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Computer simulations are used to study composition fluctuations in disordered diblock copolymer melts over a range of values of the chain lengths N, and test several theories for the structure factor $S(q)$. Specifically, we test the random-phase approximation (RPA), which is based on a self-consistent field treatment of fluctuations, the Fredrickson-Helfand theory, which was designed to treat describe fluctuations near the order-disorder transition, and the relatively new renormalized-one-loop (ROL) theory. The results confirm claims that the RPA is exact in the limit $N \to \infty$ and that the ROL yields the dominant corrections to the RPA within a systematic expansion in powers of $N^{-1/2}$, and show that the ROL is much more accurate than either older theory.

At the level of chemical repeat units, polymers are structurally similar to smaller organic molecules. Many aspects of the behavior of polymer liquids over larger length scales can, however, be described by coarse-grained models in which the details of local structure are absorbed into a few parameters. The most successful theory of dense polymer liquids such as block copolymer melts is based on a self-consistent field (SCF) approximation that treats individual chains as random walks in an inhomogeneous chemical potential landscape. The approximations underlying this and other coarse-grained theories depend on the existence of a separation of length scales between the size of a chemical repeat unit and that of a polymer coil in the limit of very long polymers.

Diblock copolymer melts can exhibit both a disordered (homogeneous) phase and a variety of periodic ordered phases.[1] The structure factor $S(q)$ of the disordered phase can be measured by small angle x-ray (SAXS) and neutron (SANS) scattering experiments. Such experiments are typically analyzed by fitting $S(q)$ to predictions of the so-called random phase approximation [2] (RPA). The RPA is based on the same SCF approximation as that often used to describe the ordered phases: $S(q)$ was derived [2] by using SCF theory to estimate the free energy cost of infinitesimal composition fluctuations of wavenumber q.

It has long been suspected that the RPA and SCF approximations are exact in the limit $N \to \infty$ of infinitely long polymers. Direct evidence for this, however, remains limited. Recent work by our group [11–14] and others [6–9] has yielded a more sophisticated theory for $S(q)$, the renormalized one-loop (ROL) theory, that reduces to the RPA in the limit $N \to \infty$, but that also appears to yield the first correction to the RPA within a systematic expansion in powers of $N^{-1/2}$.

In this Letter, we present the first quantitative test of this ROL theory, while also testing the RPA and the older Fredrickson-Helfand [3] theory of pre-critical fluctuations with an unprecedented level of precision. We focus, specifically, on testing whether the RPA and ROL do indeed become systematically more accurate with increasing N, by examining how the discrepancies between these theories and simulation results vary with changes in chain length N.

We consider the structure factor $S(q)$ in a dense liquid of symmetric AB diblock copolymers, each containing N monomers. We define

$$S(q) \equiv \int d\mathbf{r} \, \langle \delta\psi(\mathbf{r})\delta\psi(0)\rangle e^{i\mathbf{q}\cdot\mathbf{r}}, \qquad (1)$$

where $\delta\psi(\mathbf{r}) \equiv [\delta c_A(\mathbf{r}) - \delta c_B(\mathbf{r})]/2$ is a composition field, and $q \equiv |\mathbf{q}|$. Here, $\delta c_i(\mathbf{r})$ is the deviation of the number concentration $c_i(\mathbf{r})$ of i monomers from its spatial average. In a disordered diblock copolymer melt, $S(q)$ has a maximum at a nonzero wavenumber q^*.[2]

The RPA [2] predicts an inverse structure factor of the form

$$cNS_0^{-1}(q) = F(qR_{g0}) - 2\chi_e N. \qquad (2)$$

Here, $R_{g0} = (N/6)^{1/2}b$ is the radius of gyration of a random walk polymer with a statistical segment length b, c is the overall monomer concentration, and χ_e is an effective interaction parameter that quantifies the excess free energy of mixing A and B monomers. $F(x)$ is a known analytic function [2] that has a minimum at a nonzero value x^*. The RPA thus predicts a maximum in $S_0(q)$ at a nonzero wavenumber $q_0^* \equiv x^*/R_{g0}$ that is independent of χ_e, and a divergence of $S(q^*)$ when $\chi_e N$ reaches a spinodal value $(\chi_e N)_s \equiv F(x^*)/2$. For symmetric diblock copolymers, $x^* = 1.95$, $F(x^*) = 21.99$, and $(\chi_e N)_s = 10.495$. A subscript '0' is used here to denote RPA predictions for $S(q)$, R_g and q^*.

Since the 1980s, several related coarse-grained theories have been developed that attempt to improve upon the RPA for $S(q)$. [3–6, 10–14] These theories all predict corrections to the RPA with a relative magnitude proportional to a small parameter $\bar{N}^{-1/2}$, where $\bar{N} \equiv N(cb^3)^2$. Physically, $\bar{N}^{1/2}$ is a measure of polymer overlap: It is proportional to the number R^3/V of chains, each of volume $V = N/c$, that can pack into the volume R^3 pervaded by a single chain of size $R \sim \sqrt{N}b$. The first and most influential such theory, by Fredrickson and Helfand [3] (FH), was designed to describe only the dominant effects of strong fluctuations very near the order-disorder transition (ODT) for symmetric diblock copolymers. More recent work has yielded a family of closely related ROL theories of corrections to both the underlying random-walk model of single-chain correlations [7–9] and to the RPA for $S(q)$ [6, 11–14] in both polymer mixtures and diblock copolymer melts. One distinguishing feature of these ROL theories is the

introduction of systematic methods to separate non-universal effects of monomer-scale correlations from universal long-wavelength phenomena, and to absorb the effects of short-wavelength correlations into renormalized values of the RPA parameters b and χ_e. The ROL theory for $S(q)$ appears to be the first correction to the RPA within an expansion of $cNS^{-1}(q)$ in powers of $\bar{N}^{-1/2}$. Because the validity of this expansion is not restricted to the vicinity of the ODT, the ROL theory thus has a much broader potential range of validity than the older FH theory. The ROL theory of corrections to the random-walk model for single chains in homopolymer melts, by the Strasbourg group,[7, 8] is contained within the ROL theory for blends and diblocks as a special case, and has already been shown to agree quantitatively with hompolymer simulations.[7, 9]

Both the FH and ROL theories yield predictions for $S^{-1}(q)$ as a sum $S^{-1}(q) = S_0^{-1}(q) + \delta S^{-1}(q)$ in which $S_0^{-1}(q)$ is given by Eq. (2), and in which $cN\delta S^{-1}(q)$ is a function of the form

$$cN\delta S^{-1}(q) = \bar{N}^{-1/2}H(qR_{g0}, \chi_a^* N). \quad (3)$$

Here, H is a dimensionless function for which the FH and ROL theories yield different expressions. In both theories, H depends upon the self-consistently determined peak intensity $S(q^*)$. Equivalently, we may express H in terms of an "apparent" interaction parameter χ_a^* that we define by simply fitting the predicted peak intensity $S(q^*)$ to the RPA, defining

$$cNS^{-1}(q^*) \equiv 2[(\chi_e N)_s - \chi_a^* N], \quad (4)$$

where $(\chi_e N)_s = 10.495$. The FH theory for symmetric copolymers yields a function $H = B[(\chi_e N)_s - \chi_a^* N]^{-1/2}$ that is independent of q, with $B \simeq 280$. The ROL theory [11, 14] yields an expression for $H(qR_{g0}, \chi_a^* N)$ as a sum of Fourier integrals, which must be evaluated numerically.

Several limitations of the RPA have been documented by both experiments [20–22] and previous simulations.[16–19] These all show a decrease in q^* and a nonlinear dependence of $S^{-1}(q^*)$ on $1/T$ near the ODT that are not consistent with the RPA. Previous simulations have not, however, provided very precise quantitative tests of either the RPA or FH theories. The main reason for this has been the absence of a clear prescription for how to relate the parameter χ_e that is required as an input to these theories to the parameters that are controlled in a simulation. The analysis presented here uses several novel methods to avoid or minimize this ambiguity.

Our simulations use a simple bead-spring model similar to that of Grest and coworkers. [18] We use a purely repulsive Lennard-Jones nonbonded pair potential, with $v_{ij}(r) = \varepsilon_{ij}\left[4(r/\sigma)^{-12} - 4(r/\sigma)^{-6} + 1\right]$ for $r < r_c$, with $r_c = 2^{1/6}\sigma$, and a harmonic bond potential $v_{\text{bond}}(r) = \kappa(r - l_0)^2/2$. All work presented here uses parameters $\varepsilon_{AA} = \varepsilon_{BB} = kT$, $l_0 = \sigma$, and $\kappa = 400kT\sigma^{-2}$, with a monomer concentration $c = 0.7\sigma^{-3}$. The magnitude ε_{AB} of the AB repulsion is controlled by a parameter $\alpha = \varepsilon_{AB} - \varepsilon_{AA}$ that indirectly controls χ_e. We have simulated liquids containing
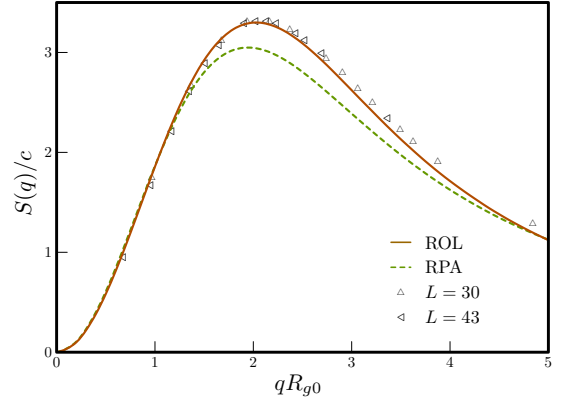

FIG. 1. q dependence of $S(q)$ for $N = 64$, at $\alpha = 0$, for $L = 30$ and $L = 43$, in units with $\sigma \equiv 1$. The RPA and ROL predictions are shown by dashed and solid lines, respectively.

chains of $N = 16$, 32, 64, and 128 beads in periodic $L \times L \times L$ cubic boxes.

We have conducted replica-exchange [23] hybrid MC simulations, using replicas with different values of α at the same T. The simulations combine a hybrid MC move, [24] in which short MD simulations are used as proposed MC moves, with end-swap, reptation, and double-rebridging [25] MC moves. Values of q^* and $S(q^*)$ were determined by fitting discrete values of $S(q)$ at allowed wavevectors to a smooth function of q. Results are presented only for for values of α for which the peak in $S(q)$ is broad enough to allow a reliable fit, and for which consistent results were obtained with two values of L.

To test the RPA, FH, and ROL theories, one needs an unambiguous way to determine values for the parameters b and χ_e that these theories all require as inputs. Our comparisons with theory all use a value $b = 1.41\sigma$ that was obtained [9] by extrapolating results obtained from homopolymer ($\alpha = 0$) melts of varying N, and defining $b^2 \equiv \lim_{N\to\infty} 6R_g^2(N)/N$. This definition of b is required for consistency with the ROL theory for single-chain statistics[8], which yields a random walk only in the limit $N \to \infty$. An analogous procedure for estimating $\chi_e(\alpha)$ is discussed below.

Limit $\chi_e = 0$: We first consider the special case $\alpha = 0$, or $\varepsilon_{AB} = \varepsilon_{AA}$, for which $\chi_e = 0$. This corresponds to a SANS experiment in which A and B monomers are labelled by differential deuteration, but are otherwise identical. In this limit, the ROL and RPA predictions differ only as result of predicted $\mathcal{O}(\bar{N}^{-1/2})$ deviations from random walk intramolecular statistics.[14]

Fig. 1 shows simulation results and predictions for $S(q)$ vs. qR_{g0} in systems with $N = 64$ ($\bar{N} = 246$) and $\alpha = 0$. Here, $R_{g0}^2 \equiv Nb^2/6$, with $b = 1.41\sigma$. The RPA (dashed line) slightly underestimates both the peak amplitude $S(q^*)$ and peak wavenumber q^*. The ROL prediction (solid line), however, fits the data almost perfectly, with no adjustable parameters. Agreement is similar for other chain lengths.

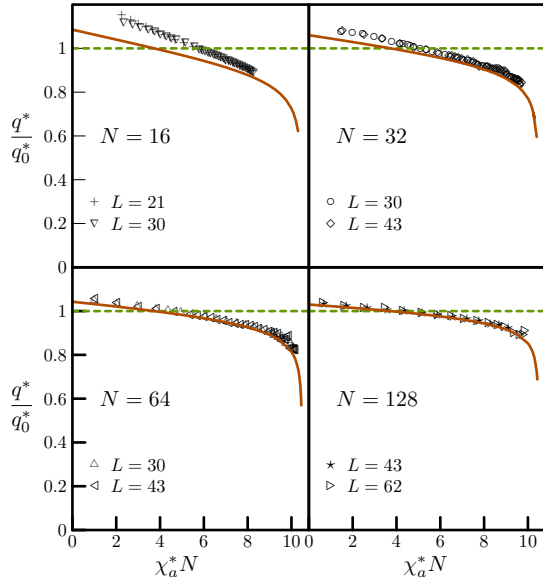*Peak wavenumber:* Fig. 2 shows the evolution of the peak

FIG. 2. Peak wavenumber q^*, normalized by the RPA prediction q_0^*, vs $\chi_a^* N$ for $N = 16$, 32, 64, and 128 ($\bar{N} = 62$, 123, 246, 492). Results for two box sizes L are shown for each N. ROL predictions are solid lines.

wavenumber q^* with changes in α. Here, we plot the ratio q^*/q_0^* of q^* to the RPA prediction $q_0^* = 1.95/R_{g0}$ vs. the quantity $\chi_a^* N$ defined in Eq. (4). Recall that χ_a^* is directly related to the peak intensity. This plot thus shows peak wavenumber vs. a measure of the peak intensity $S(q^*)$, plotted so that $S(q^*) \to \infty$ as $\chi_a^* N \to 10.495$.

Simulation results for q^* decrease monotonically with increasing χ_a^* or α, dropping 15-20 % over the range shown, as found previously.[19] Note that $q^*/q_0^* > 1$ for small values of $\chi_a^* N$, consistent with the behavior of Fig. 1 for $\alpha = 0$, but $q^*/q_0^* < 1$ for $\chi_a^* N \gtrsim 5$. ROL predictions (solid lines) reproduce this behavior quite accurately, with no adjustable parameters. Moreover, the ROL predictions seem to become systematically more accurate with increasing N, and are extremely accurate for the longest chain. This rapid convergence of predictions and simulation results with increasing N is strong evidence for the claim [11, 12] that the ROL theory is the first correction to the RPA within a systematic expansion.

Estimating $\chi_e(\alpha)$: In all of the theories considered here, the degree of incompatibility between A and B monomers is characterized by an effective interaction parameter χ_e. We can directly test predictions for the dependence of $S(q^*)$ on χ_e, however, only if we can obtain an independent estimate of how $\chi_e(\alpha)$ depends on α. The comparisons shown in Figs. 1 and Fig. 2 did not require such an estimate.

We have chosen to estimate $\chi_e(\alpha)$ using a method proposed in Ref. 15, which yields a rigorous expression for $\chi_e(\alpha)$ to first order in α within a Taylor expansion in powers of α. The method is based on a perturbation theory for the free energy of structurally symmetric blends of A and B homopolymer with a pair potential of the form $u_{ij}(r) = \varepsilon_{ij} u(r)$ used here, in

which $\alpha \equiv \varepsilon_{AB} - \varepsilon_{AA}$ is treated as a small parameter. Perturbation theory is a natural description of the homogeneous state of either a blend or a diblock copolymer melt, because the homogeneous phase remains stable only when α is less than a critical value that decreases as $1/N$ with increasing N, guaranteeing the accuracy of a Taylor expansion for sufficiently large N. By comparing the N-dependence of the free energy predicted by perturbation theory to that predicted by the ROL theory, it was shown [15] that the parameter χ_e in the ROL theory is given to $\mathcal{O}(\alpha)$ by

$$\chi_e(\alpha) \simeq \frac{\alpha z(\infty)}{kT} \qquad (5)$$

where $z(\infty)$ is the $N \to \infty$ limit of an "effective coordination number" $z(N) \equiv \int d\mathbf{r} \; g(\mathbf{r}; N)u(\mathbf{r})$, in which $g(\mathbf{r}; N)$ is the inter-molecular radial distribution function in a reference homopolymer ($\alpha = 0$) melt containing chains of length N. For the model considered here, we previously obtained [15] $z(\infty) = 0.2965$ by numerically extrapolating results of simulations of hompolymer melts with varying N.

Peak intensity: Fig. 3 shows how the inverse peak intensity $cNS^{-1}(q^*)$ varies with $\chi_e N$, plotted using Eq. (5) for $\chi_e(\alpha)$. Several qualitative features are immediately apparent: Simulation results for $cNS^{-1}(q^*)$ are greater than the RPA prediction (suppressed fluctuations) for $\chi_e N \gtrsim 6$, as predicted by the FH theory, but are actually less than the RPA prediction (enhanced fluctuations) for $\chi_e N \lesssim 6$. The ROL theory predicts this change in sign of the deviation, and accurately predicts the value of $\chi_e N \simeq 6$ at which the change in sign occurs. It also correctly predicts that results for different chain lengths nearly converge at this point. The FH predictions for $N = 64$ (upper panel) adequately describes the simulation results in the limit of very strong fluctuations ($\chi_e N \gtrsim 15$, $cNS^{-1}(q^*) \lesssim 1$) for which it was designed, but differs qualitatively from both the ROL theory and the data for lower values of $\chi_e N$. ROL prediction for the longest two chain lengths ($N = 64$ and 128) are instead accurate over the entire range of $\chi_e N$ studied. For the shortest chain shown ($N = 32$), ROL predictions are accurate for small $\chi_e N$, but differ significantly from simulation results for larger $\chi_e N$. Results for $N = 16$ (not shown) differ even more from ROL prediction at large values of $\chi_e N$.

We believe that the failure of the ROL for $S(q)$ for small N and large $\chi_e N$ is primarily due to a failure of our first-order perturbation approximation for $\chi_e(\alpha)$, Eq. (5). The comparison of theory and simulation in Fig. 3 is subject to two known types of error: (i) Errors in the ROL theory itself, due to truncation of an expansion in powers of $\bar{N}^{-1/2}$ at $\mathcal{O}(\bar{N}^{-1/2})$, and (ii) Errors in Eq. (5) for $\chi_e(\alpha)$, due to truncation of a Taylor expansion of $\chi_e(\alpha)$ at $\mathcal{O}(\alpha)$. The value of α required to obtain a specific estimate for $\chi_e N$ increases linearly with increasing $\chi_e N$ at fixed N, and also increases as $1/N$ with decreasing N at fixed $\chi_e N$. The fact that large discrepancies between ROL predictions and simulation results for $S(q^*)$ are found only for small N and large $\chi_e N$, corresponding to particularly large values of α, suggest that these discrepancies are probably due
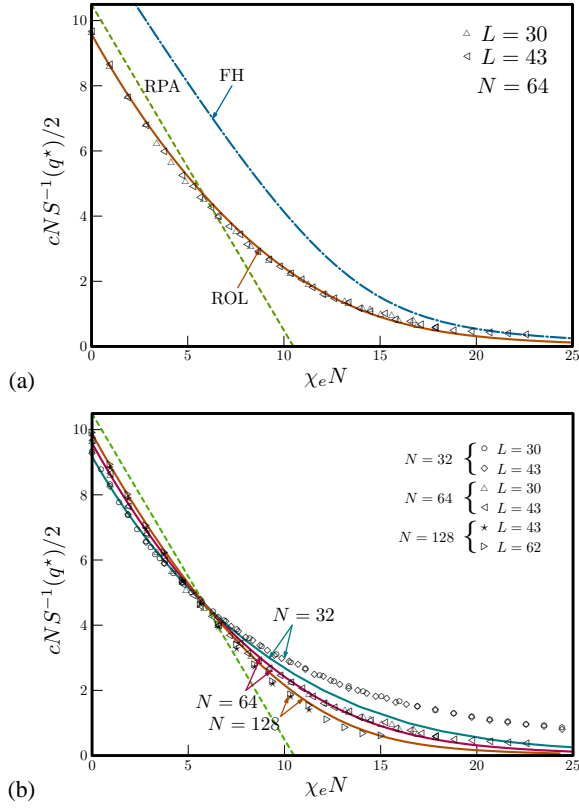
FIG. 3. Inverse peak intensity *vs.* $\chi_e N$, plotted using Eq. (5) to estimate $\chi_e(\alpha)$, with $z_c = 0.2965$. Panel (a) shows results for $N = 64$ compared to the RPA (straight dashed line), FH (dot-dashed curve) and ROL (solid lines). Panel (b) shows $N = 32$, 64, and 128 with RPA and ROL predictions. Results for two values of L are shown for each chain length N.

here. The ability of the ROL to make accurate predictions even for rather short chains suggests that it may be useful as a tool for interpreting results of experiments on blends and block copolymers of short, strongly interacting polymers, and for interpreting and extrapolating results of atomistic simulations of relatively short chains. Our results provide the clearest available evidence that the RPA is indeed exact in the limit $N \to \infty$, and strongly support the claim that the ROL theory yields the first correction to the RPA within a systematic expansion. The net effect is to significantly extend the known range of validity, and thus the potential usefulness, of the analytic theory of dense polymer liquids.

primarily to errors of type (ii). This is also suggested by the fact that much smaller errors are seen for short chains in Fig. 2, which does not rely on an estimate of $\chi_e(\alpha)$, and thus is not subject to this source of error. We will show elsewhere that the discrepancy between ROL predictions and simulation results for $S(q^*)$ for large α can be almost entirely removed if we treat $\chi_e(\alpha)$ as a nonlinear function of α (but not N) that we fit to the data. We have restricted ourselves here, however, to comparisons that involve no adjustable parameters.

We have presented an unusually systematic simulation study of the behavior of $S(q)$ in AB diblock copolymer melts over a range of chain lengths, and compared the results to several theories. The use of theoretically motivated procedures for estimating the RPA parameters b and χ_e, defined by extrapolation to $N = \infty$, allowed much more quantitative comparisons to theory than was previously possible. The range of values of $\bar{N}$ studied here, $\bar{N} \leq 500$, overlaps the lower end of the range studied in experiments, for which $\bar{N}$ is typically $10^3 - 10^4$. The new ROL theory is shown to be much more accurate than either the RPA or ROL theories, and to be strikingly accurate for the longest chain lengths studied

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