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On the chain length dependence of local correlations in polymer melts and a perturbation theory of symmetric polymer blends

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The self-consistent field (SCF) approach to the thermodynamics of dense polymer liquids is based on the idea that short-range correlations in a polymer liquid are almost independent of how monomers are connected into polymers over large scales. Some limits of this idea are explored in the context of a perturbation theory for mixtures of two structurally identical polymer species, A and B, in which the AB pair interaction differs slightly from the AA and BB interaction, and this difference is controlled by a parameter α. An expansion of the free energy to first order in α yields an excess free energy of mixing of the form $\alpha z(N)\phi_A\phi_B$, in both lattice and continuum models, where $z(N)$ is a measure of the number of inter-molecular near neighbors of each monomer in a one-component ($\alpha = 0$) reference liquid with chains of length N. This quantity decreases slightly with increasing N because the self-concentration of monomers from the same chain around each monomer is slightly higher for longer chains, creating a deeper inter-molecular correlation hole for longer chains. We present a theoretical analysis of the resulting N-dependence of local liquid structure, and predict that $z(N) = z^\infty[1 + \beta\bar{N}^{-1/2}]$, where $\bar{N}$ is an invariant degree of polymerization, and $\beta = (6/\pi)^{3/2}$ is a universal coefficient. This and related predictions are confirmed by comparison to simulations of a continuum bead-spring model, as well as to previously published lattice Monte Carlo simulations. We propose a way to estimate the effective interaction parameter appropriate for comparisons of simulation data to SCF theory and to coarse-grained theories of corrections to SCF theory, which is based on an extrapolation of coefficients in this perturbation theory to the limit $N \to \infty$. We show that a renormalized one-loop theory contains a quantitatively correct description of the N-dependence of local liquid structure that we study here.

I. INTRODUCTION

In its most general form,[1] the Flory-Huggins theory of polymer mixtures postulates that the free energy of mixing per monomer Δf in a binary polymer mixture can be expressed as a sum of the form

$$\Delta f = kT \sum_i \frac{\phi_i}{N_i} \ln \phi_i + \Delta f_{\text{int}}(\phi, T) \quad , \qquad (1)$$

where N_i is the degree of polymerization of species i, for $i = A$ or B, $\phi_A = \phi$ and $\phi_B = 1 - \phi_A$ are volume fractions, kT is thermal energy, and $\Delta f_{\text{int}}(\phi, T)$ is an interaction free energy per monomer. The original Flory-Huggins lattice model[2] was more specific, insofar as it predicted that Δf_{int} should be of the regular solution form $\Delta f_{\text{int}} = C\phi_A\phi_B$, where C is a temperature independent constant. In order to capture the variety of behaviors observed in real polymer mixtures, however, it has long been understood[1,3,4,5] that Δf_{int} must be allowed to exhibit an essentially arbitrary dependence on temperature and composition.

This generalization of the Flory-Huggins theory is very flexible, but not infinitely so: As long as $\Delta f_{\text{int}}(\phi, T)$ is assumed to be independent of the chain lengths N_A and N_B, the theory makes falsifiable predictions about how the phase diagrams for a homologous set of mixtures vary with N_A and N_B, which are generally quite accurate. The assumption that $\Delta f_{\text{int}}(\phi, T)$ is independent of chain length is the essential

physical content of the theory.

The intuitive basis of this assumption is the idea that $\Delta f_{\text{int}}(\phi, T)$ represents a contribution to the free energy that is sensitive only to the local structure of a polymer liquid. It is also assumed that this contribution is separable from contributions that arise from the entropy of mixing in homogeneous mixtures and, in a generalization to inhomogeneous liquids, from the distortion of polymer chains over large length scales. The generalized Flory-Huggins theory described above is the homogeneous limit of a correspondingly general form of the self-consistent field theory (SCFT) of inhomogeneous polymer liquids. The key assumption in this SCFT[6] is that the interaction free energy density at any point in the fluid depends only upon the temperature and the average monomer concentration very near that point, independent of chain lengths, chain architecture, or compositions at distant points.

The original Flory-Huggins lattice theory combined an implicit assumption of locality (i.e., that local fluid structure is independent of chain length) with a much cruder random mixing approximation. The original theory introduced a random mixing approximation for the free energy of a lattice model in which monomers of types i and j on neighboring lattice sites interact with a potential energy v_{ij}. In the absence of vacancies, this yields

$$\Delta f_{int} = \alpha z_{\text{latt}}\phi_A\phi_B \quad , \qquad (2)$$

where $\alpha \equiv [v_{AB} - (v_{AA} + v_{BB})/2]$, and where z_{latt} is the

lattice coordination number, i.e., the number of lattice sites neighboring each site.

The random mixing approximation is known to substantially overestimate the actual energy of mixing for lattice models. In simulations of a simple cubic lattice diluted with a modest density of vacancies, Sariban and Binder[7,8] found that the energy of mixing was roughly half that predicted by an analogous approximation for a lattice with vacancies. In more recent lattice Monte Carlo simulations of diblock copolymer melts on a diluted fcc lattice, Matsen and coworkers[9,10] also considered a lattice mean-field (i.e., random mixing) approximation for the order-disorder transition of symmetric diblocks, and found that it predicts a transition temperature more than twice that observed in their simulations, again indicating a large overestimation of the energy arising from AB pair interactions.

A. Perturbation Theory

For simple symmetric models, a much more accurate estimate for Δf in the one-phase region can be obtained from thermodynamic perturbation theory. We focus here on a class of structurally symmetric models of A-B polymer blends, on- or off-lattice, in which A and B chains are structurally identical, but in which the potential energy for AB pair interactions is slightly different than that for AA and BB interactions. Many of the coarse-grained models used in previous simulations of polymer blends fit this description, including some used in lattice Monte Carlo (MC)[7,8,11,12,13] off-lattice MC[14,15] and molecular dynamics (MD)[16] simulations.

To construct a perturbation theory, let α be a small parameter, with units of energy, that is proportional to the magnitude of the difference between AB and AA interactions. Here, we consider an expansion of the free energy as function of α at constant temperature, in a liquid containing structurally identical A and B chains of equal length N. The limit $\alpha = 0$ is thus a strongly correlated one-component liquid. At the critical composition $\phi = 1/2$, phase separation occurs when α exceeds a critical value α_c that decreases as $1/N$ with increasing N. An expansion of Δf for $\alpha < \alpha_c$ to first order in α is thus expected to become increasingly accurate with increasing N.

In Sec. III of this paper, we show that the first order expansion for the free energy of mixing is given by a function of the form

$$\Delta f \simeq kT \sum_i \frac{\phi_i}{N} \ln \phi_i + \alpha z(N) \phi_A \phi_B \quad . \quad (3)$$

for both lattice and continuum models. In this expansion, the coefficient $z(N)$ is an "effective coordination number" whose value is sensitive to local correlations in the one-component reference state. In a lattice model with nearest-neighbor interactions, $z(N)$ is found to be equal to the average number of inter-molecular nearest neighbors, i.e., the number of lattice sites neighboring a test monomer that are occupied by

monomers from a different chain than the one containing the test monomer. An analogous definition is given for $z(N)$ in a continuum model.

The main source of error in the random mixing model is the neglect of the consequences of the so-called correlation hole. The immediate environment of any monomer in a dense polymer liquid is crowded with other monomers from the same chain. In a nearly incompressible liquid, this causes a compensating depression in the number of neighboring monomers from other chains, leading to a correlation hole in the intermolecular distribution function, and thus to a decrease in the intermolecular interaction energy. The accuracy of a perturbation theory for the free energy of a system of long chains is a result of the fact that the structure of this correlation hole at all $\alpha < \alpha_c$ is very similar to that in the $\alpha = 0$ reference liquid, because of the smallness of α_c.

Several authors have previously proposed approximations that are either equivalent to first order perturbation theory, or very closely related. Müller and Binder[13] proposed a "modified Flory-Huggins" approximation for the free energy of mixing Δf of a simple lattice model that is completely equivalent to the first-order perturbation theory of Eq. (3). In discussions of the results of continuum bead-spring simulations, both Grest and coworkers[16] and Escobedo and de Pablo[15] have proposed approximations for structurally symmetric continuum models that are either equivalent[16] or nearly equivalent[15] to the perturbation theory discussed here. None of these authors explicitly described their proposed approximations as a form of perturbation theory.

Müller and Binder[13] and Escobedo and de Pablo[15] have both shown that these perturbative approximations provide extremely accurate predictions for the critical temperature T_c observed in simulations of symmetric binary blends. In both of these studies, the authors showed that critical point found from finite-size scaling analysis of simulation results is very well approximated by the expression

$$\frac{\alpha z(N) N}{k T_c(N)} \simeq 2 \quad (4)$$

that is obtained by using the first-order expansion of Eq. (3) to predict T_c. A somewhat stronger statement can be made about the lattice MC data of Binder, Mueller, and coworkers[12,13,17]: Their results for the dimensionless parameter $\alpha z(N) N / k T_c(N)$ deviate systematically from 2 for finite chains, but appear to extrapolate in the limit $N \rightarrow \infty$ to an asymptote that is equal to 2 to within statistical uncertainties. This convergence was not emphasized by Binder and coworkers, but appears to be a natural consequence of the identification of modified Flory-Huggins theory as first order perturbation theory, and the fact that deviations from any low order perturbation theory for T_c must decrease with decreasing α_c, and thus with increasing N.

B. Chain Length Dependence of Local Correlations

An important difference between the generalized Flory-Huggins theory of Eq. (1) and perturbation theory of Eq. (3), which are superficially very similar, is that the coefficient $z(N)$ in Eq.(3) actually does depend slightly upon the chain length N. Müller and Binder[13] obtained values for $z(N)$ in bond fluctuation model simulations of one-component melts for several values of N, ranging from $N =20,\ldots,160$. They found that $z(N)$ approaches a finite asymptote z^∞ as $N \to \infty$, and that deviations of $z(N)$ from z^∞ are well approximated by a function of the form

$$z(N) = z^\infty[1 + \beta \bar{N}^{-1/2}] \quad . \quad (5)$$

where $\bar{N} \equiv Nb^6/v^2$, b is the statistical segment length, v is the volume per monomer, and β is a constant that Müller and Binder determined empirically.

In Sec. IV of this paper, we analyze the chain length dependence of the short distance behavior of the intermolecular radial distribution function, and of related quantities such as $z(N)$. Our analysis starts from the (verifiable) assumption that, in a nearly incompressible liquid, the total radial distribution function, including both intra- and inter-molecular contributions, changes extremely little with changes in chain length N. The intramolecular correlation function does, however, change slightly with N, due to changes in the number of chemically distant monomers from the same chain that contribute to the self-concentration around any test monomer. This causes a systematic decrease in the depth of the intermolecular correlation function with decreasing N, and thus an increase in $z(N)$, as as chemically distant intramolecular neighbors are simply replaced by intermolecular neighbors in the immediate environment of any test monomer. The relevant concentration of chemically distant intramolecular neighbors of any test monomer is calculated using a simple random walk model.

We predict that, while z^∞ is a model dependent quantity, the coefficient β in Eq. (5) has a universal value

$$\beta = \left(\frac{6}{\pi}\right)^{3/2} = 2.64 \quad (6)$$

for any structurally symmetric model.

In Secs. V and VI we test our assumptions by comparing the resulting predictions to simulation results. In Sec. V, we verify the accuracy of Eq. (6) by comparing it to the lattice MC results of Müller and Binder. In VI, we present a more extensive comparison to the results of our own off-lattice simulations, which allow us to more directly test the assumptions underlying our analysis.

C. Comparing Blend Simulations to SCFT

Simulations of dense polymer liquids are providing increasingly precise tests of the assumptions underlying SCF theory. Lattice Monte Carlo and continuum simulations of simple coarse-grained models have been used to quantify slight deviations from the random walk model for polymer statistics in melts, and deviations from the RPA description of composition fluctuations in both polymer blends[7,12,13,16] and block copolymer melts[10,18,19,20,21].

In order to compare either simulation or experimental data to SCF predictions for multicomponent systems, however, one must somehow choose values for the SCF interaction free energy $\Delta f_{\text{int}}(\phi, T)$ and/or the effective interaction parameter

$$\chi_e = \frac{-1}{2kT} \frac{\partial \Delta f_{\text{int}}(\phi, T)}{\partial \phi^2} \quad (7)$$

relevant to the RPA analysis of long-wavelength scattering.[1] [Note that, throughout this paper, f and Δf denote free energies per monomer, though we use the same symbols elsewhere to denote free energies per volume.[6]] Because the relationship between $\Delta f_{\text{int}}(\phi, T)$ and the underlying microscopic parameters is never known *a priori*, the temperature and (sometimes) composition dependence of Δf_{int} or χ_e have thus far been determined by fitting RPA predictions to the available measurements of composition fluctuations, in the analysis of either experiment or simulations. The uncertainty introduced by this fitting procedure becomes a potentially serious problem, however, when one's goal is to precisely quantify small deviations from RPA predictions, which is necessary in order to test theories that predict corrections to SCFT, such as the one loop theory. For this purpose, it is would be very useful to have independent way of unambiguously defining and accurately calculating Δf_{int} for a simulation model, using the microscopic information that is available in a simulation. Here, we propose a way of doing this for symmetric models, which is based on an extrapolation of perturbation theory to the infinite chain limit.

SCFT has long been believed to be, in some sense, exact in the limit of infinitely long chains. The basis for this belief is, in part, the predictions of a variety of closely related one-loop theories of fluctuation effects. The one-loop theory[6,22,23,24,25,26] is a coarse-grained theory, that, when properly interpreted[6,26], predicts small corrections to the free energy of an underlying SCF theory. The relative magnitude of the fluctuation correction to the free energy is found[6,23,24,26] to decrease as $N^{-1/2}$ with increasing chain length N, implying that SCFT becomes exact as $N \to \infty$. This idea makes sense, however, only if it is understood that the definition of SCF theory used in the construction of the renormalized one-loop theory[6,26] is one in which Δf_{int} is defined by a process of extrapolation to the infinite chain limit: That is, it makes sense to say that the true free energy f convergences to some form of SCF free energy as $N \to \infty$ only if the relevant SCF is understood to be one whose parameters reflect the liquid structure of a hypothetical system of infinitely long chains.

We propose here that a useful approximation for this asymptotic SCF free energy may be obtained for simple symmetric models by considering perturbative expansions of both Δf_{int} and the true free energy f in powers of α. The idea is to

identify the coefficients in the expansion of Δf_{int} by considering the limiting behavior as $N \to \infty$ of the corresponding coefficients in the expansion of the true free energy for blends of finite chains.

Specifically, we identify the first order contribution to Δf_{int} as the $N \to \infty$ limit of the first order contribution to Eq. (3) for $\Delta f(\phi, N)$. This yields an SCF energy

$$\Delta f_{int} \simeq \alpha z^\infty \phi_A \phi_B + \mathcal{O}(\alpha^2) \tag{8}$$

to first order in α. This first order approximation yields the same dependence on composition as the original Flory-Huggins theory, but reflects the local correlations present in a hypothetical reference system of infinitely long chains.

In Sec. VII, we discuss the relationship between the $\mathcal{O}(N^{-1/2})$ contributions to $z(N)$ in the first order perturbation theory for finite N and the corrections to SCF theory predicted by a renormalized one-loop theory. To test the compatibility of one-loop predictions with our analysis of the perturbation theory, we consider the predictions of the one-loop theory for the value of the derivative $\partial \Delta f / \partial \alpha$ in a symmetric blend with $\alpha = 0$. We find that the one-loop prediction for this quantity is actually *identical* to that given by Eqs. (3), (5), and Eq. (6), with the same value for the numerical coefficient β of the $\mathcal{O}(N^{-1/2})$ correction. This implies that the renormalized one-loop theory correctly describes the chain length dependence of the correlation hole that is discussed here.

II. MODELS AND NOTATION

In what follows, we consider a general class of structurally symmetric binary polymer blends, uisng a similar language for lattice and continuum models. We consider a system containing a total of M structurally identical chains, each containing N monomers, in which $\phi_A M$ are of type A and $\phi_B M$ are of type B. Let α be a small parameter that controls the magnitude of the difference between AB and AA interactions. The state $\alpha = 0$ is thus a ideal mixture of M physically indistinguishable chains, in which a fraction ϕ_A can be chosen to be A chains at random.

A. Lattice Models

We consider a class of lattice models in which double occupancy of lattice sites is forbidden, and in which monomers on neighboring sites of types i and j interact with a pair potential $v_{ij}(\alpha)$ of the form

$$v_{ij}(\alpha) = u + \alpha b_{ij} \quad . \tag{9}$$

Here, u is the interaction between all neighboring monomers, α is a small parameter, and b_{ij} is a symmetric matrix of dimensionless coefficients, with $b_{AB} = b_{BA}$. To maintain the symmetry between the two species, we require that $b_{AA} = b_{BB}$. The value of the parameter u is relevant if and

only if the system contains vacancies, because changes in u can then effect correlations in the one-component reference liquid.

Binder, Deutsch, and Müller[12,13,17] have simulated one variant of the bond fluctuation model in which (in our notation) $b_{AA} = 0$ and $b_{AB} = 1$ and another in which $b_{AB} = 1/2$ and $b_{AA} = -1/2$.

B. Continuum Models

We also consider a class of structurally symmetric continuum models. Consider a system of M chains of length N in a volume V, giving an overall monomer concentration $c = MN/V$ or an average monomer volume $v = 1/c$. The total potential energy is the sum of intramolecular bonding potentials, which are assumed to be the same for A and B chains, plus a sum of nonbonded pair potentials. The pair potential for monomers of type i and j separated by a distance r is assumed to be of the form

$$v_{ij}(r) = u(r) + \alpha b_{ij}(r) \quad , \tag{10}$$

with $b_{AA}(r) = b_{BB}(r)$, where α has units of energy.

In the continuum model of Grest *et al*[16], $v_{ij}(r)$ is taken to be a purely repulsive shifted Lennard-Jones (LJ) interaction, with the same LJ diameter and cutoff distances for all pairs, but with an interaction energy that is slightly larger for AB pairs than for AA or BB pairs. In this model, $b_{AA}(r) = 0$, and $u(r)$ and $b_{AB}(r)$ have the same functional form, differing only by a prefactor. A very similar model is used in our own continuum simulations, which are presented in Sec. VI

C. Correlation Functions

To discuss a perturbation theory for continuum models, it is useful to introduce some notation for inter- and intra-molecular correlations in the the one-component reference liquid, with $\alpha = 0$. Let $g_{\mathrm{inter}}(\mathbf{r}, s, N)$ denote the intermolecular radial distribution function (RDF) for a test monomer with monomer index s in a reference liquid containing chains of length N, defined such that $g_{\mathrm{inter}}(\mathbf{r}, s, N) \to 1$ as $\mathbf{r} \to \infty$. The product $cg_{\mathrm{inter}}(\mathbf{r}, s, N)$ is thus the probability density (probability per volume) of finding any monomer from a different chain separated by a vector $\mathbf{r}$ from such a test monomer. Let $\omega(\mathbf{r}, s, N)$ be an intramolecular correlation function in this reference liquid, defined as the probability density for finding any other monomer from the same chain separated by a vector $\mathbf{r}$ from a test monomer with monomer index s. Let $g_{\mathrm{tot}}(\mathbf{r}, s, N)$ be the total RDF for a test monomer with a specific monomer index s, defined so that

$$cg_{\mathrm{tot}}(\mathbf{r}, s, N) = \omega(\mathbf{r}, s, N) + cg_{\mathrm{inter}}(\mathbf{r}, s, N) \quad , \tag{11}$$

and so that $g_{\mathrm{tot}}(\mathbf{r}, s, N) \to 1$ as $\mathbf{r} \to \infty$. Let $\bar{g}_{\mathrm{inter}}(\mathbf{r}, N)$, $\bar{g}_{\mathrm{tot}}(\mathbf{r}, N)$, and $\bar{\omega}(\mathbf{r}, N)$ denote the averages

of $g_{\text{inter}}(\mathbf{r}, s, N)$, $g_{\text{tot}}(\mathbf{r}, s, N)$, and $\omega(\mathbf{r}, s, N)$, respectively, with respect to s.

III. PERTURBATION THEORY

We consider a first-order perturbation theory for the free energy per monomer

$$f \equiv \frac{-kT}{MN} \ln Z \qquad (12)$$

for either type of model. Here,

$$Z = \int D[\mathbf{R}] e^{-H/kT} \qquad (13)$$

is the partition function, H is the total potential energy and $\int D[\mathbf{R}]$ denotes an integral or (in a lattice model) sum over distinguishable microstates. Differentiation of f with respect to α yields

$$\frac{\partial f}{\partial \alpha} = \theta \qquad (14)$$

where

$$\theta(\phi, \alpha) \equiv \frac{1}{MN} \left\langle \frac{\partial H}{\partial \alpha} \right\rangle \quad . \qquad (15)$$

To first order in α, the free energy per monomer in a system with a composition $\phi \equiv \phi_A$, is thus given by

$$f(\phi, \alpha) \simeq f_0 + \frac{kT}{N} \sum_i \phi_i \ln \phi_i + \alpha \theta(\phi, 0) \qquad (16)$$

Here, f_0 is the free energy per monomer of a corresponding one-component reference state, with $\alpha = 0$, when all of the chains are treated as indistinguishable in the calculation of entropy. The ideal free energy of mixing term accounts for the combinatorial entropy associated with the random labelling of chains as A or B. The quantity $\theta(\phi, \alpha = 0)$ is evaluated in the resulting ideal mixture.

In the simple case of a lattice model with $v_{AA} = u$ and $v_{AB} = u + \alpha$, θ is simply equal to the total number of AB neighbor pairs in the system, divided by the total number MN of monomers.

In a continuum model with $b_{AA} = b_{BB} = 0$, θ is given by the sum of values of $b_{AB}(r)$ for all interacting AB monomer pairs, divided by MN.

The composition dependence of θ within the ideal mixture can be determined by simple combinatorial arguments. To show this, we consider lattice and continuum models separately.

A. Lattice Models

Let $z_c(N)$ be the average number of sites neighboring each monomer that are occupied by monomers from a different chain, evaluated in the reference state $\alpha = 0$ (i.e., the average number of inter-molecular neighbors per monomer). Let $w_c(N)$ be the average number of neighboring sites that are occupied by monomers from the same chain (the average number of intra-molecular neighbors). Let

$$y_c(N) = z_c(N) + w_c(N) \qquad (17)$$

be the average total number of occupied neighbors. In the absence of vacancies, $y_c(N)$ must equal the latice coordination number.

In the reference state, the labelling of chains as type A or B is random. The probability that any given pair of inter-molecular neighbors will belong to different chains labelled with types i and j, respectively, is thus simply $\phi_i \phi_j$. Similarly, the probability that any two intramolecular neighbors will belong to a chain of type i is simply ϕ_i. Thus, for $\alpha = 0$,

$$\theta = \frac{1}{2} w(N) \sum_i \phi_i b_{ii} + \frac{1}{2} z(N) \sum_{ij} \phi_i \phi_j b_{ij} \quad , \qquad (18)$$

The prefactors of $1/2$ correct for the double counting of pairs. A bit of rearrangement yields

$$\theta = \frac{1}{2} y(N) + z(N) \phi_A \phi_B \quad , \qquad (19)$$

where we have defined

$$\begin{aligned} y(N) &\equiv y_c(N) b_{AA} \\ z(N) &\equiv z_c(N)(b_{AB} - b_{AA}) \quad . \end{aligned} \qquad (20)$$

The free energy per monomer is thus given to first order in α by

$$f \simeq f_0 + \frac{1}{2} \alpha y(N) + \Delta f \quad , \qquad (21)$$

where Δf is given by Eq. (3), with the definition of $z(N)$ discussed above. The resulting first order expansion of Δf is identical to the modified Flory-Huggins approximation of Müller and Binder.[13]

B. Continuum Models

In a continuum model, for any value of α,

$$\theta = \frac{v}{2} \sum_{ij} \int d\mathbf{r} \, \langle c_i(\mathbf{r}) c_j(0) \rangle b_{ij}(\mathbf{r}) \quad , \qquad (22)$$

where $c_i(\mathbf{r})$ is the instantaneous concentration of monomers of type i and $v = V/MN$ is the volume per monomer. In an ideal mixture, with $\alpha = 0$, random labelling of a fraction ϕ_A of the chains as A and the remainder as B yields

$$\langle c_i(\mathbf{r}) c_j(0) \rangle = \delta_{ij} c\bar{\omega}(\mathbf{r}, N) \phi_i + c^2 \bar{g}_{\text{inter}}(\mathbf{r}, N) \phi_i \phi_j \quad . \qquad (23)$$

Using expression in Eq. (22) yields an expression for $\theta(\phi, 0)$ of the same form as that given in Eq. (19), and a free energy of the form given in Eqs. (21) and (3), in which the quantities $y(N)$ and $z(N)$ are given for a continuum model by the integrals

$$
\begin{aligned}
y(N) &\equiv c \int d\mathbf{r}\, \bar{g}_{\text{tot}}(\mathbf{r}) b_{AA}(\mathbf{r}) \\
z(N) &\equiv c \int d\mathbf{r}\, \bar{g}_{\text{inter}}(\mathbf{r}) \Delta b(\mathbf{r}) \quad,
\end{aligned} \tag{24}
$$

where

$$
\Delta b(\mathbf{r}) \equiv b_{AB}(\mathbf{r}) - b_{AA}(\mathbf{r}) \quad. \tag{25}
$$

In what follows, we will also consider the analogous quantities

$$
\begin{aligned}
y(s, N) &\equiv c \int d\mathbf{r}\, g_{\text{tot}}(\mathbf{r}, s, N) b_{AA}(\mathbf{r}) \\
z(s, N) &\equiv c \int d\mathbf{r}\, g_{\text{inter}}(\mathbf{r}, s, N) \Delta b(\mathbf{r}) \quad,
\end{aligned} \tag{26}
$$

for a test monomer with a known monomer index s, with $1 \leq s \leq N$.

IV. DEPENDENCE OF LOCAL LIQUID STRUCTURE ON CHAIN LENGTH

In this section, we consider how properties of a one-component melt that are sensitive to short range correlations, such as $z(N)$, depend upon overall chain length N. Our reasoning applies equally well to lattice and continuum models, but we will hereafter adopt a notation appropriate to a continuum model. To proceed, we first consider how the intramolecular correlation function $\omega(\mathbf{r}, s, N)$ depends upon s and N, and then consider how this translates into a corresponding s- and N-dependence of $g_{\text{inter}}(\mathbf{r}, s, N)$.

A. Intra-molecular distribution

Each monomer in the one-component reference liquid is surrounded by a concentration $\omega(\mathbf{r}, s, N)$ of other monomers from the same chain, in addition to a concentration $c g_{\text{inter}}(\mathbf{r}, s, N)$ of monomers from other chains. Let

$$
\omega(\mathbf{r}, s, N) \equiv \sum_{s'} P(\mathbf{r}, s', s, N) \tag{27}
$$

where $P(\mathbf{r}, s', s, N)$ is probability density of finding a specific pair of monomers from the same chain, with monomer indices s' and s, separated by a vector $\mathbf{r}$. The distribution $\omega(\mathbf{r}, s, N)$ is dominated, for small values of $\mathbf{r}$, by contributions from monomers for which $|s' - s|$ is small. As a result, for monomers that are far from either chain end (i.e., far from

$s = 1$ and $s = N$), $\omega(\mathbf{r}, s, N)$ depends only weakly on chain length N and index s.

In the limit $N \to \infty$, $P(\mathbf{r}, s, s', N)$ approaches a function

$$
P^\infty(\mathbf{r}, |s - s'|) \equiv \lim_{N \to \infty} P(\mathbf{r}, s, s', N) \tag{28}
$$

that depends only on $|s - s'|$, and $\omega(\mathbf{r}, s, N)$ approaches a function

$$
\omega^\infty(\mathbf{r}) \equiv \lim_{N \to \infty} \omega(\mathbf{r}, s = N/2, N) \tag{29}
$$

that is independent of s, for s not too close to either chain end.

For finite chains, $\omega(\mathbf{r}, s, N)$ contains a small correction to $\omega^\infty(\mathbf{r})$, which depends upon both s and N. Let

$$
\delta\omega(\mathbf{r}, s, N) \equiv \omega^\infty(\mathbf{r}) - \omega(\mathbf{r}, s, N) \quad, \tag{30}
$$

where $\omega^\infty(\mathbf{r})$ and $\omega(\mathbf{r}, s, N)$ are evaluated at the same temperature and concentration. To estimate $\delta\omega(\mathbf{r}, s, N)$, we assume that infinite chains and long finite chains have very similar conformational statistics. We thus approximate the difference $\delta\omega(\mathbf{r}, s, N)$ for monomers that are not too close to either chain end by the contributions to $\omega^\infty(\mathbf{r})$ from monomers with $s' \leq 0$ and $s' > N$. In this approximation,

$$
\delta\omega(\mathbf{r}, s, N) \simeq \sum_{s'=-\infty}^{0} P^\infty(\mathbf{r}, \Delta s) + \sum_{s'=N+1}^{\infty} P^\infty(\mathbf{r}, \Delta s) \quad, \tag{31}
$$

where $\Delta s \equiv |s' - s|$. The content of this equation is shown schematically in Fig. 1.

For values of $\Delta s \gg 1$, we may further approximate $P^\infty(\mathbf{r}, \Delta s)$ by a Gaussian distribution

$$
P_{\text{id}}(\mathbf{r}, \Delta s) = \left(\frac{3}{2\pi \Delta s b^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2\Delta s b^2}\right) \quad, \tag{32}
$$

for a continuous random walk, with $\Delta s = |s - s'|$. The use of random walk statistics is justified by the fact that, for $s \gg 1$ and $|N - s| \gg 1$, $|s' - s| \gg 1$ for every term in the relevant sums. In the same limit, we may also approximate sums over s' by integrals to obtain an analytic approximation for $\delta\omega_{\text{id}}(\mathbf{r}, s, N)$. Here and hereafter, a subscript id (for "ideal") is used to indicate approximations obtained using this idealized continuous random-walk chain model.

The effective coordination number $z(s, N)$ is sensitive only to the distribution of monomers that lie within the range of the pair potential from a test monomer. To characterize how the self-concentration $\omega(\mathbf{r}, s, N)$ within this small region depends upon s and N, we consider the s- and N-dependence of the distribution $\delta\omega_{\text{id}}(\mathbf{r} = 0, s, N)$ for a random walk, evaluated at the the position $\mathbf{r} = 0$ of the test monomer. The random-walk model yields a deviation

$$
\begin{aligned}
\delta\omega_{\text{id}}(0, s, N) &= \left(\frac{3}{2\pi b^2}\right)^{3/2} \left[\int_s^\infty \frac{d\Delta}{\Delta^{3/2}} + \int_{N-s}^\infty \frac{d\Delta}{\Delta^{3/2}}\right] \\
&= \left(\frac{3}{2\pi}\right)^{3/2} \frac{2}{b^3} \left[\frac{1}{\sqrt{s}} + \frac{1}{\sqrt{N-s}}\right] \quad, \tag{33}
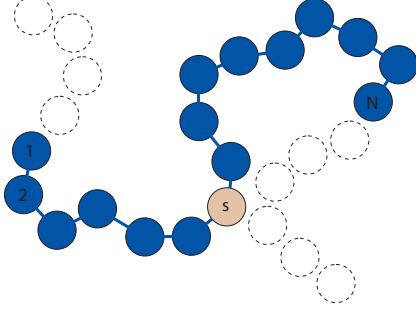\end{aligned}
$$

FIG. 1: Schematic view of Eq. (31) for the difference $\delta\omega(\mathbf{r}, s, N)$ between the intramolecular function $\omega^\infty(\mathbf{r})$ for an infinite chain and the corresponding correlation function $\omega(\mathbf{r}, s, N)$ for monomer s on a chain of length N. This difference is attributed to the contributions to $\omega^\infty(\mathbf{r})$ of the monomers $s \leq 0$ and $s > N$ that are "missing" from the finite chain. The concentration of these missing monomers near the test monomer (i.e., near $\mathbf{r} = 0$) can be estimated using a random walk model, if s is not too near either chain end. As the chain length is decreased from ∞, chemically distant monomers from the same chain are simply replaced by monomers from other chains, while leaving the total RDF $g_{\text{tot}}(\mathbf{r}, s, N)$ almost unchanged.

where $\Delta \equiv |s - s'|$. The random walk approximation clearly breaks down for s near the chain ends, as expected on physical grounds, since Eq. (33) predicts a $1/\sqrt{s}$ divergence at either chain end.

The free energy will be shown to depend upon on the average value

$$\delta\bar{\omega}(\mathbf{r}, N) \equiv \frac{1}{N} \sum_s \delta\omega(\mathbf{r}, s, N) \quad . \tag{34}$$

Using the above random walk model for $\delta\omega(\mathbf{r} = 0, s, N)$ yields

$$\delta\bar{\omega}_{\text{id}}(\mathbf{r} = 0, N) = \frac{1}{v} \left(\frac{6}{\pi}\right)^{3/2} \frac{1}{\bar{N}^{1/2}} \tag{35}$$

in which $\bar{N} \equiv N b^6 / v^2$. The quantity $v\delta\bar{\omega}_{\text{id}}(\mathbf{r} = 0, N) = (6/\pi)^{3/2}\bar{N}^{-1/2}$ is the corresponding volume fraction of the "missing" monomers in the vicinity of a randomly chosen test monomer.

Note that the integral with respect to s required to calculate $\omega_{\text{id}}(\mathbf{r} = 0, N)$ converges, despite the divergence of Eq. (33) for the integrand at both chain ends. This reflects the fact that the average with respect to s is dominated not by the contributions of a few monomers near the chain ends, but by that of many interior monomers. As a result, our use of a random walk model is sufficiently accurate to correctly calculate the prefactor of the dominant $\mathcal{O}(N^{-1/2})$ to $\delta\omega(\mathbf{r} = 0, s, N)$.

Further corrections that arise from the breakdown of the random walk model near both chain ends are expected to yield subdominant contributions of $\mathcal{O}(N^{-1})$.

B. Inter-molecular distribution

We now consider how the N-dependence of the intramolecular correlation function is reflected in intermolecular correlations.

1. A simple argument for $z(N)$

Each monomer in a dense melt is surrounded by an environment that contains both monomers from other chains and chemically distant monomers from the same chain. Near any test monomer, the local concentration of chemically distant monomers from the same chain is lower than that found for an infinite chain by a concentration $\delta\omega(0, s, N)$, which is calculated above. We assume that, in an incompressible liquid, this decrease in the self-concentration of a finite chain with decreasing N must be almost exactly compensated by a corresponding increase in the concentration of inter-molecular near neighbors. We assume furthermore that, in a structurally symmetric model with $\alpha = 0$, the contribution of chemically distant monomers on the same chain to the overall radial distribution function $g_{\text{tot}}(\mathbf{r}, s, N)$ within the small region near a test monomer that lies within the range of the potential is the same, per monomer, as the contribution of monomers from other chains. Only intermolecular near neighbors, however, contribute to the quantity $z(N)$. We thus expect a decrease in the local self-concentration by a volume fraction $v\delta\omega(0, s, N)$ is to increase the effective coordination number by a fractional amount $v\delta\omega(0, s, N)$, due to a direct replacement of chemically distant intramolecular neighbors by intermolecular neighbors. This yields a predicted coordination number

$$z(N) = z^\infty[1 + v\delta\bar{\omega}(0, s, N)] \tag{36}$$

or

$$z(N) \simeq z^\infty \left[1 + \left(\frac{6}{\pi}\right)^{3/2} \frac{1}{\bar{N}^{1/2}}\right] \quad , \tag{37}$$

where z^∞ is the limiting value of $z(N)$ in the limit $N \to \infty$.

2. A more detailed view

The same conclusion may be obtained from a set of more explicit assumptions about intra- and inter-molecular correlation functions in a dense liquid. Let $g_{\text{tot}}^\infty(\mathbf{r})$ and $g_{\text{inter}}^\infty(\mathbf{r})$ denote the limits of the g_{tot} and g_{inter}, respectively, in the limit $N \to \infty$. The value of $z(N)$ depends only upon the behavior

of the intermolecular distribution $g_{\text{inter}}(\mathbf{r}, s, N)$ for small $\mathbf{r}$, for which $|\mathbf{r}|$ is less than the range of the pair potential. We make the following assumptions about how the small-$|\mathbf{r}|$ behavior of $g_{\text{tot}}^\infty(\mathbf{r}, s, N)$ and $g_{\text{inter}}(\mathbf{r}, s, N)$ depends upon chain length, in a dense melt in which the polymer coil size $\sqrt{N}b$ is much larger than the range of the pair potential:

(1) In an almost incompressible liquid, we assume that the total RDF $g_{\text{tot}}(\mathbf{r}, s, N)$ is almost independent of both s and N, except for monomers very close to one of the chain ends. In this problem, this is what is meant when we say that the melt is effectively "incompressible". If true, this implies that

$$g_{\text{tot}}(\mathbf{r}, s, N) \simeq g_{\text{tot}}^\infty(\mathbf{r}) \quad , \qquad (38)$$

for all monomers except a few near the chain ends. For this to be true for all N, however, the decrease in the intramolecular self-concentration $\omega(\mathbf{r}, s, N)$ with decreasing N must be exactly compensated by an increase in $cg_{\text{inter}}(\mathbf{r}, s, N)$. This implies

$$cg_{\text{inter}}(\mathbf{r}, s, N) \simeq cg_{\text{inter}}^\infty(\mathbf{r}) + \delta\omega(\mathbf{r}, s, N) \quad , \qquad (39)$$

where $\delta\omega(\mathbf{r}, s, N)$ is defined by Eq. (30).

Corrections to assumption (38) can arise, even for values of s that are far from either chain end, from contributions to $g_{\text{tot}}^\infty(\mathbf{r}, s, N)$ due to correlations between an interior monomer test monomer and an end monomer. The resulting end-effect corrections (discussed in more detail in the subsection) are of order $1/N$, and are found to be negligible compared to the $1/\sqrt{N}$ corrections that are obtained from the N dependence of $\delta\omega(\mathbf{r}, s, N)$.

(2) The spatial distribution around a test monomer of chemically distant monomers from the same chain is assumed to closely mimic the local distribution g_{inter} of monomers from other chains, which we can approximate by the RDF $g_{\text{inter}}^\infty(r)$ for a system of infinite chains. We thus assume that the distribution $\delta\omega(\mathbf{r}, s, N)$ of the chemically distant "missing" monomers (those that must be removed from an infinite chain to form the finite chain of interest) is of the form

$$\delta\omega(\mathbf{r}, s, N) \propto g_{\text{inter}}^\infty(\mathbf{r}) \qquad (40)$$

for large N, values of s far from either chain end, and values $|\mathbf{r}|$ less than the range of the potential.

(3) The constant of proportionality in Eq. (40) depends on an overall concentration of "missing" monomers over a region larger than the range of the potential. We assume that an average concentration of missing monomers near a test monomer can be obtained by using the random-walk model for the return probability $\delta\omega(\mathbf{r} = 0, s, N)$. More precisely, we assume that

$$\delta\omega(\mathbf{r}, s, N) \simeq \delta\omega_{\text{id}}(0, s, N)g_{\text{inter}}^\infty(\mathbf{r}) \qquad (41)$$

under the same conditions that Eq. (40) applies.

By combining assumptions (39) and (41), we find that

$$g_{\text{inter}}(\mathbf{r}, s, N) \simeq g_{\text{inter}}^\infty(\mathbf{r})\left[\,1 + v\delta\omega_{\text{id}}(0, s, N)\,\right] \qquad (42)$$

Using this approximation yields

$$z(s, N) \simeq z^\infty\left[1 + v\delta\omega_{\text{id}}(0, s, N)\right] \quad , \qquad (43)$$

where $\omega_{\text{id}}(0, s, N)$ is given by Eq. (33), where

$$z^\infty \equiv c \int d\mathbf{r}\, g_{\text{inter}}^\infty(\mathbf{r})\Delta b(\mathbf{r}) \quad . \qquad (44)$$

Averaging with respect to N yields Eq. (37).

C. End Effects

In addition to the dominant $\mathcal{O}(\bar{N}^{-1/2})$ corrections to $z(N)$ predicted above, we also expect to find subdominant $\mathcal{O}(1/N)$ corrections to both $y(N)$ and $z(N)$ that arise from true end effects, due to the perturbation of the liquid structure near chain ends.

First, consider the contribution of end-effects to the total correlation function $g_{\text{tot}}(\mathbf{r}, s)$, and to the corresponding integral $y(s, N)$. Let $g_{\text{tot}}(\mathbf{r}, s, s', N)$ be a distribution function for pairs of monomers with specified monomer indices s and s', defined so that $(c/N)g_{\text{tot}}(\mathbf{r}, s, s', N)$ is the probability per unit volume of finding any monomer with index s' separated by $\mathbf{r}$ from a test monomer with index s, and so that

$$g_{\text{tot}}(\mathbf{r}, s) = \frac{1}{N}\sum_{s'} g_{\text{tot}}(\mathbf{r}, s, s', N) \qquad (45)$$

We assume that the deviation of $g_{\text{tot}}(\mathbf{r}, s, s', N)$ from $g_{\text{tot}}^\infty(\mathbf{r})$ is dominated by pairs of values where either s or s' (but not both) are near one of the chains, and the other is somewhere in the interior of the chain. Reflecting this assumption, we assume that $g_{\text{tot}}(\mathbf{r}, s, s', N)$ can be approximated by a function of the form

$$g_{\text{tot}}(\mathbf{r}, s, s', N) = g_{\text{tot}}^\infty(\mathbf{r}) + \delta g_{\text{end}}(\mathbf{r}, s) + \delta g_{\text{end}}(\mathbf{r}, s') \quad (46)$$

where $\delta g_{\text{end}}(\mathbf{r}, s)$ is a deviation that is large only for s near 1 or N, and vanishes for interior monomers. This functional form assumes that the correction $\delta g_{\text{end}}(\mathbf{r}, s)$ that arises from s near one of the chain ends is independent of s' when s' is an interior monomer, and similarly for the correction $\delta g_{\text{end}}(\mathbf{r}, s')$. This approximation captures the dominant $\mathcal{O}(N^{-1})$ corrections to $\bar{g}_{\text{tot}}(\mathbf{r})$, but ignores smaller $\mathcal{O}(N^{-2})$ corrections arising from contributions in which both s and s' are near chain ends. Within this $\mathcal{O}(N^{-1})$ approximation, evaluating the sum with respect to s' yields

$$g_{\text{tot}}(\mathbf{r}, s) = g_{\text{tot}}^\infty(\mathbf{r}) + \delta g_{\text{end}}(\mathbf{r}, s) + \frac{1}{N}d_{\text{end}}(\mathbf{r}) \qquad (47)$$

where

$$d_{\text{end}}(\mathbf{r}) \equiv \sum_{s'} \delta g_{\text{end}}(\mathbf{r}, s') \quad . \qquad (48)$$

Within the above approximation, we thus predict that, for interior monomers, $g_{\text{tot}}(\mathbf{r}, s)$ should deviate from $g_{\text{tot}}^\infty(\mathbf{r})$ by an amount that is proportional to $1/N$ but independent of s.

This approximation for $g_{\text{tot}}(\mathbf{r}, s)$ also implies that we expect to find

$$y(s, N) \simeq y^{\infty} + \frac{\delta}{N} \quad , \tag{49}$$

for interior monomers. The $1/N$ correction to $y(s, N)$ for interior monomers is the result of occasional close contact between an interior test monomers and end monomers, and is assumed to be independent of the monomer index s of the interior test monomer. In addition, we expect to see a much larger $\mathcal{O}(1)$ deviation from y^{∞} for the last few monomers at either chain end.

Similar reasoning suggests that the quantity $z(s, N)$ for s far from either chain end should also exhibit an $\mathcal{O}(1/N)$ contribution, due to close contacts between the interior test monomer and end monomers of other chains, in addition to the $\mathcal{O}(N^{-1/2})$ correction described above. The same reasoning suggests that this $\mathcal{O}(1/N)$ correction for interior monomers should be independent of s, implying a functional form

$$z(s, N) \simeq z^{\infty} [\, 1 + v\delta\omega_{\text{id}}(0, s, N)\,] + \frac{\gamma}{N} \tag{50}$$

in which z^{∞} and γ are material parameters.

V. COMPARISON TO LATTICE SIMULATIONS

Fig. 2 shows a comparison of theoretical predictions to the lattice Monte Carlo results of Müller and Binder[13] for $z(N)$ for two different variants of the bond fluctuation model. In both variants of the model, a monomer is taken to occupy 8 sites within a cubic lattice, from which other monomers are excluded. The volume fraction of occupied sites is 50%. The top panel of Fig. 2 shows results for $z(N)$ for chains of length $N = 20, \ldots, 160$ for a model in which each monomer interacts with monomers that are located at any of 54 neighbors. The bottom panel shows results for a model in which each monomer interacts only with monomers at the 6 nearest possible positions in a cubic lattice. We have compared both sets of data to a prediction

$$z(N) \simeq z^{\infty} \left[1 + \beta \bar{N}^{-1/2} \right] + \gamma'/N \quad , \tag{51}$$

in which β is given by Eq. (6), but in which z^{∞} and γ' are treated as adjustable parameters. The γ'/N term is included to account both for the $1/N$ contribution to Eq. (50) for interior monomers, and for contributions to the average over s arising from $\mathcal{O}(1)$ deviations from z^{∞} for monomers near either chain end.

In the absence of a prediction for the coefficient β, Müller and Binder fit each of these data sets to a function $z(N) = z^{\infty}[1 + \beta_{fit} \bar{N}^{-1/2}]$, while treating both z^{∞} and β_{fit} as adjustable parameters. This yields best fit parameters $\beta_{fit} = 2.846$ for z^{54} and $\beta_{fit} = 3.330$ for z^6 slightly higher than
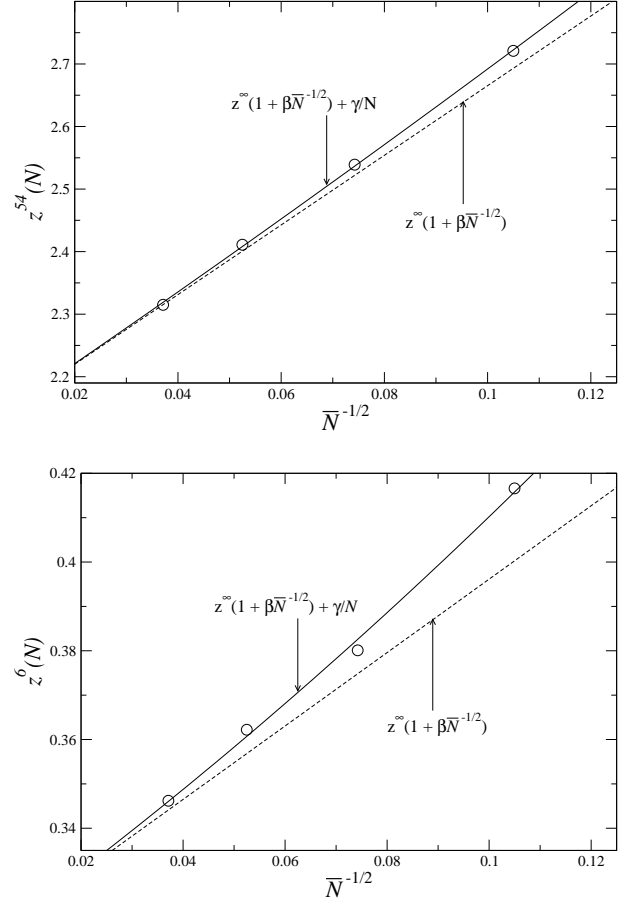

FIG. 2: Lattice MC results of Müller and Binder[13] for $z(N)$ (symbols) vs. $\bar{N}^{-1/2}$ for two different variants of the bond fluctuation model. The top panel shows results for a model in which each site interacts with monomers located on any of 54 nearby sites, while the bottom shows results for a model in which each site can interact with only 6 neighboring sites. In each panel, the solid line is a best fit to Eq. (51), using the predicted value of $\beta = (6/\pi)^{3/2}$. This fit yields $z^{\infty} = 2.109$ and $\gamma' = 0.588$ for the model with 54 neighbors and $z^{\infty} = 0.3134$ and $\gamma' = 0.310$ for the model with 6 neighbors. Dashed lines show the estimated asymptote $z^{\infty}[1 + \beta \bar{N}^{-1/2}]$, with the same value for z^{∞}, in order to show the predicted asymptotic slope.

the predicted value of 2.64. The quality of the fit is approximately the same with either functional form.

Our predictions of a univeral value for the asymptotic slope in these plots is consistent with this data. Inclusion of the $1/N$ end correction is necessary to adequately fit this data for modest values of N, however, particularly for the model with very short range interactions.

VI. CONTINUUM SIMULATIONS

In order to test the predictions of Sec. IV in more detail, we have also conducted off-lattice Monte Carlo simulations

of a simple bead-spring model.

Our simulations use a model of flexible polymers with a short-range repulsive nonbonded pair potential and a harmonic bond potential. The non-bonded pair potential $v_{\text{pair}}(r)$ in our one-component reference liquid is a purely repulsive shifted Lennard-Jones potential, of the form

$$
\begin{aligned}
v_{\text{pair}}(r) &= \epsilon F(r) \\
F(r) &= 4[(\sigma/r)^{12} - (\sigma/r)^6] + 1
\end{aligned}
\tag{52}
$$

for r less than than a cutoff $r_c = \sigma 2^{1/6}$, and $v_{\text{pair}}(r) = F(r) = 0$ for $r > r_c$. The bond potential is a harmonic spring,

$$
v_{\text{bond}}(r) = \frac{1}{2}\kappa(r - l)^2 \quad .
\tag{53}
$$

All of our simulations have used parameter $\epsilon = kT$, $l = \sigma$, and $\kappa = 400kT$.

We have simulated chains of of length $N = 16, 32, 64, 128$, and 256 at a fixed monomer concentration of $c = 0.7\sigma^{-3}$. For these parameters, we obtain an asymptotic statistical segment length $b = 1.335$, which was obtained by extrapolating the slope of a plot of mean squared end-to-end vector versus N to $N = \infty$. All simulations use a cubic $L \times L \times L$ simulation cell with periodic boundary conditions. We have simulated systems containing $M = 1176, 588\ 294, 146$, and 146 chains for $N = 16, 32, 64, 128$, and 256, respectively. This correspond to $L \simeq 29.955\sigma$ for $N \leq 128$, and $L \simeq 37.7$ for $N = 256$. The Monte Carlo simulations reported here were carried out using a combination of hybrid Monte Carlo / Molecular Dynamics (MC/MD), reptation, and double-rebridging[27] moves.

Fig. 3 shows the distribution functions $\bar{g}_{\text{tot}}(\mathbf{r})$ and $\bar{g}_{\text{inter}}(\mathbf{r})$ in the one-component liquid for chains of length $N = 16, \ldots, 256$. Results for $\bar{g}_{\text{tot}}(\mathbf{r})$ for chains of different length are indistinguishable at the scale of the main plot, but the correlation hole in $\bar{g}_{\text{inter}}(\mathbf{r})$ becomes visibly deeper with increasing N. The slight dependence of $\bar{g}_{\text{tot}}(\mathbf{r}, N)$ on N is visible in the inset.

A. Intermolecular Coordination Number

We consider a perturbation theory for a model of blends in which the nonbonded pair potential is of the form used by Grest and Lacasse[16]. In this model, the pair potential for i and j monomers is taken to be a repulsive LJ potential $v_{ij}(r) = \epsilon_{ij}F(r)$, where $F(r)$ is given by Eq. (52), in which $\epsilon_{AA} = \epsilon_{BB} = \epsilon$ and $\epsilon_{AB} = \epsilon + \alpha$, while the same LJ diameter σ and cutoff distance $r_c = 2^{1/6}\sigma$ is used for all i and j. For this model,

$$
z(s, N) = c \int d\mathbf{r}\, g_{\text{inter}}(\mathbf{r}, s, N)F(r) \quad ,
\tag{54}
$$

and $z(N)$ is the corresponding average with respect to s.

Fig. 4 shows our results for $z(N)$. To compare this data to theoretical predictions, we have fit values of $z(N)$ for all but
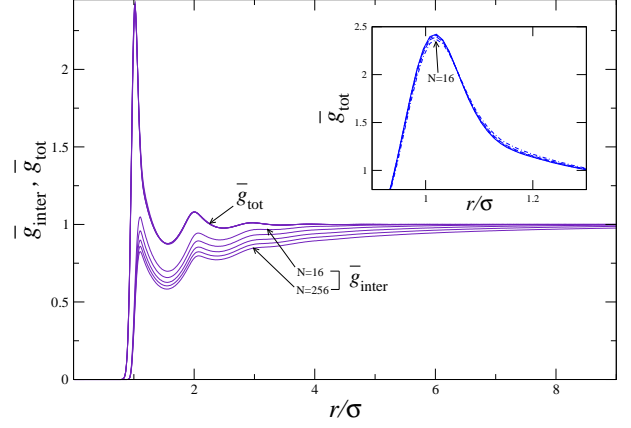

FIG. 3: Intermolecular and total radial distribution functions $\bar{g}_{\text{inter}}(\mathbf{r})$ and $\bar{g}_{\text{tot}}(\mathbf{r})$ for chains of length $N = 16, \ldots, 256$. Results for $\bar{g}_{\text{tot}}(\mathbf{r})$ for chains of different length are indistinguishable in the main plot. Inset: $\bar{g}_{\text{tot}}(\mathbf{r})$ in an expanded scale, in which the slight dependence on N is visible.
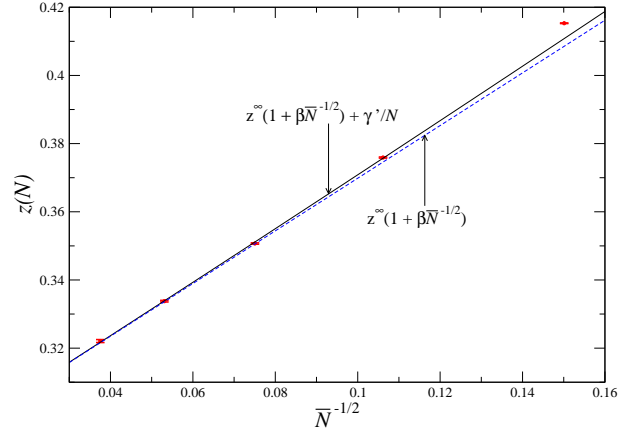

FIG. 4: Simulation results for $z(N)$ (symbols) vs. $\bar{N}^{-1/2}$, compared to the prediction of Eq. (51), using the predicted value of $\beta = (6/\pi)^{3/2}$. A best fit to the four longest chain lengths ($N = 32, \ldots, 256$), shown by the solid line, yields parameters $z^{\infty} = 0.2926$ and $\gamma' = 0.0361$. The dashed line is the asymptotic line $z^{\infty}[1 + \beta\bar{N}^{-1/2}]$, with the same values for z^{∞} and β. Error bars are shown, but are very small on this scale.

the shortest chain ($N = 16$) to Eq. (51). We chose to exclude the data for $N = 16$ from this fit because the predictions are an asymptotic expansion that is expected to be accurate only for sufficiently long chains, and because excluding the shortest chains from this data substantially improved the quality of the fit. The fit for the 4 longest chains, $N = 32, \ldots, 256$, agrees with the data to within our (very small) statistical errors.

Fig. 5 shows a corresponding comparison of theoretical predictions to simulation results for the quantity

$$
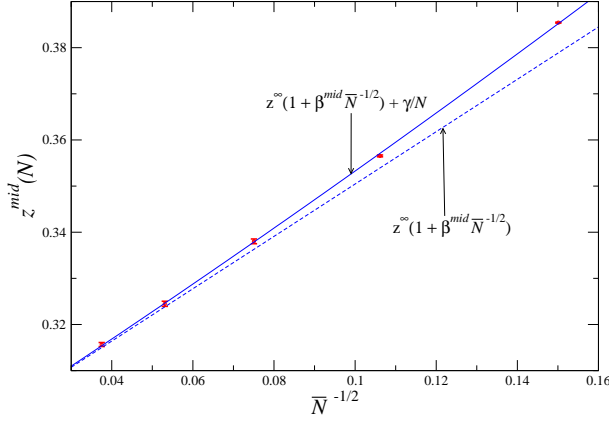z^{mid}(N) \equiv \frac{2}{N} \sum_{s=N/4+1}^{3N/4} z(s, N) \quad .
\tag{55}
$$

FIG. 5: Simulation results for $z^{mid}(N)$ (symbols) vs. $\bar{N}^{-1/2}$, compared to the prediction of Eq. (56), using Eq. (57) for β^{mid}. A best fit, shown by the solid line, yields parameters $z^\infty = 0.2937$ and $\gamma = 0.1014$. The dashed line is the asymptote $z^\infty[1 + \beta\bar{N}^{-1/2}]$.

This is the average of $z(s, N)$ over the middle half of each chain. This quantity, unlike the average $z(N)$ over all monomers, excludes contributions from monomers very near the chain ends. By using Eq. (50) for $z(s, N)$, and approximating the sum over s in Eq. (55) by an integral over $N/4 < s < 3N/4$, we obtain a predicted N-dependence

$$z^{mid}(N) = z^\infty \left[1 + \beta^{mid}\bar{N}^{-1/2}\right] + \frac{\gamma}{N} \quad , \quad (56)$$

in which

$$\beta^{mid} \equiv (\sqrt{3} - 1)\left(\frac{6}{\pi}\right)^{3/2} = 1.932 \quad . \quad (57)$$

The approximation of a sum over s by an integral gives rise to errors of $\mathcal{O}(N^{-3/2})$, which lie beyond the $\mathcal{O}(1/N)$ accuracy of Eq. (50) for the summand $z(s, N)$. Because the sum over s that defines $z^{mid}(N)$ only includes interior monomers, for which we expect Eq. (50) for $z(s, N)$ to be valid, we may identify the constant γ in this fit with the constant γ in Eq. (50). The prediction fits the data for all $N = 16, \ldots, 256$ to within the (small) statistical errors. A fit of the same data to $z^\infty[1 + \beta_{fit}^{mid}\bar{N}^{-1/2}]$, in which β_{fit}^{mid} is treated as an adjustable parameter, yields a slightly worse fit, and a value $\beta^{mid} = 2.1233$ slightly higher than the predicted value of β^{mid}.

Fig. 6 shows our simulation results for $z(s, N)$ for monomers $s = 1, \ldots, N/2$ on chains of length $N = 16, \ldots, 256$. Results for each chain length are compared to the predictions of Eq. (50), shown by dashed lines. Values for the two parameters z^∞ and γ have been taken from the fit of $z^{mid}(N)$ shown in Fig. 5. Because Eq. (33) for $\delta\omega_{\rm id}(0, s, N)$ was derived using continuous Gaussian chain model, and yields a value that diverges at both chain ends, we have taken

$$\delta\omega_{\rm id}(0, s, N) = \left(\frac{3}{2\pi}\right)^{3/2}\frac{2}{b^3}\left[\frac{1}{\sqrt{s - a}} + \frac{1}{\sqrt{N + a - s}}\right] , \quad (58)$$
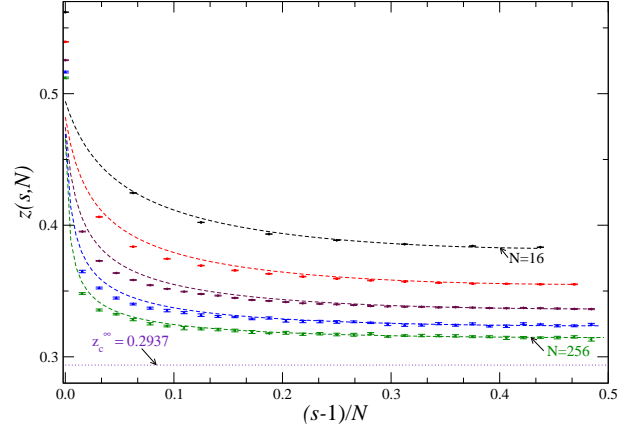

FIG. 6: Simulation results for $z(s, N)$ (symbols) vs. s, for $s = 1, \ldots, N/2$ and chains of length $N = 16, \ldots, 256$, compared to the prediction of Eqs. (50) and (58), shown by dashed lines. Values for the two parameters z^∞ and γ were taken from the fit of $z^{mid}(N)$ shown in Fig. 5.

to apply Eq. (33) to a discrete chain with monomer indices $s = 1, \ldots, N$, with $a = 1/2$. Different choices for the value of the offset a yield predictions that differ by a correction of $\mathcal{O}(N^{-3/2})$. The value $a = 1/2$ was chosen to minimize the discretization error arising from our use of integral to approximate a sum over s in the derivation of Eq. (56).

Agreement between this data for $z(s, N)$ and Eq. (50) is excellent for all N, and for all s except values near the chain ends, for which all analytic approximations are expected to fail.

B. Total Coordination Number

We have also considered a quantity

$$y(s, N) = c\int d\mathbf{r}\, g_{\rm tot}(\mathbf{r}, s, N)F(r) \quad (59)$$

that depends on the total RDF $g_{\rm tot}$. For the blend model considered here, for which $b_{AA}(\mathbf{r})$, the quantity $y(N)$ that appears in the perturbation theory actually vanishes. We have nonetheless considered the quantity defined above as a way to test our assumptions about the chain length dependence of $g_{\rm inter}(\mathbf{r}, s, N)$.

Fig. 7 shows our results for the average

$$y^{mid}(N) \equiv \frac{2}{N}\sum_{s=N/4+1}^{3N/4} y(s, N) \quad (60)$$

of the total coordination number $y(s, N)$ over the middle half of each chain, and for $y(s, N)$ itself, respectively. Results for $y^{mid}(N)$ have been fit to a predicted form $y^{mid}(N) = y^\infty + \delta/N$, which follows immediately from Eq. (49) for
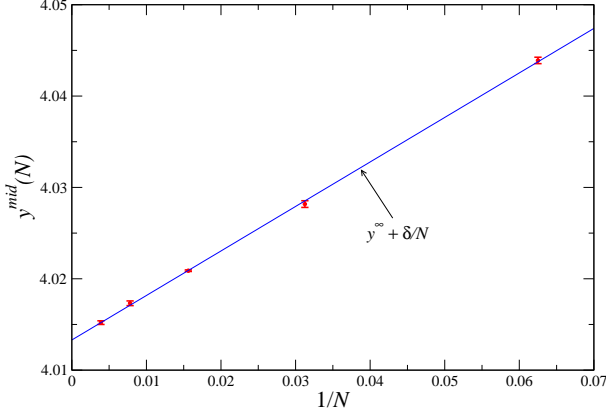
FIG. 7: Simulation results for $y^{mid}(N)$ (symbols) vs. $1/N$. A best fit to $y^{mid}(N) = y^{\infty} + \delta/N$, shown by the solid line, yields parameters $y^{\infty} = 4.0133$ and $\delta = 0.4872$.
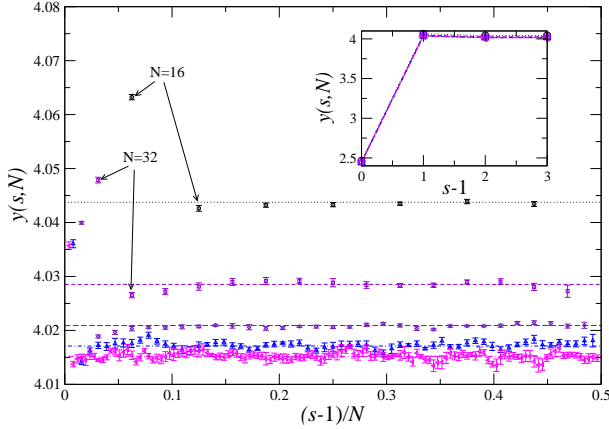

FIG. 8: Simulation results for $y(s, N)$ (symbols) vs. s for $s = 1, \ldots, N/2$ and $N = 16, \ldots, 256$, compared to the prediction $y(s, N) = y^{\infty} + \delta/N$ (dashed lines). Values for the parameters y^{∞} and δ were taken from the fit shown in Fig. 8.

$y(s, N)$ for interior monomers. Note that the fractional deviations of $y^{mid}(N)$ from y^{∞} are much smaller than those found for $z^{mid}(N)$: For the shortest chains, with $N = 16$, $y^{mid}(N)$ deviates from y^{∞} by about 1%, whereas $z^{mid}(N)$ deviates from z^{∞} by roughly 30%.

In Fig. 8, we compare data for $y(s, N)$ for all s and N to the functional form predicted in Eq. (49) for interior monomers. Here, we have used the values of y^{∞} and δ obtained from the fit shown in Fig. 7. This data clearly confirms that the small deviations $y(s, N)$ from y^{∞} for interior monomers are independent of s and proportional to $1/N$, as expected if the dominant corrections to y^{∞} arise from occasional contact of interior monomers with end monomers. The inset to Fig. 8 shows the much larger $\mathcal{O}(1)$ deviation of $y(s, N)$ from y^{∞} for the last bead at each chain end.

VII. SCFT AND ONE-LOOP THEORY

There are good reasons to believe that a generalized form of SCFT becomes increasingly accurate with increasing chain length, and is exact in the limit of infinitely long chains. The strongest theoretical evidence for this hypothesis comes from investigation of corrections to SCFT within the context of the renormalized one-loop theory[6], as discussed below. The hypothesis that SCFT is exact in the limit of long chains is, of course, also consistent with the striking success of the Flory-Huggins and (particularly) RPA theories in describing experimental data from mixtures of long finite polymers.

The renormalized one-loop theory yields a prediction for the free energy per monomer of the form

$$f = kT \sum_i \frac{\phi_i}{N_i} \ln \phi_i + f_{\text{int}}(\phi, T) + f^* \quad , \quad (61)$$

in which f^* is a one-loop correction to generalized Flory-Huggins theory. For symmetric models of the type considered here, the predicted correction f^* is a function of the form

$$f^*(\phi, \chi_{\text{e}}, N) = \frac{kT}{N \bar{N}^{1/2}} \hat{f}^*(\phi, \chi_{\text{e}} N) \quad (62)$$

where $\hat{f}^*$ is a dimensionless function of ϕ and $\chi_{\text{e}} N$. Here, χ_{e} is an effective interaction parameter that is related to $\Delta f_{\text{int}}(\phi, T)$ by Eq. (7). The SCF interaction free energy f_{int}, which is required as an input to the theory, can have an arbitrary composition dependence. To compare one-loop predictions to our perturbation theory of symmetric mixtures, we must also allow f_{int} to depend upon the parameter α of the underlying microscopic model.

A. SCFT

Because the one-loop contribution f^* decreases as $N^{-1/2}$ with increasing chain length, the SCF contribution f_{int} may be identified by considering the limit $N \to \infty$ of the true free energy f. As discussed in the introduction, an expansion of f_{int} to first order in α may thus be obtained by simply taking the limit $N \to \infty$ of the corresponding first order expansion of f, which is given in Eq.(3). This yields

$$f_{\text{int}} = f_0 + \frac{1}{2} \alpha y^{\infty} + \alpha z^{\infty} \phi_A \phi_B \quad . \quad (63)$$

An expression for the corresponding contribution Δf_{int} to the free energy of mixing is given in Eq. (8). This result yields an expansion of effective SCF interaction parameter χ_{e}, to first order in α, as

$$\chi_{\text{e}} = \frac{\alpha z^{\infty}}{kT} \quad . \quad (64)$$

The fact that this expansion for χ_{e} is independent of composition is a special feature of the expansion of this class of

symmetric models to first order in α: We do not expect it to survive any generalization to structurally asymmetric models or to higher order in α. Nothing rigorous can be said about the temperature dependence, even in this first order expansion, because the expansion with respect to α has been carried out at constant T, and z^∞ thus has an unknown dependence on T. The coefficient z^∞ would be independent of T only in an athermal reference system, such as a lattice model with no vacancies or a model of tangent hard spheres.

B. One-Loop Contribution

Both the one-loop theory for f and the simple perturbative expansion of f predict corrections to the SCF free energy, as defined above, that are of order $\bar{N}^{-1/2}$. The one-loop theory is simply not a perturbation theory, since it predicts a correction $f^*(\phi, \chi_\mathrm{e} N)$ that is a nonlinear function of $\chi_\mathrm{e} N$, and that exhibits singular behavior near the spinodal. We can test whether one-loop predictions are *consistent* with our analysis of a more microscopic perturbation theory, however, by considering the predictions of the one-loop theory for the derivative $\theta = \partial f / \partial \alpha$ at $\alpha = 0$, and comparing expressions for the $\mathcal{O}(\bar{N}^{-1/2})$ contribution to this coefficient.

The one-loop expression for $\theta \equiv \partial f / \partial \alpha$ at $\alpha = 0$ can be expressed as a sum

$$\frac{\partial f}{\partial \alpha} = \frac{\partial f_{int}}{\partial \alpha} + \frac{\partial f^*}{\partial \alpha} \quad . \tag{65}$$

The SCF contribution is simply

$$\left.\frac{\partial f_{int}}{\partial \alpha}\right|_{\alpha=0} = \frac{1}{2} y^\infty + z^\infty \phi_A \phi_B \tag{66}$$

and $\theta^* \equiv \partial f^* / \partial \alpha$. The one-loop correction is of the form

$$\frac{\partial f^*}{\partial \alpha} = \frac{\partial \chi_\mathrm{e}(\phi, \alpha)}{\partial \alpha} \frac{\partial f^*(\phi, \chi_\mathrm{e}, N)}{\partial \chi_\mathrm{e}} \quad . \tag{67}$$

It is straightforward to show, by using the functional form given in Eq. (62), that this correction is proportional to $\bar{N}^{-1/2}$.

In the accompanying paper, we explicitly calculate the required derivative of the one-loop correction f^*, and find that

$$\left.\frac{\partial f^*}{\partial \alpha}\right|_{\alpha=0} = v \delta \bar{\omega}_{\mathrm{id}}(\mathbf{r} = 0, N) \phi_A \phi_B \quad . \tag{68}$$

Combining this with Eqs. (65-67) and Eq. (64) for χ_e yields

$$\left.\frac{\partial f}{\partial \alpha}\right|_{\alpha=0} = \frac{1}{2} y^\infty + z^\infty \phi_A \phi_B \left[1 + v \delta \bar{\omega}_{\mathrm{id}}(\mathbf{r} = 0, N)\right] \quad . \tag{69}$$

This is identical to the expression obtained in Sec. IV.

We thus conclude that the one-loop theory implicitly contains a correct description of the N-dependence of the correlation hole. This is enough to guarantee that the one-loop theory will yield a very accurate description of corrections to SCFT in weakly non-ideal symmetric blends, with $\chi_\mathrm{e} N \ll 1$. In an accompanying paper, we confirm that this is true by comparing one-loop predictions to simulation results for composition fluctuations in such blends. There, we also examine the accuracy of the one loop theory for larger values of α, up to the critical value, for which perturbation theory becomes inadequate.

VIII. CONCLUSIONS

A simple physical picture has been given for how intra- and inter-molecular correlation functions vary with chain length in a polymer melt. A theory based on this picture is in excellent agreement with computer simulation results. The structure of a one-component melt is related by perturbation theory to the free energy of mixing in corresponding structurally symmetric blends. The $\mathcal{O}(N^{-1/2})$ contribution to the depth of the intramolecular correlation hole in the melt of finite chains leads to a slightly higher free energy of mixing in mixtures of shorter chains. This simply reflects the fact that monomers on shorter chains are less strongly screened from contact with other chains. Perturbation theory may be used to estimate the SCF interaction free energy appropriate for comparison of SCF theory to simulations, by identifying SCF theory with the $N \to \infty$ limit of the perturbation theory. If this prescription is used identify SCF parameters, the predictions of the one-loop theory for corrections to SCF theory is found to be consistent with the perturbation theory presented here, insofar as both theories give identical results for a $\mathcal{O}(N^{-1/2})$ correction to the apparent interaction parameter in weakly non-ideal symmetric mixtures, with $\chi N \ll 1$.

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