between CL-FTS and L-FTS is remarkable, as evident from the inset. The agreement with Eq. (1) is less precise, but nevertheless within 0.04 units of χN . This difference can be attributed to the fact that Eq. (1) contains some degree of inaccuracy, particularly at large $\bar{N}$, because it was derived from fits to particle-based simulations with $\bar{N} \lesssim 8000$.^{5,6}

IV. DISCUSSION

As mentioned previously, the CL-FTSs were able to locate the ODT for $\bar{N} \gtrsim 10^8$ without the use of dynamical stabilization. This, however, does not mean that hot-spot formation was not an issue. In the absence of a restoring force, the system diffuses along the line of complex-saddle extending from the real saddle-point.³⁹ Therefore, in time, the system will inevitably end up deep in the complex plane where hot spots readily form, causing the CL-FTS to fail. We intentionally initialized our simulations with real-valued fields from a L-FTS to ensure that the system started off near the real saddle-point of SCFT, so as to maximize the time before failure. For the large $\bar{N}$, this was sufficient to collect adequate statistics.

For $\bar{N} \gtrsim 10^5$, the dynamical stabilization was able to keep the system in close proximity to the real saddle-point without significantly biasing the statistics, allowing us to accurately locate the ODT. Although this still does not match what is possible with L-FTSs, it is nevertheless a considerable improvement. We tried different forms of the restoring force, but they did not offer significant improvement over the simple linear form in Eq. (10). In any case, the performance of the dynamical stabilization far surpasses that of the translation cooling in Ref. 39.

Field-theoretic simulations have already proven superior to conventional particle-based simulations for the high molecular-weight regime,⁵³ where block copolymer phase behavior becomes universal. Not only do they readily provide quantitative results calibrated with respect to the standard GCM, they can easily handle complicated block copolymer architectures^{12–14} as well as blends in a wide range of ensembles.^{15–17} Another important advantage is the ability to evaluate accurate free energies,^{44,54} which facilitates the calculation of order-order transitions and thus the means of constructing complete phase diagrams.¹¹ FTSs are still relatively new, and hence there remains considerable scope for other major developments that would further enhance their competitive advantage.

It is a tremendous simplification that block copolymer systems reduce to the standard GCM, although this is only true if N is sufficiently large. Unfortunately, there is no *a priori* way of determining what is sufficient. In practice, one concludes that N is large enough by confirming that a reasonable number of quantities conform to their universal values. Indeed, this is our justification that $N = 90$ is sufficient for our compressible model with $\zeta = 1$.¹¹ If there were too few monomers, then the monomer-scale details would become important and could no longer be absorbed into a small number of effective parameters, four in the case of monodisperse diblock copolymer melts.

It is well understood that the saddle-point approximation of SCFT eliminates the UV divergence, and thus the partial saddle-point approximation (PSPA) is certain to affect the UV divergence as well. Hence, the differences

between CL-FTSs and L-FTSs reported by Quah *et al.*³⁵ are of no surprise. It is remarkable, though, that these differences virtually vanish once the results are mapped onto the standard GCM by the Morse calibration. This was illustrated previously for the lamellar period and the peak in the disordered-state structure function,¹¹ and again here for the position of the order-disorder transitions in Fig. 10. The implication is that the PSPA has little impact beyond its effect on the UV divergence.

Given that the inaccuracy of the PSPA is compensated for by the Morse calibration, it makes little difference accuracy-wise whether one applies CL-FTSs or L-FTSs. The advantage of L-FTSs is that they do not become unstable at small $\bar{N}$. Instead, the limiting factors are statistical inaccuracies and the eventual breakdown of the Morse calibration. There is a high computational cost of performing the PSPA though, but this is partially compensated for by the ability to handle exceptionally large Langevin steps. In fact, it can be further compensated for by solving for $w_+(\mathbf{r})$ with machine learning.⁵⁵ In any case, the ability to handle smaller values of $\bar{N}$ without sacrificing universality makes L-FTSs a preferred choice for many block copolymer systems.

Although the PSPA is proving to be accurate, as was the case in the current study, there will be situations where it breaks down. As such, it would be preferable to dispense with the PSPA, and dynamical stabilization goes a long way to making this possible. Of course, dynamical stabilization introduces its own inaccuracy, but it is a controllable one that can be tested, as we have done in this study. There will undoubtedly be ways of further stabilizing CL-FTSs. Indeed, this was the primary reason for adding compressibility to our model. Likewise, we could switch to finite-range interactions, provided that the range is not so large as to compromise the universality. Note, however, that this would require modifications to Eqs. (12) and (14) as well as a recalibration of c_2 in Eq. (13). A more thorough understanding of hot-spot formation may suggest other ways of improving the stability of CL-FTSs.

V. SUMMARY

Dynamical stabilization has been found to greatly improve the stability of complex-Langevin field-theoretic simulations (CL-FTSs). The method involves adding an imaginary force to the Langevin equation for the composition field, $W_-(\mathbf{r})$. The force acts to minimize the imaginary component of $W_-(\mathbf{r})$, so as to keep the system in close proximity to real-valued saddle-point of self-consistent field theory (SCFT), which reduces the propensity to form ‘hot spots’ in the fields causing CL-FTSs to fail. The amplitude of the force, α_{ds} , has to be chosen large enough to prevent hot-spot formation but small enough not to significantly bias the ensemble averages. The application to diblock copolymer melts allowed us to calculate accurate order-disorder translations

(ODTs) for invariant polymerization indices, $\bar{N}$, several orders of magnitude smaller than what was possible without dynamical stabilization. The increased stability also permits the use of the Leimkuhler-Matthews algorithm for solving the Langevin equations,⁴⁵ which greatly improves the efficiency of the CL-FTSs.

We compared the ODTs calculated by CL-FTSs to those calculated by L-FTSs using the partial saddle-point approximation (PSPA)^{30,31} and to the universal prediction in Eq. (1) obtained from conventional particle-based simulations.^{5,7} There was remarkable agreement between CL-FTSs and L-FTSs when compared using the effective χ in Eq. (13). This is consistent with the previous agreement found for domain sizes in the ordered and disordered phases,¹¹ suggesting that the PSPA has little effect other than to alter the nature of the ultraviolet divergence. The PSPA does, however, increase the computational cost, but that is partially compensated for by an ability to handle remarkably large Langevin steps.

As a result of their stability, L-FTSs hold an advantage over CL-FTSs for their ability to access the universal behavior of block copolymer systems in the large- N regime.¹¹ However, dynamical stabilization has greatly reduced this advantage. Dynamical stabilization introduces a degree of inaccuracy as does the PSPA, but this one is a controllable inaccuracy that can be rendered negligible by choosing a sufficiently small force. While this was not always possible in the current study, dynamical stabilization could be combined with other ways of improving the stability. In fact, we did so by adding compressibility to our model, and likewise one could switch from contact forces to short-range interactions. Further improvements might also emerge from a better understanding of hot-spot formation. In light of these opportunities, the prospects for more robust CL-FTSs are promising.

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