

Statistical segment length in complex-Langevin field-theoretic simulations

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A method is introduced for calculating the average end-to-end length, R_0 , of polymers in complex-Langevin field-theoretic simulations (CL-FTSs). The statistical segment length, a , is then obtained by extrapolating R_0 to the long-chain limit. Because a has not been available to previous CL-FTSs, results have been expressed in terms of the bare statistical segment length, a_b , of an isolated polymer, which introduces inaccuracies even though the simulation method itself is inherently exact. In a few cases, a has been estimated by a weak-field approximation, but its accuracy remains uncertain. This study focuses on the fluctuation correction, $a - a_b$, for compressible melts of discrete Gaussian chains with finite-range interactions and compares it to the weak-field approximation. The approximation underestimates the fluctuation correction by up to 20%, but this is not particularly serious given that the correction itself is a small effect. Notably, our technique for evaluating R_0 can be generalized to any single-chain observable, which allows access to all the intramolecular correlations.

I. INTRODUCTION

The advent of field-theoretic simulations (FTSs) by Fredrickson and coworkers¹ has led to a remarkably efficient method for evaluating the equilibrium phase behavior of polymeric systems. The approach uses Hubbard-Stratonovich identities to convert the particle-based Hamiltonian, $H_p[\{\mathbf{r}_i\}]$, of a system to a field-based Hamiltonian, $H_f[W]$, involving fields, $W(\mathbf{r})$, rather than monomer coordinates, $\{\mathbf{r}_i\}$.¹⁻⁵ $H_f[W]$ has two parts, an integral involving the fields and the free energy of noninteracting polymers subjected to the fields, both of which can be readily evaluated. However, $H_f[W]$ turns out to be complex valued, which means that the Boltzmann weight, $\exp(-H_f/k_B T)$, is no longer positive definite. This results in the so-called sign problem, which Fredrickson and coworkers dealt with by applying complex-Langevin (CL) simulations.⁶⁻⁹

Although CL-FTSs¹⁰ are ‘exact’ and far more efficient than particle-based simulations for high-molecular-weight polymers,¹¹ they are not without their problems. CL simulations, in general, have well-known stability issues,¹²⁻¹⁵ and the polymer simulations are no exception.¹⁶⁻¹⁹ When the fluctuations become large, sharp spikes, known as ‘hot spots’, begin to appear in the field configurations,^{16,17} often causing the simulations to crash. Although this can be prevented by using adaptive time steps,¹⁶ the observables, nevertheless, exhibit an abnormal occurrence of extreme values.¹⁷⁻¹⁹ In fact, it appears that this problem begins as a ‘silent’ failure, before it escalates to the point where it can be readily detected in a histogram.²⁰ Thus, one has to be careful to stay well away from the parameter region where hot spots form.

When they work, CL-FTSs are not only exceptionally fast, they can also cope with complicated systems that are well beyond the capabilities of conventional particle-based simulations. For instance, they can handle block copolymers with elaborate architectures²¹⁻²³ involving numerous monomer types.^{24,25} It is also straightforward to include electrostatic interactions.²⁶⁻²⁹ Furthermore, they can handle multi-component systems in a variety of ensembles.³⁰⁻³² There are also efficient methods of evaluating the free energy,³³⁻³⁵ which is particularly valuable for constructing phase diagrams.^{36,37}

Admittedly, the evaluation of observables is generally less straightforward than in particle-based simulations. This is because observables are typically defined in terms of particle coordinates, and therefore they need to be re-expressed in terms of the field variables. An important example is the statistical segment length, a , which is generally obtained by measuring either the average end-to-end length, $R_0 = aN^{1/2}$, or the radius of gyration, $R_g = a(N/6)^{1/2}$, of linear chains of large polymerization N . Previous CL-FTSs have approximated the segment length, a , by that of an isolated polymer, which we refer to as the bare statistical segment length, a_b . However, a polymer expands when immersed in a melt,³⁸ and therefore the actual segment length, a , is generally larger (i.e., $a > a_b$). This difference, $a - a_b$, increases as the fluctuations become stronger.

An inaccurate segment length affects the predictions for domain sizes and wavevectors, since they are generally calibrated with respect to R_0 or R_g . Furthermore, the inaccuracy affects the measures used to quantify fluctuation effects, such as the dimensionless polymer concentration, $C = \rho_0 R_0^3/N$, or the invariant polymerization index, $\bar{N} = C^2$, where ρ_0 is the bulk monomer density. Although CL-FTSs provide exact results, apart from the statistical inaccuracies, this advantage is diminished if one is unable to accurately quantify the various length scales or the level of fluctuations. Here, this issue is re-

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solved with a technique for evaluating the true value of a in CL-FTSs.

II. FIELD-THEORETIC SIMULATIONS

In this study, we consider a melt of volume V involving n linear polymers of polymerization N . The 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 polymer concentration is given by

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

As usual, we divide by the bulk monomer density, $\rho_0 \equiv nN/V$, to create a dimensionless concentration. As such, the fluctuations from bulk density are given by

$$\delta\hat{\phi}(\mathbf{r}) \equiv \hat{\phi}(\mathbf{r}) - 1. \quad (2)$$

The Hamiltonian of our polymers,

$$H_p[\{\mathbf{r}_{\alpha,i}\}] = U_b[\{\mathbf{r}_{\alpha,i}\}] + U_{\text{int}}[\{\mathbf{r}_{\alpha,i}\}], \quad (3)$$

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

$$\frac{U_b}{k_B T} = \frac{3}{2a_b^2} \sum_{\alpha=1}^n \sum_{i=1}^{N-1} |\mathbf{r}_{\alpha,i+1} - \mathbf{r}_{\alpha,i}|^2, \quad (4)$$

where a_b is the bare statistical segment length of an isolated polymer. The nonbonded interactions are modeled by a Helfand-type compressibility,

$$\frac{U_{\text{int}}}{k_B T} = \frac{\rho_0 \zeta}{2} \int |\delta\hat{\phi}_{\Gamma}(\mathbf{r})|^2 d\mathbf{r}, \quad (5)$$

which is controlled by a dimensionless compression modulus, ζ .³⁹ Following Fredrickson and coworkers,^{27–29,36} the interactions are evaluated in terms of a smeared concentration, $\delta\hat{\phi}_{\Gamma}(\mathbf{r})$, obtained by a convolution,

$$f_{\Gamma}(\mathbf{r}) \equiv \int f(\mathbf{r} - \mathbf{r}') \Gamma(r') d\mathbf{r}', \quad (6)$$

with a ‘smearing’ function that satisfies $\int \Gamma(r) d\mathbf{r} = 1$. This is mathematically equivalent to finite-range interactions, given that Eq. (5) can be re-expressed as

$$\frac{U_{\text{int}}}{k_B T} = \frac{\rho_0 \zeta}{2} \int \delta\hat{\phi}(\mathbf{r}) u_{\text{int}}(|\mathbf{r} - \mathbf{r}'|) \delta\hat{\phi}(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (7)$$

where

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

We use the same Gaussian smearing function,

$$\Gamma(r) = \frac{1}{(2\pi a_{\text{int}}^2)^{3/2}} \exp(-r^2/2a_{\text{int}}^2), \quad (9)$$

as Fredrickson and coworkers, which corresponds to an interaction profile of

$$u_{\text{int}}(r) = \frac{1}{(4\pi a_{\text{int}}^2)^{3/2}} \exp(-r^2/4a_{\text{int}}^2). \quad (10)$$

Note that this expression reduces to that of contact interactions, $u_{\text{int}}(r) = \delta(r)$, in the limit where the interaction range, a_{int} , becomes zero.

To calculate the average end-to-end length of the polymers,

$$R_0 \equiv \langle |\mathbf{r}_{\alpha,N} - \mathbf{r}_{\alpha,1}|^2 \rangle^{1/2}, \quad (11)$$

which is the same for all α , we insert a harmonic potential connecting the chain ends. The Hamiltonian for this system is

$$H_{p,\eta}[\{\mathbf{r}_{\alpha,i}\}] = H_p[\{\mathbf{r}_{\alpha,i}\}] + \eta U_R[\{\mathbf{r}_{\alpha,i}\}], \quad (12)$$

where η controls the strength of the potential,

$$\frac{U_R}{k_B T} = \sum_{\alpha=1}^n |\mathbf{r}_{\alpha,N} - \mathbf{r}_{\alpha,1}|^2. \quad (13)$$

The average end-to-end length of the polymers is then obtained from the derivative,

$$\left. \frac{\partial F_{\eta}}{\partial \eta} \right|_{\eta=0} = \left\langle \left. \frac{\partial H_{p,\eta}}{\partial \eta} \right|_{\eta=0} \right\rangle, \quad (14)$$

$$= \langle U_R \rangle, \quad (15)$$

$$= nk_B T R_0^2, \quad (16)$$

of the free energy, $F_{\eta} = -k_B T \ln Z_{\eta}$, corresponding to the partition function,

$$Z_{\eta} = \int \exp\left(-\frac{H_{p,\eta}}{k_B T}\right) d\{\mathbf{r}_{\alpha,i}\}. \quad (17)$$

Note that the angle brackets above denote ensemble averages over the polymer coordinates, $\{\mathbf{r}_{\alpha,i}\}$, with $\eta = 0$.

To proceed, we transform this particle-based representation into a field-theoretic representation, by replacing the Boltzmann weight of U_{int} in Eq. (5) with the Hubbard-Stratonovich identity,

$$\exp\left(-\frac{U_{\text{int}}}{k_B T}\right) \propto \int \exp\left(\rho_0 \int \left[\frac{W^2}{2\zeta} - W \delta\hat{\phi}_{\Gamma}\right] d\mathbf{r}\right) \mathcal{D}W. \quad (18)$$

In order for the integral over $W(\mathbf{r})$ to converge, the integration is performed along the imaginary axis. (Alternatively, one could replace $W(\mathbf{r})$ by $iW(\mathbf{r})$ and integrate along the real axis.^{1–3}) The fact that $\delta\hat{\phi}_{\Gamma}(\mathbf{r})$ appears linearly in the exponential of Eq. (18) allows us to integrate

over the polymer coordinates in Eq. (17). This reduces the partition function to a functional integral over $W(\mathbf{r})$,

$$Z_\eta = \int \exp\left(-\frac{H_{f,\eta}}{k_B T}\right) \mathcal{D}W, \quad (19)$$

where the Boltzmann weight now involves the field-theoretic Hamiltonian,

$$\frac{H_{f,\eta}}{k_B T} = -n \ln Q_\eta - \rho_0 \int \left(\frac{W^2}{2\zeta} + W \right) d\mathbf{r}. \quad (20)$$

The logarithmic term in Eq. (20) corresponds to the free energy of n noninteracting polymers, where

$$Q_\eta[W] = \frac{1}{V} \int \exp\left(-\frac{H_1 + \eta |\mathbf{r}_N - \mathbf{r}_1|^2}{k_B T}\right) d\{\mathbf{r}_i\} \quad (21)$$

is the partition function of the single-chain Hamiltonian,

$$\frac{H_1}{k_B T} = \frac{3}{2a_b^2} \sum_{i=1}^{N-1} |\mathbf{r}_{i+1} - \mathbf{r}_i|^2 + \sum_{i=1}^N W_\Gamma(\mathbf{r}_i), \quad (22)$$

supplemented with a harmonic attraction between the chain ends. Applying the identity in Eq. (16) to the field-theoretic Hamiltonian in Eq. (20) gives

$$R_0^2 = - \left\langle \frac{\partial \ln Q_\eta}{\partial \eta} \bigg|_{\eta=0} \right\rangle, \quad (23)$$

$$= \left\langle \frac{\int |\mathbf{r}_N - \mathbf{r}_1|^2 \exp(-H_1/k_B T) d\{\mathbf{r}_i\}}{\int \exp(-H_1/k_B T) d\{\mathbf{r}_i\}} \right\rangle. \quad (24)$$

This time, the angle brackets denote an ensemble average over the field configurations, $W(\mathbf{r})$.

The integral in the denominator of Eq. (24) is evaluated in the usual manner⁴⁰ by generating partial partition functions, $q_i(\mathbf{r})$, using the recursion relation,

$$q_{i+1}(\mathbf{r}) = h(\mathbf{r}) \int q_i(\mathbf{r} - \mathbf{R}) g(R) d\mathbf{R}, \quad (25)$$

with the initial condition $q_1(\mathbf{r}) = h(\mathbf{r})$. Here,

$$g(R) = \left(\frac{3}{2\pi a_b^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2a_b^2}\right) \quad (26)$$

is the Boltzmann weight for an individual bond of length R and

$$h(\mathbf{r}) = \exp(-W_\Gamma(\mathbf{r})) \quad (27)$$

is the Boltzmann weight for a monomer at position $\mathbf{r}$ acted upon by the smeared field. The integral in the numerator of Eq. (24) is evaluated in a similar fashion. In this case, we pin the $i = 1$ monomer to the origin, and evaluate an analogous partial partition function, $\tilde{q}_i(\mathbf{r})$, that obeys the same recursion relation in Eq. (25), but with the initial condition $\tilde{q}_1(\mathbf{r}) = h(\mathbf{r})\delta(\mathbf{r})$. In terms of these partial partition functions, Eq. (24) becomes

$$R_0^2 = \left\langle \frac{\int r^2 \tilde{q}_N(\mathbf{r}) d\mathbf{r}}{\int q_N(\mathbf{r}) d\mathbf{r}} \right\rangle. \quad (28)$$

Strictly speaking, we should average over the position of the $i = 1$ monomer, but this is taken care of by the ensemble average over $W(\mathbf{r})$ as a result of the translational symmetry.

All the spatially-dependent quantities [e.g., $W(\mathbf{r})$ and $q_i(\mathbf{r})$] are defined in an $L \times L \times L$ cubic box with periodic boundary conditions. To represent them on the computer, the box is overlaid with an $m \times m \times m$ grid of uniform spacing, $\Delta = L/m$. Hence, each cell of the grid occupies a volume of $V_{\text{cell}} = V/M$, where $V = L^3$ is the total volume of the box and $M = m^3$ is the total number of cells. The convolution integrals in Eqs. (6) and (25) are conveniently solved in Fourier space.

The next task is to perform the average in Eq. (28) over an ensemble of $W(\mathbf{r})$ configurations. This is done using CL-FTSs, where $W(\mathbf{r})$ is permitted to explore the entire complex plane. In particular, we employ the Leimkuhler-Matthews algorithm,⁴¹

$$W^{(k+1)}(\mathbf{r}) = W^{(k)}(\mathbf{r}) + \Lambda^{(k)}(\mathbf{r})\delta\tau + \frac{i}{2}[\mathcal{N}^{(k)}(\mathbf{r}) + \mathcal{N}^{(k-1)}(\mathbf{r})], \quad (29)$$

which generates a Markov sequence of field configurations over a fictitious time $\tau = k\delta\tau$ for $k = 0, 1, 2, \dots$. The deterministic force is given by

$$\Lambda(\mathbf{r}) \equiv \frac{1}{k_B T \rho_0} \frac{D H_f}{D W(\mathbf{r})} = \phi_\Gamma(\mathbf{r}) - 1 - \frac{W(\mathbf{r})}{\zeta}, \quad (30)$$

where $\phi_\Gamma(\mathbf{r})$ is obtained by smearing

$$\phi(\mathbf{r}) = \frac{\sum_{i=1}^N q_i(\mathbf{r}) q_{N+1-i}(\mathbf{r})}{h(\mathbf{r}) \int q_N(\mathbf{r}) d\mathbf{r}}. \quad (31)$$

The stochastic forces, $\mathcal{N}(\mathbf{r})$, are generated from a Gaussian distribution of real-valued numbers with a mean of zero and a variance of $\sigma^2 = 2\delta\tau/V_{\text{cell}}\rho_0$. The only difference from the common Euler-Maruyama algorithm, which uses separate stochastic forces at each time step, is that the Leimkuhler-Matthews algorithm averages the stochastic forces generated at the current step with those of the preceding step. With this simple modification, the algorithm remains accurate to much larger time steps. We generally use $N\delta\tau = 0.5$.

III. RESULTS

Our study begins by examining the N -dependence of the average end-to-end length, R_0 , of linear polymers. Figure 1 plots R_0 for a melt relative to the unperturbed value of an isolated polymer, $a_b(N-1)^{1/2}$, as a function of polymerization, N , calculated for an average monomer concentration of $\rho_0 = 30/a_b^3$, a compression modulus of $\zeta = 1$, contact interactions, and a grid resolution of $\Delta = 1.5a_b$. As demonstrated by the plot, the fluctuating field causes an expansion of R_0 relative to $a_b(N-1)^{1/2}$. The solid curve in Fig. 1 compares the weak-field approximation, Eq. (A17), derived in the Appendix. Al-

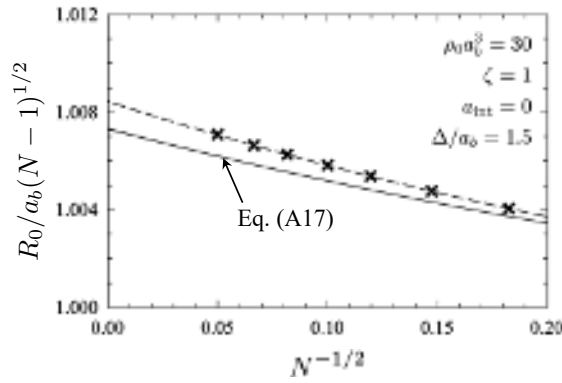


FIG. 1. Average end-to-end length, R_0 , as a function of polymerization, N , calculated for melts with a monomer density of $\rho_0 = 30/a_b^3$, a compression modulus of $\zeta = 1$, contact interactions, and a grid resolution of $\Delta = 1.5a_b$. The dashed curve is a fit to the CL-FTS results (crosses) and the solid curve shows the weak-field approximation from Eq. (A17).

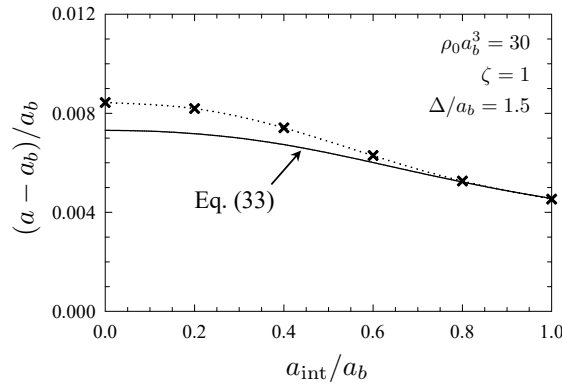


FIG. 2. Fluctuation correction of the segment length, a , as a function of the interaction range, a_{int} . The dotted curve is a guide to the eye and the solid curve shows the approximation in Eq. (33).

though the approximation captures the general dependence on N , it nevertheless underestimates the expansion by roughly 10%.

As usual, the statistical segment length, a , is obtained by extrapolating $R_0/(N-1)^{1/2}$ to $N \rightarrow \infty$, while keeping all the other parameters constant, including the grid spacing, Δ . To avoid significant effects from the periodic boundary conditions, we generally require $L \gtrsim 5R_0$. As such, the number of grid points must satisfy $M \gtrsim 125(\Delta/a_b)^{-3}N^{3/2}$. We also require exceptional accurate statistics, given that highly-stretched chains have a significant influence on R_0 despite their relatively low population. The combination of these two issues limits the polymerizations to $N \lesssim 400$. Nevertheless, we are able to obtain accurate extrapolations using the fact that the leading correction to $R_0/(N-1)^{1/2}$ scales as $N^{-1/2}$.^{42–45} This is done by fitting the difference between the calculated value, $R_0^{(\text{FTS})}$, and the weak-field approximation,

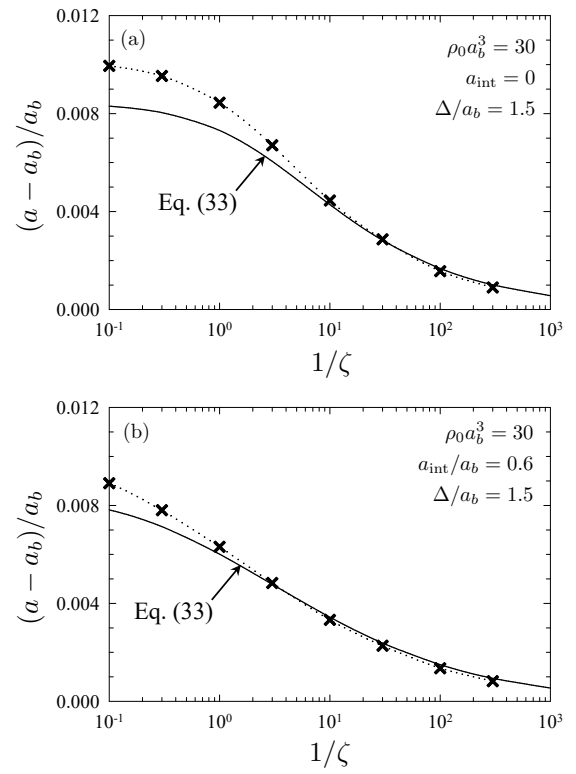


FIG. 3. Fluctuation correction of the segment length, a , as a function of compressibility, ζ , calculated for (a) contact interactions and (b) finite-range interactions. The dotted curve is a guide to the eye and the solid curve shows the approximation in Eq. (33).

$R_0^{(\text{approx})}$, to the functional form

$$\frac{R_0^{(\text{FTS})} - R_0^{(\text{approx})}}{a_b(N-1)^{1/2}} = c_0 + \frac{c_1}{N^{1/2}} + \frac{c_2}{N}, \quad (32)$$

where c_0 , c_1 , and c_2 are fitting parameters. Based on the fit in Fig. 1 (dashed curve), the fluctuation correction of the segment length is $(a - a_b)/a_b = 0.00844$. From the large- N limit of $R_0^{(\text{approx})}$, we obtain the weak-field approximation

$$\frac{a - a_b}{a_b} \approx \frac{a_b^2}{72(2\pi)^3 \rho_0} \int \frac{k^2 d\mathbf{k}}{s^2(k)[1 + t(k)/\zeta]}, \quad (33)$$

where

$$s(k) \equiv \sinh(k^2 a_b^2/12), \quad (34)$$

$$t(k) \equiv \tanh(k^2 a_b^2/12)/\Gamma^2(k), \quad (35)$$

with the integration extending between $k_\nu = \pm\pi/\Delta$ in each dimension, $\nu = x, y$, and z . For the current parameters, Eq. (33) predicts $(a - a_b)/a_b \approx 0.00731$, which underestimates the actual value by 13%. The rest of our study examines how the accuracy of Eq. (33) varies with the system parameters.

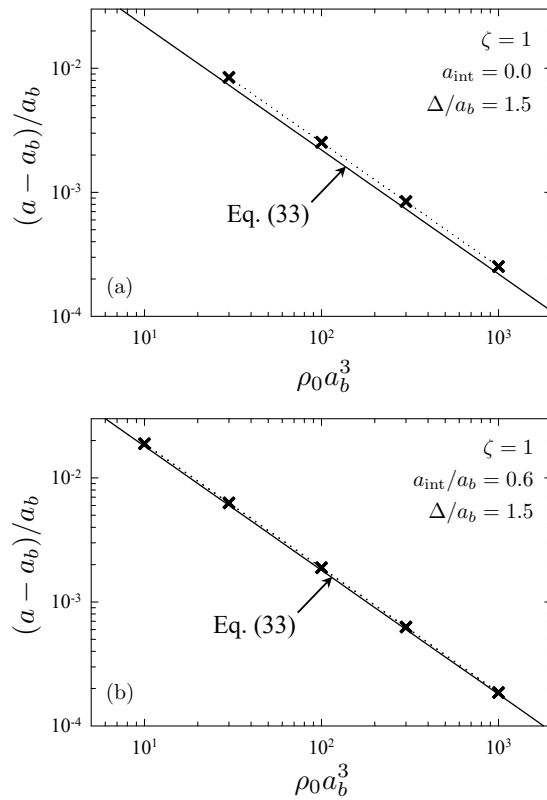


FIG. 4. Fluctuation correction of the segment length, a , as a function of the monomer density, ρ_0 , calculated for (a) contact interactions and (b) finite-range interactions. The dotted curve is a guide to the eye and the solid curve shows the approximation in Eq. (33). The logarithmic scale confirms that $a - a_b \propto \rho_0^{-1}$.

We first study the effect of increasing the range of the interactions, a_{int} , on the fluctuation correction, $a - a_b$. Figure 2 plots CL-FTS results (crosses) up to relatively large ranges, which, for polymers of $N = 100$, would be comparable to those typically used by Fredrickson and coworkers.^{16,35,36} The solid curve compares the analytical approximation from Eq. (33). The 13% inaccuracy we previously observed for contact interactions decreases continuously as the interaction range is increased. Beyond $a_{\text{int}} \gtrsim 0.8a_b$, Eq. (33) is found to agree with the CL-FTS results to within our numerical accuracy.

Next, we investigate the effect of compressibility, ζ . Figure 3(a) compares the actual fluctuation correction, $a - a_b$, to the weak-field approximation for the case of contact interactions, $a_{\text{int}} = 0$. The inaccuracy is most severe in the incompressible limit (i.e., $\zeta \rightarrow \infty$), where Eq. (33) underestimates the CL-FTS results by about 20%. However, the weak-field approximation improves as the compressibility increases, to the point where it is indistinguishable from the CL-FTS results for $\zeta \lesssim 0.1$. Incidentally, this inequality is satisfied for the levels of compressibility previously used by Fredrickson and coworkers^{26–29} to mimic polymer solutions. Figure 3(b) repeats the com-

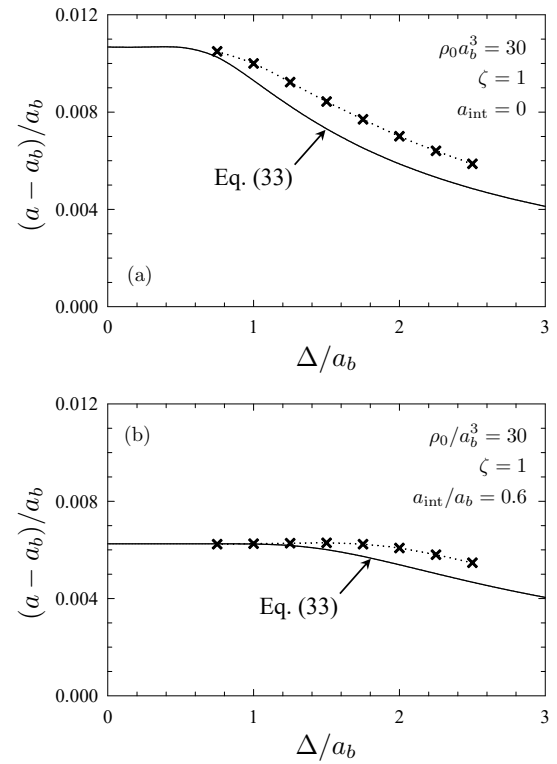


FIG. 5. Fluctuation correction of the segment length, a , as a function of the grid spacing, Δ , calculated for (a) contact interactions and (b) finite-range interactions. The dotted curve is a guide to the eye and the solid curve shows the approximation in Eq. (33).

parison for finite-range interactions of $a_{\text{int}} = 0.6a_b$. As before, increasing the range of the interactions improves the accuracy of the weak-field approximation.

As previously predicted for incompressible melts with contact interactions,^{38,46} the fluctuation correction for the statistical segment length in Eq. (33) is inversely proportional to the monomer density, ρ_0 . Figure 4 tests this prediction with a logarithmic plot of $a - a_b$ versus ρ_0 . The calculations are performed for contact interactions ($a_{\text{int}} = 0$) and finite-range interactions ($a_{\text{int}} = 0.6a_b$). As before, the CL-FTS results exceed the analytical prediction in Eq. (33), although less so as the interaction range increases. Remarkably, the CL-FTS results follow the ρ_0^{-1} scaling almost perfectly, in both cases.

To conclude, we examine the effect of grid resolution, which up to now has been fixed at $\Delta = 1.5a_b$. Figure 5(a) shows results for the case of contact interactions. According to the weak-field approximation (solid curve), the fluctuation correction increases as the grid spacing is reduced, eventually converging to a well-defined value once $\Delta \lesssim a_b$. Although our calculations are limited by the fact that the required number of grid points scales as $M \sim \Delta^{-3}$, the CL-FTS results (crosses) appear to converge to a similar value as $\Delta \rightarrow 0$. Figure 5(b) shows analogous results for finite-range interactions, which accelerates the convergence. For long-range interactions,

the results should converge once $\Delta \lesssim a_{\text{int}}$.

IV. DISCUSSION

The improved accuracy of Eq. (33) in Figs. 2 and 3 at low compressibility and long-range interactions, respectively, is entirely expected. The main source of inaccuracy is the weak-field approximation for $\ln Q$ in Eq. (A3). It is evident from the Hamiltonian in Eq. (20) that decreasing ζ reduces the magnitude of the field fluctuations. An increase in a_{int} also has a similar effect, given that $\ln Q$ is evaluated with the smeared field, $W_{\Gamma}(\mathbf{r})$. We also found that the accuracy of Eq. (33) in Fig. 5 improved for finer grids, but in this case there is no obvious reason. The main effect of reducing Δ is to add short-wavelength fluctuations, but presumably this does little to improve the accuracy associated with the long-wavelength fluctuations. Therefore, we attribute the good agreement, in this case, to a fortuitous cancellation of inaccuracies.

In most numerical calculations, the grid spacing, Δ , is reduced until the results converge, at least, to within some acceptable error tolerance. However, field-theoretic simulations involving contact interactions are known to exhibit an ultraviolet (UV) divergence, in which case convergence does not generally occur regardless of how small Δ is.^{17,20,47} Although the segment length, a , is UV convergent for discrete Gaussian chains as evident in Fig. 5(a), other quantities such as the free energy are not. Even with finite-range interactions, it may not be feasible to reduce Δ sufficiently to obtain convergence. Nevertheless, it is possible to remove the grid dependence with an appropriate renormalization of the system parameters.²⁰ Although, the relevant length scales of the system may still depend on Δ , their ratios do not. It is for this reason that we did not restrict our study to the small values of Δ required for convergence.

The tendency for hot spots (i.e., spikes) to form in strongly fluctuating fields limited our ability to simulate small values of $\rho_0 a_b^3$. Even when the hot spots were not severe enough to crash the program, they corrupted the statistics as evident by the occurrence of random spikes in the value of the Hamiltonian.^{17–19} Notably, introducing compressibility and finite-range interactions diminishes the problem to some degree. In hopes of reducing the problem further, we tried applying dynamical stabilization,^{12–15} where a small force is added to $\Lambda(\mathbf{r})$ to counter the formation of hot spots.^{17,19,20} Unfortunately, we were unable to obtain a meaningful improvement without significantly biasing the statistics. Nevertheless, the fact that our CL-FTS results conformed to the $a - a_b \propto \rho_0^{-1}$ scaling so precisely gives us confidence that our conclusions extend to values of $\rho_0 a_b^3$ well below those that we were able to simulate.

Our current study was motivated by a previous suspicion that Eq. (33) may become seriously inaccurate for large fluctuations. Particle-based simulations have provided strong evidence that block copolymer melts exhibit

universal behavior in the long-chain limit.^{48–51} However, CL-FTSs in Ref. 20 for symmetric diblock copolymers deviated from the universality for invariant polymerizations of $\bar{N} \lesssim 10^4$, even though L-FTSs, which avoid the sign problem by invoking a partial saddle-point approximation (PSPA), continued to obey universality.^{47,52} One proposed explanation was that Eq. (33) severely underestimated the fluctuation correction of the segment length. The L-FTSs would be immune from this inaccuracy, because the fluctuation correction is absent on account of the PSPA. However, the inaccuracy we detected in Eq. (33) is not nearly large enough to account for the departure from universality observed in the CL-FTSs.

The other explanation, which now seems even more likely, is that the CL-FTSs for the block copolymer melts in Ref. 20 experienced a ‘silent’ failure preceding the visible occurrence of hot spots. In reality, any such failure should emerge continuously, and thus we should expect subtle inaccuracies to occur prior to any detectable signature. Indeed, there exist numerous documented examples of silent failures in CL simulations of other systems.^{7,9,15,53–58} It is for this reason that we stayed well clear of the parameter region where hot spots were observed. Naturally, we can never be absolutely certain that our results were not affected. Nevertheless, the general consistency with the weak-field predictions and, in particular, the precise scaling of the fluctuation correction, $a - a_b$, with ρ_0^{-1} bodes well for the validity of our results.

As indicated in Eq. (15), our technique evaluates the ensemble average of the functional U_R defined in Eq. (13). Because U_R involves the same single-chain observable summed over all the polymers, its Boltzmann weight can be absorbed into the single-chain partition function, $Q_{\eta}[W]$, in the transformation to the field-theoretic Hamiltonian. As such, the average of U_R is then given by its expectation in the system of noninteracting polymers ensemble averaged over the field configurations. Indeed, the ratio of the integrals in Eq. (28) is just the expectation of $|\mathbf{r}_N - \mathbf{r}_1|^2$ for a single polymer chain acted upon by the field, $W(\mathbf{r})$. This technique can be readily applied to any single-chain observable, which therefore gives us access to all the intramolecular correlations of the polymer. This coupled with the fact that CL-FTSs can be easily applied to complicated polymer architectures should allow researchers to address problems that are far beyond the capabilities of conventional simulations.

V. SUMMARY

A method was introduced for evaluating the average end-to-end length, R_0 , of linear polymers of polymerization, N , in a melt, using complex-Langevin field-theoretic simulations (CL-FTSs). From that, we extracted the statistical segment length, a , by extrapolating $R_0/(N-1)^{1/2}$ to infinite N . The calculations were performed for melts of discrete Gaussian chains involving harmonic bonds of

unperturbed length a_b with a compressibility controlled by nonbonded interactions of finite range. Our study examined the dependence of the fluctuation correction of the segment length, $a - a_b$, on the range of the interactions, a_{int} , the modulus of the compressibility, ζ , and the bulk monomer density, ρ_0 . Given that it is not strictly necessary to remove the grid dependence in CL-FTSs, we also investigated the dependence on the grid spacing, Δ .

The fluctuation correction, $a - a_b$, from the CL-FTSs was compared to the weak-field approximation in Eq. (33).²⁰ The approximation proved to be exceptionally accurate for high degrees of compressibility and for polymers with long-range interactions. However, in the limit of incompressible melts ($\zeta \rightarrow \infty$) with contact interactions ($a_{\text{int}} \rightarrow 0$), it underestimated the correction by up to 20%. We expect this to be true over a wide range of monomer densities, ρ_0 , due to the fact that the CL-FTS results accurately obeyed the ρ_0^{-1} scaling predicted by Eq. (33). Nevertheless, this level of inaccuracy is generally tolerable, given that the fluctuation correction is a relatively small effect.

Our technique for evaluating R_0 involves two steps that can be applied to any single-chain observable. The first step is to perform an ensemble average of the observable over the configurations of a single polymer chain acted upon by the field, $W(\mathbf{r})$. The second step is to average the result over the ensemble of field configurations. As such, this approach can be used to access all the intramolecular correlations of the polymer, and thus it adds to the growing list of useful techniques in field-theoretic simulations.

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APPENDIX: CALCULATION OF R_0 FOR FINITE N

Here, we evaluate the average end-to-end length, R_0 , of linear polymers in the weak-field limit. This is done by generalizing a calculation introduced by Wang³⁸ for incompressible melts of continuous Gaussian chains with contact interactions to compressible melts of discrete Gaussian chains with finite-range interactions. The generalization is analogous to that of Ref. 20 except that we now avoid any assumption that the polymerization, N , is large.

To start, the field-theoretic Hamiltonian in Eq. (20) is expressed as

$$\frac{H_{\eta,f}}{k_B T} = -n \ln Q_\eta[W] - \frac{\rho_0}{2\zeta V} \sum_{\mathbf{k}} W(\mathbf{k})W(-\mathbf{k}) - \rho_0 W(\mathbf{0}), \quad (\text{A1})$$

in terms of the Fourier transformed field,

$$W(\mathbf{k}) = \int W(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}. \quad (\text{A2})$$

The single-chain partition function from Eq. (21) is then approximated to second-order in the field as⁵⁹

$$\ln Q_\eta[W] \approx \ln Q_\eta[0] - \frac{N}{V} W(\mathbf{0}) + \frac{N(N-1)}{2V^2} \sum_{\mathbf{k} \neq \mathbf{0}} S_\eta(k) W(\mathbf{k})W(-\mathbf{k}), \quad (\text{A3})$$

where

$$S_\eta(k) = \frac{\Gamma^2(k)}{N(N-1)} \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \exp\left(-\frac{k^2}{6} \langle(\mathbf{r}_i - \mathbf{r}_j)^2\rangle\right) \quad (\text{A4})$$

is evaluated in the absence of a field. Inserting Eq. (A3) into Eq. (A1) gives

$$\frac{H_{\eta,f}}{k_B T} = -n \ln Q_\eta[0] + \frac{\rho_0}{2\zeta V} |W(\mathbf{0})|^2 + \frac{\rho_0}{2V} \sum_{\mathbf{k} \neq \mathbf{0}} [\zeta^{-1} + N S_\eta(k)] |W(\mathbf{k})|^2, \quad (\text{A5})$$

where we have used the fact that $W(-\mathbf{k}) = -W^*(\mathbf{k})$ for imaginary fields. In this weak-field approximation, each Fourier component of the field behaves as a harmonic oscillator, and thus

$$\langle |W(\mathbf{k})|^2 \rangle = \frac{V}{\rho_0} [\zeta^{-1} + N S_\eta(k)]^{-1}. \quad (\text{A6})$$

Applying the relationship in Eq. (16), it follows that

$$R_0^2 = - \left. \frac{\partial \ln Q_\eta[0]}{\partial \eta} \right|_{\eta=0} + \frac{1}{2n} \sum_{\mathbf{k} \neq \mathbf{0}} \frac{1}{\zeta^{-1} + N S_\eta(k)} \left. \frac{\partial N S_\eta(k)}{\partial \eta} \right|_{\eta=0}. \quad (\text{A7})$$

Given the definition of $Q_\eta[W]$ in Eq. (21), it immediately follows that the first term in Eq. (A7) is just the value of R_0^2 in the absence of a field, $a_b^2(N-1)$. To evaluate the second term in Eq. (A7), we expand $N S_\eta(k)$ to first-order in η . The harmonic potential, $\eta|\mathbf{r}_1 - \mathbf{r}_N|^2$, connecting the chain ends creates a ring polymer, for which³⁸

$$\frac{\langle(\mathbf{r}_i - \mathbf{r}_j)^2\rangle}{a_b^2} = \left(\frac{1}{|i-j|} + \frac{1}{\bar{\eta}^{-1} + N - |i-j|} \right)^{-1}, \quad (\text{A8})$$

$$\approx |i-j| - \bar{\eta}(i-j)^2, \quad (\text{A9})$$

where $\bar{\eta} = \frac{2}{3}a_b^2\eta$. Thus, the zeroth-order term for $N S_\eta(k)$ is

$$N S_0(k) = \Gamma^2(k)g(x), \quad (\text{A10})$$

where

$$g(x) = \frac{1}{N-1} \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} e^{-x|i-j|}, \quad (\text{A11})$$

$$= \frac{1}{\tanh(x/2)} - \frac{1 - e^{-(N-1)x}}{2(N-1)\sinh^2(x/2)}, \quad (\text{A12})$$

and $x = k^2 a_b^2/6$. Similarly, the first-order term is given by

$$\left. \frac{\partial N S_\eta(k)}{\partial \eta} \right|_{\eta=0} = \frac{2}{3} a_b^2 \Gamma^2(k) r(x), \quad (\text{A13})$$

where

$$r(x) = \frac{x}{N-1} \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} (i-j)^2 e^{-x|i-j|}, \quad (\text{A14})$$

$$= x \frac{d^2}{dx^2} g(x). \quad (\text{A15})$$

Inserting these results into Eq. (A7), we obtain

$$R_0^2 = a_b^2(N-1) + \frac{a_b^2}{3n} \sum_{\mathbf{k} \neq 0} \frac{\Gamma^2(k) r(x)}{\zeta^{-1} + \Gamma^2(k) g(x)}. \quad (\text{A16})$$

The last step is to approximate the sum by an integral, which gives

$$\frac{R_0}{a_b \sqrt{N-1}} \approx 1 + \frac{N}{6(2\pi)^3 \rho_0(N-1)} \int \frac{\Gamma^2(k) r(x) d\mathbf{k}}{\zeta^{-1} + \Gamma^2(k) g(x)}, \quad (\text{A17})$$

where the integration is over the interval $-\pi/\Delta \leq k_\nu \leq \pi/\Delta$ in each dimension, $\nu = x, y$, and z .

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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