

Renormalization of the one-loop theory of fluctuations in polymer blends and diblock copolymer melts

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Attempts to use coarse-grained molecular theories to calculate corrections to the random-phase approximation (RPA) for correlations in polymer mixtures have been plagued by an unwanted sensitivity to the value of an arbitrary cutoff length, i.e., by an ultraviolet (UV) divergence. We analyze the UV divergence of the inverse structure factor $S^{-1}(k)$ predicted by a “one-loop” approximation similar to that used in several previous studies. We consider both miscible homopolymer blends and disordered diblock copolymer melts. We show, in both cases, that all UV divergent contributions can be absorbed into a renormalization of the values of the phenomenological parameters of a generalized self-consistent field theory (SCFT). This observation allows the construction of an UV convergent theory of corrections to SCFT phenomenology. The UV-divergent one-loop contribution to $S^{-1}(k)$ is shown to be the sum of (i) a k -independent contribution that arises from a renormalization of the effective χ parameter, (ii) a k -dependent contribution that arises from a renormalization of monomer statistical segment lengths, (iii) a contribution proportional to k^2 that arises from a square-gradient contribution to the one-loop fluctuation free energy, and (iv) a k -dependent contribution that is inversely proportional to the degree of polymerization, which arises from local perturbations in fluid structure near chain ends and near junctions between blocks in block copolymers.

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I. INTRODUCTION

The statistical mechanics of polymer mixtures and block copolymer melts exhibit some universal features that are well described by self-consistent field theory (SCFT). The phase behavior of homopolymer mixtures is reasonably well described by Flory-Huggins theory. Various inhomogeneous structures formed by flexible polymers, such as interfaces and ordered phases of block copolymers, are accurately described by a SCFT of inhomogeneous liquids, which reduces to Flory-Huggins theory in the case of a homogeneous mixture. A self-consistent field approximation also underlies the so-called random-phase approximation (RPA) for the structure function $S(k)$ in homogeneous mixtures. The RPA is obtained by using SCFT to calculate the susceptibility of a liquid to a hypothetical infinitesimal perturbation, and using the correlation-response theorem to relate this linear susceptibility to the corresponding correlation function.

SCFT is a highly successful theory, but not a perfect one. Among its limitations is the inability of the RPA to accurately describe fluctuations very near a critical point in a polymer blend or near an order-disorder transition (ODT) in a symmetric diblock copolymer melt. The range of temperatures over which deviations from the RPA are significant is believed to decrease with increasing degree of polymerization N . The fractional width of this so-called Ginzburg region is predicted to decrease as N^{-1} with molecular weight N in a homopolymer blend [1–3], and as $N^{-1/3}$ in a symmetric diblock copolymer melt [4]. For molecular weights typical of experiments, however, fluctuation effects that are ignored by SCFT have significant observable consequences.

The form of SCFT that has proved useful for the analysis of experimental data is a phenomenological theory. It contains several parameters whose values are sensitive to details of monomer scale structure, which must be determined by

comparison to experiment. In the simplest form of SCFT for systems with two types of monomers, these parameters are a Flory-Huggins interaction parameter $\chi(T)$, and the statistical segment lengths of both species. SCFT does not predict how these parameters depend upon the details of molecular structure. Its usefulness arises instead from its ability to predict phase behavior, equilibrium structures, and diffuse scattering for systems containing polymers that are comprised of the same types of monomers, but that have different molecular weights and/or architectures.

Any attempt to systematically calculate corrections to this SCFT, however, must start with some sort of micromechanical model. (We need a Hamiltonian to do statistical mechanics.) Here, as in several previous studies [5–10] we start from a coarse-grained model of Gaussian chains with pairwise-additive interactions between monomers. Each coarse-grained monomer in such a model represents a subchain of many chemical repeat units, within a chain that contains many such monomers. Such models are thus implicitly coarse-grained to some cutoff length intermediate between the chemical monomer size and the polymer coil size.

The long wavelength composition fluctuations that become important near the critical point of a blend, or the ODT of a symmetric diblock copolymer, exhibit a universal phenomenology of their own. For a blend, sufficiently close to the critical point, this is the critical behavior of the Ising universality class. One might hope that our theoretical description of these long wavelength fluctuations would be insensitive to the value chosen for a cutoff length, or to other arbitrary details of how our coarse-grained model behaves at very short length scales. Unfortunately, this is not so, at least not in the simplest sense. Numerical values predicted for a variety of quantities turn out to be very sensitive to the value chosen for the cutoff length. The purpose of this paper is to show how this may be remedied by an appropriate renormalization scheme.

A. Field theory and mean-field theory

The calculations presented here make use of the auxiliary field representation of the partition function that was introduced into polymer physics by Edwards [11,12]. This approach has been used in several previous studies of fluctuation effects in polymer blends [5–8]. Let

$$Z \equiv \int D[\mathbf{R}] e^{-U[\mathbf{R}]} \quad (1)$$

denote the partition function for a model with a potential energy U , where $\int D[\mathbf{R}]$ denotes an integral over all particle positions. The auxiliary field approach makes use of an exact transformation of the partition function for any model in which U is a sum of intramolecular potential and a pairwise additive potential for interactions between monomers. This transformation can be applied to either the canonical or grand-canonical partition function. The transformation yields a representation of Z (in either ensemble) as a functional integral of the form

$$Z = \int D[J] e^{\mathcal{L}[J]}, \quad (2)$$

where J is an auxiliary field (or a pair of such fields, one for each monomer type) that has units of monomer chemical potential. This approach is discussed in more detail in Sec. IV.

A saddle-point approximation to the auxiliary field functional integral is known to yield a very simple form of mean-field theory. The free-energy functional obtained in this saddle-point approximation is the sum of the free energy of an ideal gas of polymers plus a mean-field approximation for the interaction energy. The average interaction energy obtained in this approximation is the same as that obtained by a “random mixing” approximation in which we ignore all correlations among the monomer positions. The underlying assumption of microscopically random mixing is analogous to that used in the Poisson-Boltzmann theory of electrolytes, or the original Flory-Huggins lattice model, which are both “mean-field” theories in the same sense. Like other microscopic mean-field theories of this type, the resulting theory makes very simple, but generally inaccurate, predictions about the relationship between microscopic interaction parameters and macroscopic parameters, such as the effective χ parameter observed in scattering experiments. We will make a distinction in what follows between this microscopic mean-field theory and the phenomenological SCFT that is used to fit experimental data, which contains several adjustable parameters.

B. Ultraviolet divergence and renormalization

One appealing feature of the auxiliary field approach is that it allows the effects of fluctuations of the auxiliary field about this mean-field approximation to be treated by standard methods of diagrammatic perturbation theory, analogous to those used in the study of critical phenomena [13]. Several studies have attempted to calculate corrections to the simple mean field theory for binary polymers blends [5–8]

by introducing a Gaussian approximation for distribution of fluctuations of the auxiliary J about its saddle point. In any perturbative field theory, a Gaussian approximation for fluctuations about the saddle point can be expressed diagrammatically in terms of Feynman diagrams that involve only a single “loop,” or a single wave vector integration. For this reason, this approximation is often referred to (and will be referred to here) as a “one-loop” approximation.

In all of these calculations, it was found that the predictions of the one-loop approximation for corrections to the mean-field free-energy density and for the inverse structure factor [5–8] are dominated by the contributions of short-wavelength fluctuations, with wavelengths of the order of a coarse graining length or (equivalently) a cutoff length. If the relevant Fourier integrals are cut off at a wave number Λ , predictions for the apparent χ parameter are found to contain terms proportional to Λ and Λ^3 , which diverge in the limit $\Lambda \rightarrow \infty$. In the jargon of field theory, the one-loop approximation was thus found to be ultraviolet (UV) divergent.

This UV divergence is not peculiar to studies that rely on the auxiliary field approach, but arises in all coarse-grained models of fluctuation effects in polymer liquids. The most influential theory of fluctuation effects in diblock copolymer blends is that of Brazovskii [14], Fredrickson, and Helfand (BFH) [4]. The BFH theory and its descendants [15–19] are based on an effective Hamiltonian formalism in which the partition function is approximated as a functional integral with respect to a fluctuating monomer concentration field, rather than with respect to a fluctuating chemical potential. A saddle-point approximation for the functional integral used in the effective Hamiltonian approach yields the same mean-field theory as that obtained by a saddle-point approximation in the auxiliary field approach. The BFH theory is based on a self-consistent one-loop approximations for fluctuations about this saddle point. As emphasized by Kudlay and Stepanow [18], this approach leads to UV divergences analogous to those encountered in the auxiliary field approach.

The physical reason for this sensitivity to the value chosen for the cutoff length Λ^{-1} is not hard to understand. The total free energy of a polymer liquid is only subtly different from that of a corresponding liquid of oligomers, because both are dominated by the effects of monomer scale liquid structure. It should thus be no surprise that the free-energy density of a coarse-grained model is sensitive to our choice of cutoff length: The total free energy is sensitive to every detail of local fluid structure, at the shortest wavelength relevant to whatever model we consider.

Phenomenological SCFT assumes that this sensitivity to local structure can be encapsulated within a few phenomenological parameters. Phenomenological SCFT is widely believed to be asymptotically exact in the high molecular-weight limit, except within a Ginzburg region very near the spinodal. If we assume this to be true, however, we should nonetheless expect to obtain different estimates for the values of the SCFT phenomenological parameters from different mathematical approximations for the properties of a given microscopic model. Specifically, we should expect to obtain different approximations for the χ parameter and statistical segment lengths from a one-loop approximation than those obtained from the simple mean-field approximation.

One-loop corrections to the predictions of the simplest mean-field theory should thus be understood to contain two conceptually different kinds of corrections:

(1) Corrections to mean-field estimates of the *parameters* of SCFT, e.g., of the statistical segment lengths and effective interaction parameters.

(2) Corrections to the *phenomenology* of SCFT, which cannot be absorbed into corrections to these parameters. We expect these to become small in the limit $N \rightarrow \infty$, except within a narrow temperature window near the spinodal.

We expect corrections to the SCFT parameters to be sensitive to our treatment of short wavelength correlations, and thus, in a coarse-grained theory, to our choice of cutoff wave number. Conversely, we expect corrections to the phenomenology of SCFT, such as corrections to Gaussian chain statistics or to RPA predictions of the functional form of $S(k)$, to arise primarily from longer wavelength fluctuations, and to be independent of Λ . One goal of this paper is to provide mathematical evidence for the consistency of this physical picture.

Our ultimate goal is to construct a renormalized perturbation theory that allows us to unambiguously calculate corrections to phenomenological SCFT. We assume (subject to confirmation) that a SCFT with renormalized parameters is asymptotically exact in the limit $N \rightarrow \infty$. We thus hope to construct a theory in which all corrections to this form of SCFT can be shown to vanish in the limit $N \rightarrow \infty$. The assumption that SCFT becomes exact as $N \rightarrow \infty$ implies, however, that all large, UV divergent contributions to the calculated correlation functions (which generally do not vanish in the limit $N \rightarrow \infty$) must preserve the dependence on wave vector, chain length, and architecture predicted by SCFT. This is possible only if all of the UV divergent terms in the one-loop approximation can somehow be absorbed into corrections to the values of the phenomenological parameters used in SCFT.

This criteria for “renormalizability” imposes some nontrivial constraints on the allowed functional forms of UV divergent corrections. It implies, for instance, that any UV divergent contribution to $S^{-1}(k)$ that we wish to interpret as a renormalization of χ be completely independent of k and N , and that it have the same value in a polymer blend and a diblock copolymer melt of the same composition, as is assumed for the χ parameter in SCFT. Similarly, it requires that any contribution to $S^{-1}(k)$ that we associate with a renormalization of a statistical segment length exhibit the nontrivial but predictable k dependence of the change in the RPA prediction for $S^{-1}(k)$ that would be caused by a slight swelling or a contraction of Gaussian chains due to a change in statistical segment length. We show here that these criteria are actually satisfied by the one-loop approximation.

C. UV divergences in prior work

The UV divergence of the one-loop theory has inspired a variety of responses in prior work.

In studies of fluctuation effects in polymer blends, several authors have introduced a cutoff Λ that is assumed to be of order the inverse monomer size, and simply reported the

dominant UV divergent contributions as functions of Λ [5–7,20]. These results have sometimes been interpreted as meaningful predictions for the dependence of the χ parameter [5–7] or the statistical segment length [20] upon microscopic structure. We believe that this interpretation is misguided: When a prediction of a coarse-grained model for some quantity depends upon a microscopic cutoff length, it indicates only that the value of that quantity is sensitive to details of local fluid structure that such a model should not be expected to accurately describe.

Holyst and Vilgis [9,10] have instead argued for the introduction a cutoff length of the order of the polymer coil size $R \propto \sqrt{Nb}$ as a way of controlling the UV divergence. Their reasoning is worth recounting: Holyst and Vilgis [9] posed the question of whether the cutoff length that was needed as a result of the UV divergence of their theory should be taken to be a length of the order of the monomer size b or the coil size R . They noted that a cutoff length of order b would lead to corrections to the mean-field (i.e., saddle-point) theory that do not become small in the limit $N \rightarrow \infty$. They thus rejected this option in favor of the introduction of an *ad hoc* cutoff length of order R . These authors were thus led into a quandary, in part, because they did not make the conceptual distinction made here between the microscopic mean-field theory, which is certainly not exact in the limit $N \rightarrow \infty$, and phenomenological SCFT theory, which (we argue) is.

In Brazovskii’s analysis of weakly first-order crystallization, he considers a UV divergent integral expression for $S^{-1}(k)$, but never mentions its divergence. This UV divergence is also not mentioned by Fredrickson and Helfand [4] in their application of Brazovskii’s analysis to diblock copolymer melts. Instead, these authors all report the UV convergent part of the integral, which develops an infrared (IR) divergence at the SCFT spinodal, and discard the UV divergent contribution without comment. This approach is consistent with that normally taken in field theoretic studies of, e.g., the Ising critical point [21], in which it is well known that an analogous UV divergence of the one-loop theory can be absorbed into a renormalization of the critical temperature. This interpretation of the divergence in the Brazovskii model was made more explicit by Dobrynin and Erukhimovich [15], who noted (in their Appendix) that it could also be absorbed into a shift in the critical temperature.

This approach is the only appropriate one in the study of very generic models, such as the original Brazovskii model, in which the critical temperature is treated from the outset as an unknown parameter. It becomes problematic only when such a field theoretic treatment of fluctuations is grafted onto a SCFT theory that we expect to become exact in the limit $N \rightarrow \infty$. SCFT predicts nontrivial relationships between critical temperatures and order-disorder temperatures of homologous systems containing polymers that are constructed from the same monomers, but which have different lengths or architectures (e.g., blends and diblock copolymer melts). If we were to treat the transition temperatures for different such systems as completely independent parameters, we would forego the ability to say anything about corrections to SCFT predictions for these relationships. UV divergent contributions to the one-loop theory can be made truly benign only if they can be related to the parameters of SCFT.

We are aware of two previous attempts to renormalize the theory of fluctuations in blends or copolymer melts, similar in spirit to that given below:

Kudlay and Stepanow [18] attempted to renormalize a refined version of the one-loop approximation for $S^{-1}(k)$ in a diblock copolymer melt introduced by Fredrickson and Helfand. These authors proposed (in effect) that the UV divergence of $S^{-1}(k)$ could be tamed if it could be absorbed into a renormalization of the Flory-Huggins χ parameter. They concluded, however, that this interpretation was not tenable for the theory that they considered, because the UV divergence of $S^{-1}(k)$ in this theory was shown to exhibit a non-trivial dependence on k , and because different results for the UV divergent contribution were obtained for a diblock copolymer melt and for a binary blend of the same composition.

The first successful attempt to renormalize a prediction of a one-loop theory to our knowledge was given by Wang [8]. Wang used the Edwards' auxiliary field approach to derive an expression for a one-loop correction to the $k=0$ limit of $S^{-1}(k)$ in a binary homopolymer blend. He showed that the result was the sum of a UV divergent part that he interpreted as a renormalization of χ , and a UV convergent contribution that vanishes in the limit $N \rightarrow \infty$, as suggested by the physical picture discussed above. The main limitation of Wang's calculation is that the method that he and others [5–7] have used to calculate $S^{-1}(k=0)$ in a blend is not easily generalizable to allow the calculation of $S^{-1}(k)$ at $k \neq 0$, or to study fluctuations in block copolymer melts. Wang was thus not able to examine either the k dependent or the architecture dependence of his results. As such, Wang's calculation left open the question of whether his proposed renormalization scheme would have passed the more stringent consistency requirements imposed by Kudlay and Stepanow. Wang's analysis is discussed in detail in Sec. III. Our analysis builds directly upon Wang's, and removes many of its limitations.

D. Outline

The paper is organized as follows: Section II introduces the coarse-grained model of interest, as well as several mathematical and conceptual definitions that are needed to discuss our results. Section III contains an overview of our renormalization procedure and results, beginning with a review of Wang's results. We hope that readers who are interested in understanding only the main physical ideas and results will be able to follow to this point.

Sections IV–XII present the technical details of our analysis. Section IV reviews the auxiliary field method, and the Gaussian and/or one-loop approximation. Section V reviews the one-loop calculation of the free energy density of a homogeneous binary blend, and a corresponding analysis of $S^{-1}(0)$, in which we retain some subdominant terms that previous authors ignored. In Sec. VI, we give a self-contained derivation of the one-loop correction to $S^{-1}(k)$ at arbitrary k by functional differentiation of the Gaussian approximation for the free-energy functional. In Sec. VII, we review the general diagrammatic rules obtained in Ref. [13]. These provide an alternate path to the same expressions for $S(k)$, and

also allow us to separate intramolecular from intermolecular correlations. In Sec. VIII, we convert our expression for the one-loop correction to $S^{-1}(k)$ at fixed chemical potential (grand-canonical ensemble) to a corresponding correction for a closed system (canonical ensemble). In Sec. X, we analyze the UV divergence of the one-loop approximation for $S^{-1}(k)$ for a binary blend. In Sec. XI, we present the corresponding calculation for a diblock copolymer melt. In Sec. XII, we show that $O(1/N)$ corrections to the UV divergent part of $S^{-1}(k)$ can be consistently interpreted as the result of end effects, and of a square-gradient contribution to the interaction free energy.

Section XIII presents a power counting analysis of the UV divergence of an arbitrary diagram, at any order in a loop expansion. We also show there that a renormalized loop expansion will yield an asymptotic expansion of corrections to SCFT in powers of $1/\sqrt{N}$. Section XIV discusses the relationship between this work and the extensive literature on the excluded volume problem in polymer solutions. Concluding remarks are given in Sec. XV.

II. MODEL AND DEFINITIONS

In what follows, we explicitly consider binary homopolymer blends and diblock copolymer melts. We adopt a notation that allows for a mixture of any number of molecular species constructed from a palette of any number of monomer types. Let ρ_a be the number concentration of molecules of species a in a mixture. Let $c_i(\mathbf{r})$ be the fluctuating number concentration of monomers of type i at point \mathbf{r} . If $\mathbf{R}_{ami}(s)$ denotes the position of monomer s of monomer type i on molecule number m of species a , then

$$c_i(\mathbf{r}) \equiv \sum_{sma} \delta(\mathbf{r} - \mathbf{R}_{ami}(s)). \quad (3)$$

Here, the sum over s is taken over monomers of type i on molecules of species a , the sum over m is taken over molecules of species a , and the sum over a is taken over all species that contain i monomers. We will consider a nearly incompressible liquid with an average volume v per monomer, in which v is the same for all monomer types, and independent of composition in a mixture.

A. A coarse-grained model

Consider a coarse-grained model for polymer liquids in which the total potential energy is a sum

$$U = U_{\text{chain}} + U_{\text{int}} + U_{\text{ext}}[h], \quad (4)$$

of an intramolecular potential energy U_{chain} , a pair interaction potential

$$U_{\text{int}} \equiv \frac{1}{2} \sum_{ij} \int d\mathbf{r} \int d\mathbf{r}' U_{ij}(\mathbf{r} - \mathbf{r}') c_i(\mathbf{r}) c_j(\mathbf{r}'), \quad (5)$$

and an external potential

$$U_{\text{ext}}[h] = - \sum_i \int d\mathbf{r} h_i(\mathbf{r}) c_i(\mathbf{r}). \quad (6)$$

Here, $U_{ij}(\mathbf{r}-\mathbf{r}')$ is a pair potential for interactions between monomers of types i and j , and $h_i(\mathbf{r})$ is an external potential field conjugate to $c_i(\mathbf{r})$. The external potential fields are introduced as a mathematical convenience, and are set to zero in all final expressions.

In what follows, we sometimes use a compact notation in which a binary operator “ $*$ ” is used to indicate integration over a shared coordinate (or wave vector) and summation over a shared monomer type index. For example,

$$U_{\text{int}} = \frac{1}{2} c * U * c, \quad (7)$$

$$U_{\text{ext}} = - h * c, \quad (8)$$

in this notation.

We assume in what follows that U_{chain} is adequately approximated at the length scales of interest by the stretching energy of a continuous Gaussian chain. Let b_i denote the statistical segment length for monomers of type i on an isolated chain (with $U_{\text{int}}=0$), and

$$l_i \equiv v/b_i^2 \quad (9)$$

be the corresponding packing length for monomers of type i .

We consider a class of models in which the Fourier transform $U_{ij}(\mathbf{k})$ of the pair potential $U_{ij}(\mathbf{r}-\mathbf{r}')$ is of the form

$$U_{ij}(\mathbf{k}) = \bar{U}_{ij} \hat{F}(\mathbf{k}/\Lambda), \quad (10)$$

where \bar{U}_{ij} is a matrix of interaction strengths with dimensions of volume, Λ is an inverse range of interaction, and $\hat{F}(\mathbf{k}/\Lambda)$ is a function that approaches 1 as $\mathbf{k}/\Lambda \rightarrow 0$. This corresponds to a pair potential in coordinate space

$$U_{ij}(\mathbf{r}-\mathbf{r}') = \bar{U}_{ij} \Lambda^3 F(\Lambda|\mathbf{r}-\mathbf{r}'|), \quad (11)$$

where the function F is the inverse Fourier transform of \hat{F} , and satisfies the normalization condition $\int d\mathbf{x} F(\mathbf{x}) = 1$. The interaction matrix \bar{U}_{ij} is taken to be of the form

$$\bar{U}_{ij} = v \begin{bmatrix} B_0 & B_0 + \chi_0 \\ B_0 + \chi_0 & B_0 \end{bmatrix}. \quad (12)$$

The resulting potential energy reduces in the limit of slow spatial variations, in which the characteristic scale for gradients is much larger than Λ^{-1} , to a continuum approximation

$$U_{\text{int}} \approx v \int d\mathbf{r} \left\{ \frac{1}{2} B_0 (c_1 + c_2)^2 + \chi_0 c_1 c_2 \right\}, \quad (13)$$

in which B_0/v is the mean-field compression modulus.

The analysis presented here can be carried out in either canonical or grand-canonical ensemble, with only minor differences. We will work in grand-canonical ensemble. Let $Z[h]$ denote the grand canonical partition function, for some choice of chemical potentials. Let $F[\langle c \rangle]$ be the corresponding free energy expressed as a functional of the average

monomer concentration fields. This is defined by the Legendre transform

$$F[\langle c \rangle] = - \ln Z[h] + h * \langle c \rangle. \quad (14)$$

Here, h is the external field required to establish a monomer concentration $\langle c \rangle$, which is related to F by a functional derivative

$$h_i(\mathbf{r}) = \frac{\delta F[\langle c \rangle]}{\delta \langle c_i(\mathbf{r}) \rangle}. \quad (15)$$

In Eq. (14), and hereafter, we use energy units in which $k_B T = 1$.

B. Correlation functions

We focus on the calculation of the correlation function

$$S_{ij}(\mathbf{r}, \mathbf{r}') = \langle \delta c_i(\mathbf{r}) \delta c_j(\mathbf{r}') \rangle \quad (16)$$

and its Fourier transform

$$S_{ij}(\mathbf{k}) \equiv \int d\mathbf{r}' S_{ij}(\mathbf{r}, 0) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (17)$$

where $\delta c_i(\mathbf{r}) \equiv c_i(\mathbf{r}) - \langle c_i(\mathbf{r}) \rangle$. This quantity obeys the identities

$$S_{ij}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 \ln Z[h]}{\delta h_i(\mathbf{r}) \delta h_j(\mathbf{r}')}, \quad (18)$$

$$S_{ij}^{-1}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 F[\langle c \rangle]}{\delta \langle c_i(\mathbf{r}) \rangle \delta \langle c_j(\mathbf{r}') \rangle}. \quad (19)$$

The inverse S^{-1} is defined in coordinate space by requiring that $S * S^{-1} = \delta$, where δ denotes $\delta(\mathbf{r}, \mathbf{r}') \delta_{ik}$, or in Fourier space by requiring (for a homogenous liquid) that $\sum_j S_{ij}^{-1}(\mathbf{k}) S_{jk}(\mathbf{k}) = \delta_{ik}$.

We define an intramolecular correlation

$$\Omega_{a,ij}(\mathbf{r}, \mathbf{r}') \equiv \sum_m \langle c_{ami}(\mathbf{r}) c_{amj}(\mathbf{r}') \rangle, \quad (20)$$

that describes correlations between pairs of monomers on the same molecule m of a specified species a , in which

$$c_{ami}(\mathbf{r}) \equiv \sum_s \delta(\mathbf{r} - \mathbf{R}_{ami}(s)) \quad (21)$$

is the concentration of monomers of type i on a specific molecule m of species a . The sum over m in Eq. (20) is over all molecules of type a . The sum over s in Eq. (21) is over all monomers of type i on molecule m .

In a molecular mixture, let $\Omega_{ij}(\mathbf{r}, \mathbf{r}')$, with no species index a , denote the total contribution

$$\Omega_{ij}(\mathbf{r}, \mathbf{r}') \equiv \sum_a \Omega_{a,ij}(\mathbf{r}, \mathbf{r}'), \quad (22)$$

of intramolecular correlations to $S_{ij}(\mathbf{r}, \mathbf{r}')$. Here, the sum is taken over all species a that contain both i and j monomers. In a binary mixture of homopolymers of species $a=1$ and 2 , the only nonzero element of $\Omega_{1,ij}$ for homopolymer 1 is the

element $i=j=1$, while the only nonzero elements of Ω_{ij} are the diagonal elements, with $i=j$. In a single component copolymer melt, $\Omega_{a,ij}$ and Ω_{ij} are identical.

C. Self-consistent field theory

Polymer SCFT is a density functional theory of inhomogeneous polymer liquids. It is based upon an approximation of the free energy functional $F[\langle c \rangle]$ as a sum

$$F[\langle c \rangle] = F_{\text{chain}}[\langle c \rangle] + F_{\text{int}}[\langle c \rangle], \quad (23)$$

in which F_{chain} is the free energy of a hypothetical reference system of noninteracting polymers with a specified average concentration profile, and $F_{\text{int}}[\langle c \rangle]$ is an additional ‘‘interaction’’ free-energy functional.

The functional $F_{\text{chain}}[\langle c \rangle]$ is the free energy of a hypothetical system of noninteracting chains, with $U_{\text{int}}=0$, in which a monomer concentration $\langle c \rangle$ is maintained by a potential $U_{\text{ext}}[\tilde{h}]$, with an applied field \tilde{h} . The field \tilde{h} thus satisfies an identity

$$\tilde{h}_i(\mathbf{r}) = \frac{\delta F_{\text{chain}}[\langle c \rangle]}{\delta c_i(\mathbf{r})} \quad (24)$$

as a special case of Eq. (15). Applying Eq. (15) to Eq. (23) for $F[\langle c \rangle]$ yields a self-consistent field equation

$$\tilde{h}_i(\mathbf{r}) = h_i(\mathbf{r}) - \frac{\delta F_{\text{int}}[\langle c \rangle]}{\delta c_i(\mathbf{r})}. \quad (25)$$

Here, $h_i(\mathbf{r})$ is the external field that must be applied to the interacting fluid to establish a monomer concentration field $\langle c \rangle$, $\tilde{h}_i(\mathbf{r})$ is the field required to establish the same concentration field in the noninteracting reference system, and $\delta F_{\text{int}}/\delta c$ is an ‘‘internal’’ field contribution.

By itself, Eq. (23) is merely a definition of F_{int} , rather than a predictive theory. The standard coarse-grained model for dense multicomponent liquids of flexible polymers [22] may be obtained by supplementing this with the following physical assumptions:

(a) *Gaussian chains*. Polymer conformations are adequately described at the mesoscopic scales of interest as Gaussian random walks.

(b) *Locality*. The interaction free-energy F_{int} may be adequately approximated by a local functional of the form

$$F_{\text{int}}[\langle c \rangle] = \int d\mathbf{r} f_{\text{int}}(c_1(\mathbf{r}), c_2(\mathbf{r})), \quad (26)$$

where $f_{\text{int}}(c_1(\mathbf{r}), c_2(\mathbf{r}))$ is a free-energy density at point \mathbf{r} that depends only upon the monomer concentrations at point \mathbf{r} . More precisely, it is assumed that the range of any nonlocality in F_{int} is of the order of the monomer size, and that this is small compared to the length scales of interest in applications of the coarse-grained theory.

(c) *Incompressibility*. It is often assumed that liquid is essentially incompressible at the length scales of interest. If coarse-grained 1 and 2 monomers have been defined so as to occupy the same volume v , this may be expressed by a constraint

$$v^{-1} = \langle c_1(\mathbf{r}) \rangle + \langle c_2(\mathbf{r}) \rangle. \quad (27)$$

The simplest form of phenomenological SCFT for systems with two types of monomers assumes, in addition, that f_{int} in an incompressible liquid may be adequately described by the Flory-Huggins expression, $f_{\text{int}}=v\chi\langle c_A(\mathbf{r}) \rangle \langle c_B(\mathbf{r}) \rangle$ with an interaction parameter χ . This simple assumed composition dependence is not a necessary or essential part of the theory.

To precisely define the decomposition of F into F_{chain} and F_{int} in Eq. (23), we must make a choice of what single-chain reference Hamiltonian to use to define the ideal gas free energy F_{chain} . The physical reasoning underlying SCFT suggests that this reference Hamiltonian should yield chain conformations that, in a homogenous state, are similar to those in the liquid of interest. Even chains that are approximately Gaussian in a dense liquid generally have statistical segment lengths that are slightly different from those of a corresponding system of noninteracting chains [20]. In what follows, we will thus define F_{chain} to be the free energy of a hypothetical system of noninteracting chains in which the single-chain reference Hamiltonian is chosen so as to yield exactly the same single-chain probability distribution as that found for chains in the homogeneous state of the liquid of interest. The intramolecular reference Hamiltonian used to calculate F_{chain} should thus be understood to be a single-chain potential of mean force, rather than the bare intramolecular potential U_{chain} . This is equivalent to defining $F_{\text{chain}}[\langle c \rangle]$ to be the Legendre transform of the generating functional for the intramolecular correlation functions in the homogeneous state of the dense liquid. The 2-point intramolecular correlation function $\Omega_{ij}(\mathbf{k})$ in the dense liquid is thus related to F_{chain} , if defined in this way, by an identity

$$\Omega_{ij}^{-1}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 F_{\text{chain}}[\langle c \rangle]}{\delta c_i(\mathbf{r}) \delta c_j(\mathbf{r}')} \quad (28)$$

analogous to Eq. (19). Our results indicate that the UV divergent part of the one-loop contribution to the remaining free-energy F_{int} is actually a local functional only if F_{chain} and F_{int} are defined in this way.

D. Ornstein-Zernicke relation

It is useful to introduce a generalized Ornstein-Zernicke (OZ) relation [23–26]

$$S_{ij}^{-1}(\mathbf{r}, \mathbf{r}') = \Omega_{ij}^{-1}(\mathbf{r}, \mathbf{r}') - C_{ij}(\mathbf{r}, \mathbf{r}') \quad (29)$$

or

$$S_{ij}^{-1}(\mathbf{k}) = \Omega_{ij}^{-1}(\mathbf{k}) - C_{ij}(\mathbf{k}) \quad (30)$$

in a homogeneous liquid. Equation (29) defines the direct correlation function C_{ij} .

The single-chain correlation function $\Omega_{ij}(\mathbf{k})$ is related to the reference free-energy $F_{\text{chain}}[\langle c \rangle]$ as defined above by Eq. (28). The direct correlation function is intimately related to the interaction free-energy F_{int} . Combining Eqs. (19), (28), and (29) with Eq. (23) for F yields an identity

$$C_{ij}(\mathbf{r}, \mathbf{r}') = - \frac{\delta^2 F_{\text{int}}[\langle c \rangle]}{\delta \langle c_i(\mathbf{r}) \rangle \delta \langle c_j(\mathbf{r}') \rangle}. \quad (31)$$

Assuming that F_{int} is a local functional thus implies that the Fourier transform $C_{ij}(\mathbf{k})$ should be independent of \mathbf{k} .

In the case of a binary blend of two homopolymers, the $\mathbf{k} \rightarrow 0$ limit of the transform $C_{ij}(\mathbf{k})$ is related to the composition dependence of the free-energy density of a homogeneous mixture. Consider a homogeneous blend of two homopolymers, in which N_i is the degree of polymerization of i homopolymers, $c_i = N_i \rho_i$ is the macroscopic (i.e., spatial average) concentration of i monomers, and $f_{\text{int}}(c_1, c_2)$ is the interaction free-energy density of the mixture. Then

$$\lim_{\mathbf{k} \rightarrow 0} C_{ij}(\mathbf{k}) = - \frac{\partial^2 f_{\text{int}}}{\partial c_i \partial c_j}. \quad (32)$$

E. Incompressible limit

A simplified expression for $S_{ij}(\mathbf{k})$ may be obtained in the limit of an incompressible liquid. In a nearly incompressible liquid containing two types of monomer of equal volume, the 2×2 matrix $S_{ij}(\mathbf{k})$ has two widely disparate eigenvalues: In this limit, one eigenvector of $S_{ij}(\mathbf{k})$ must approach a pure ‘‘composition’’ mode, $[\delta \langle c_1(\mathbf{k}) \rangle, \delta \langle c_2(\mathbf{k}) \rangle] \propto [1, -1]$, which satisfies the constraint $\delta \langle c_1(\mathbf{k}) \rangle + \delta \langle c_2(\mathbf{k}) \rangle = 0$, and thus avoids the large free-energy penalty for changes in total monomer density. The second eigenvector must have a vanishing inner product with the first, and so must approach a pure ‘‘compression’’ mode, $[\delta \langle c_1(\mathbf{k}) \rangle, \delta \langle c_2(\mathbf{k}) \rangle] \propto [1, 1]$.

The incompressible limit of $S_{ij}(\mathbf{k})$ may be obtained by assuming that the eigenvectors approach the limits described above, and taking the eigenvalue of the compression mode to vanish. Alternatively, it may be obtained by assuming $C_{ij}(\mathbf{k})$ to be of the form $C_{ij}(\mathbf{k}) = -\bar{B} + \delta C_{ij}(\mathbf{k})$, and taking \bar{B} to infinity while keeping $\delta C_{ij}(\mathbf{k})$ finite. Either method yields a matrix correlation function of the form

$$\mathbf{S}(\mathbf{k}) = S(\mathbf{k}) \begin{bmatrix} +1 & -1 \\ -1 & +1 \end{bmatrix}, \quad (33)$$

with a scalar correlation function

$$S(\mathbf{k}) = \frac{|\Omega(\mathbf{k})|}{\Omega_+(\mathbf{k}) - 2v\chi_a(\mathbf{k})|\Omega(\mathbf{k})|} \quad (34)$$

where

$$\Omega_+(\mathbf{k}) \equiv \Omega_{11}(\mathbf{k}) + \Omega_{22}(\mathbf{k}) + \Omega_{12}(\mathbf{k}) + \Omega_{21}(\mathbf{k}),$$

$$|\Omega(\mathbf{k})| \equiv \Omega_{11}(\mathbf{k})\Omega_{22}(\mathbf{k}) - \Omega_{12}(\mathbf{k})\Omega_{21}(\mathbf{k}) \quad (35)$$

are the sum of elements of $\Omega_{ij}(\mathbf{k})$ and its determinant, respectively, and where

$$\chi_a(\mathbf{k}) \equiv \frac{1}{2v} [C_{11}(\mathbf{k}) + C_{22}(\mathbf{k}) - 2C_{12}(\mathbf{k})] \quad (36)$$

is a wave-number-dependent ‘‘apparent’’ χ parameter. This definition was introduced by Schweizer and Curro [25,26] using similar reasoning.

In an incompressible binary homopolymer blend, the long-wavelength limit

$$\chi_a(0) \equiv \lim_{\mathbf{k} \rightarrow 0} \chi_a(\mathbf{k}) \quad (37)$$

may be expressed as a derivative

$$\chi_a(0) = - \frac{v \partial^2 f_{\text{int}}(\phi_1)}{2 \partial \phi_1^2}, \quad (38)$$

where f_{int} is expressed as a function of the total volume fraction $\phi_1 \equiv v c_1$ of one of the two homopolymers.

III. OVERVIEW

In this section, we provide an overview of our renormalization procedure, and summarize our main results.

A. Mean-field theory

A saddle-point approximation to the Edwards auxiliary field theory yields a very simple mean-field theory. This is a form of SCFT in which $F_{\text{chain}}[\langle c \rangle]$ is approximated by the free-energy functional for a gas of noninteracting chains, with a single-chain Hamiltonian U_{chain} , and in which

$$F_{\text{int}} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \langle c_i(\mathbf{r}) \rangle U_{ij}(\mathbf{r} - \mathbf{r}') \langle c_j(\mathbf{r}') \rangle. \quad (39)$$

This approximation yields a self-consistent (saddle-point) field

$$\tilde{h}_i(\mathbf{r}) = h_i(\mathbf{r}) - \int d\mathbf{r}' U_{ij}(\mathbf{r} - \mathbf{r}') \langle c_j(\mathbf{r}') \rangle. \quad (40)$$

In this approximation, the internal contribution to $\tilde{h}_i(\mathbf{r})$ (i.e., the convolution integral in the above) is literally a ‘‘mean’’ field, insofar as it is approximated by the ensemble average of the fluctuating potential field $-\int d\mathbf{r}' U_{ij}(\mathbf{r} - \mathbf{r}') c_j(\mathbf{r}')$ at point \mathbf{r} .

The characteristic features of this microscopic mean-field theory, however it is obtained, are that (i) F_{int} is approximated by an expression for the average interaction energy $\langle U_{\text{int}} \rangle$ that neglects all correlations in monomer density, and (ii) intramolecular correlations are taken to be identical to those of a gas of noninteracting molecules. This theory yields a direct correlation function $C_{ij}(k) = -U_{ij}(k)$, an apparent χ -parameter $\chi_a(k) \simeq \chi_0$ for $k \ll \Lambda$, and statistical segment lengths equal to those of the noninteracting chains.

B. One-loop approximation for free energy

The treatment of fluctuation effects given in this paper is based on a one-loop (or Gaussian) approximation. Several authors [5–8] have previously obtained a one-loop approximation for $\chi_a(0)$ by calculating the free energy of a homogeneous blend as a function of composition, and applying Eq. (38). All of these studies started from an idealized model in which chains are treated as continuous Gaussian threads, the pair interaction is taken to be nominally pointlike and in which the liquid is taken to be nominally incompressible.

When these assumptions are all taken literally, the resulting one-loop correction to $\chi_a(0)$ is given by a Fourier integral that diverges at large wave number, i.e., that is UV divergent. The divergence can be removed either by introducing a discrete chain model or by introducing a nonzero range for two-body interactions [13]. In all of these previous studies, the integral expression for $\chi_a(0)$ was regularized by restricting the integral to wave numbers less than a cutoff wave-number Λ .

This regularized one-loop approximation for binary homopolymer blends, which is presented in Sec. V, yields an apparent χ parameter of the form

$$\chi_a(0) = \chi_0 + A\Lambda^3 + B\chi_0\Lambda + \sum_{i=1}^2 \frac{H_i}{N_i} \Lambda + \delta\chi^*(0), \quad (41)$$

where

$$\begin{aligned} A &= \frac{(l_1 - l_2)^2 v}{24\pi^2 \bar{l}^2}, \\ B &= -\frac{6l_1^2 l_2^2}{\pi^2 \bar{l}^3}, \\ H_1 &= -l_1(l_1 - l_2) \frac{3l_1 l_2}{2\pi^2 \bar{l}^3}, \\ H_2 &= -l_2(l_2 - l_1) \frac{3l_1 l_2}{2\pi^2 \bar{l}^3}, \end{aligned} \quad (42)$$

and

$$\bar{l}(\phi_1) \equiv \phi_1 l_1 + \phi_2 l_2. \quad (43)$$

Here, $\delta\chi^*(0)$ is a contribution that remains finite in the limit $\Lambda \rightarrow \infty$ (i.e., that is UV convergent).

The dominant UV divergent parts of this result have been reported previously. De la Cruz *et al.* [5] considered the structurally symmetric case $b_1 = b_2$, for which $A = 0$, and reported the contribution of the form $B\chi_0\Lambda$. Fredrickson and Liu [6,7] instead considered the athermal case $b_1 \neq b_2$ and $\chi_0 = 0$, and so found the $A\Lambda^3$ contribution. Wang [8] retained both of these contributions. The terms proportional to Λ/N have not been retained or analyzed in previous work.

Wang was the only one to attempt to renormalize this theory, in the sense proposed here, by absorbing the strongly cutoff-dependent contributions to χ_a into a redefinition of the SCFT χ parameter. Wang proposed that the χ parameter used in phenomenological SCFT theory be identified, within the one-loop approximation, with a sum

$$\chi_{\text{eff}} \equiv \chi_0 + A\Lambda^3 + B\chi\Lambda. \quad (44)$$

This definition of χ_{eff} is independent of chain length and architecture, and is thus consistent with the physical picture of χ in SCFT as a parameter that is sensitive to details of local fluid structure, but insensitive to changes in chain connectivity at longer length scales.

By absorbing the dominant cutoff-dependent terms into a renormalization of χ , while ignoring the contributions of order Λ/N , Wang was able to isolate the remaining UV convergent contribution $\delta\chi^*(0)$. It is this quantity that contains predictions of the renormalized theory for corrections to SCFT phenomenology. By introducing several further approximations, Wang obtained an approximate analytic expression for $\delta\chi^*(0)$. Both Wang's analytic approximation $\delta\chi^*(0)$ and the full one-loop integral expression for this quantity may be expressed in the nondimensionalized form

$$N\delta\chi^*(0) = \frac{1}{\bar{N}^{1/2}} \delta\tilde{\chi}^*(\chi N, \phi_1, N_1/N_2, b_1/b_2), \quad (45)$$

in which $\delta\tilde{\chi}^*$ is a dimensionless function of all of the dimensionless variables relevant to SCFT. Here, N is a reference degree of polymerization (e.g., typically N_1 or N_2),

$$\bar{N} = Nb^6/v^2 \quad (46)$$

is an invariant degree of polymerization, and b is a reference statistical segment length (e.g., b_1 or b_2). The value of χ used in the integral that defines the right-hand side (RHS) of Eq. (45) may be taken to be either χ_{eff} , to obtain a renormalized perturbation theory, or may be replaced by $\chi_a(0)$ to obtain the type of self-consistent one-loop approximation considered by Wang. In either variant of the theory, the resulting correction to SCFT vanishes in the limit $N \rightarrow \infty$ as a result of the prefactor of $\bar{N}^{-1/2}$.

After showing how to remove the UV divergence from this calculation, Wang focused primarily on a discussion of $\delta\chi^*(0)$ near the spinodal, which determines the critical behavior of a blend. We will defer our own discussion of this subject, and other physical predictions of the one-loop theory, to a subsequent publication.

C. One-loop approximation for $S(k)$

In Secs. X and XI, we analyze the UV divergent contributions to $S^{-1}(k)$ in homopolymer blends and diblock copolymers, respectively. The physical assumptions underlying phenomenological SCFT allow for the possibility that both the χ parameter and the statistical lengths may be different in a one-loop approximation from those obtained in mean-field theory. Renormalization of a local χ parameter is expected to introduce a k -independent change in $S^{-1}(k)$. Changes in statistical segment length would give rise to changes in $S^{-1}(k)$ with a nontrivial, but foreseeable, wave number dependence. To distinguish these effects, we use the OZ expression for $S_{ij}^{-1}(k)$, and calculate separate one-loop contributions to the single-chain correlation function $\Omega_{ij}(k)$ and to the direct correlation function $C_{ij}(k)$. As in the simpler calculation of $\chi_a(k=0)$ discussed above, we divide the one-loop contribution to each of these quantities into a UV-divergent part that we calculate explicitly, and a remaining UV-convergent part that will be examined elsewhere.

1. Intramolecular correlations

The standard SCFT assumes that polymers are approximately Gaussian in a dense mixture, but not that the statisti-

cal segment lengths are necessarily the same as those in a reference system of noninteracting chains. Let $\tilde{\Omega}_{ij}(k; b)$ denote the single-chain correlation function for a Gaussian chain with a specified statistical segment length b , or (for a diblock copolymer) with a specified pair of statistical segment, $b \equiv (b_1, b_2)$. For a homopolymer, $\tilde{\Omega}_{ij}(k)$ with $i=j$ is proportional to a Debye function. If the only effect of interactions upon the single-chain correlation function $\Omega_{ij}(k)$ were to change the values of the statistical segment lengths, we would expect to find

$$\Omega_{ij}(k) \simeq \tilde{\Omega}_{ij}(k; b_0 + \delta b), \quad (47)$$

where b_0 is the ‘‘bare’’ statistical segment length (or lengths) for noninteracting chains, and δb is a correction arising from interactions. This correction is calculated here to first order in a loop expansion. To first order in an expansion in powers of δb , or to first order in a loop expansion, we would expect a renormalization of b to yield a result of the form

$$\Omega_{ij}(k) \simeq \tilde{\Omega}_{ij}(k; b_0) + \sum_k \frac{\partial \tilde{\Omega}_{ij}(k; b)}{\partial b_k} \delta b_k. \quad (48)$$

In the case of a homopolymer blend, the only nonzero terms in the sum are those with $i=j=k$. The more general notation is required for a diblock copolymer melt, in which $\tilde{\Omega}_{12}(k; b)$ is a nonzero function of both b_1 and b_2 . In addition to this renormalization of the statistical segment lengths, we expect to find small corrections to Gaussian chain statistics. We thus expect to find a total one-loop contribution to $\Omega_{ij}(\mathbf{k})$ of the form

$$\delta \Omega_{ij}(k) \simeq \sum_k \frac{\partial \tilde{\Omega}_{ij}(k; b)}{\partial b_k} \delta b_k + \delta \Omega_{ij}^*(k), \quad (49)$$

in which $\delta \Omega_{ij}^*(k)$ is an UV convergent correction that vanishes in the limit $N \rightarrow \infty$.

Our results for the one-loop contribution to $\Omega_{ij}(k)$ are completely consistent with the above discussion: We find that the UV-divergent parts of the one-loop contribution to $\Omega_{ij}(k)$ in both homopolymer blends and diblock copolymer melts have precisely the wave-number dependence suggested by Eq. (48). The calculated fractional change in statistical segment length b_i , to first order in a loop expansion, is given by an expression

$$\frac{\delta b_i}{b_i} = \frac{l_i^2}{\pi^2 \bar{l}} \Lambda \quad (50)$$

that increases linearly with Λ . Identical expressions for δb_k are obtained from calculations of $\tilde{\Omega}_{ij}(k)$ in a homopolymer blend and in a disordered diblock copolymer melt with the same overall composition. Equation (50) for δb_k was obtained previously by Wang [20] by considering the effect of fluctuations upon the end-to-end vector of a single chain in a binary blend.

The UV convergent one-loop contribution $\delta \Omega_{ij}^*$ can be isolated by subtracting the above UV divergence from the total one-loop contribution. Our result for this quantity is

given by a convergent Fourier integral that can be expressed, in either blends or diblock copolymer melts, in nondimensional form

$$\frac{v}{N} \delta \Omega_{ij}^*(k) = \frac{1}{\bar{N}^{1/2}} \delta \hat{\Omega}_{ij}^*(kR, \chi N, \dots) \quad (51)$$

in which $\delta \hat{\Omega}_{ij}^*$ is a dimensionless function of all of the dimensionless variables of SCFT (i.e., χN , ϕ , N_1/N_2 , and b_1/b_2 in a blend, or of χN , f , and b_1/b_2 in a diblock copolymer melt), and of a nondimensionalized wave vector kR . Here, $R = \sqrt{N}b$, N is a reference degree of polymerization (i.e., N_1 or N_2 in a blend or N in a diblock copolymer melt), and b is a reference statistical segment length (i.e., b_1 or b_2).

2. Intermolecular correlations

We now consider intermolecular correlations, as characterized by the direct correlation function $C_{ij}(k)$. We showed in Sec. II D that $C_{ij}(k)$ can be expressed as a functional derivative of the SCFT interaction free energy F_{int} . The standard SCFT assumes that F_{int} is a local functional of monomer concentration fields, and is independent of chain length and architecture. If these assumptions were rigorously correct, the quantities $C_{ij}(k)$ and $\chi_a(k)$ would be completely independent of k , chain length and architecture, but could depend upon composition.

In Sec. X, we show that the one-loop approximation for $\chi_a(k)$ in a binary blend can be expressed as a sum

$$\chi_a(k) = \chi_{\text{eff}} + \sum_{i=1}^2 \frac{H_i(kR_i)}{N_i} \Lambda + \delta \chi^*(k) \quad (52)$$

in which χ_{eff} is the renormalized χ parameter given explicitly in Eq. (44), which is independent of k . Here, $\delta \chi^*(k)$ is a UV convergent contribution that becomes significant only near a spinodal, while $H_i(kR_i)$ is a dimensionless function that approaches the constant H_i given in Eq. (41) in the limit $k \rightarrow 0$. The corresponding expression for $\chi_a(k)$ in a diblock copolymer melt, which is analyzed in Sec. XI, is of the form

$$\chi_a(k) = \chi_{\text{eff}} + \frac{H(kR)}{N} \Lambda + \delta \chi^*(k), \quad (53)$$

where N is the length of the diblock. Both calculations confirm that the contributions to $S^{-1}(k=0)$ that Wang absorbed into χ_{eff} do indeed correspond, for $k \neq 0$, to quantities that are independent of k and chain architecture, consistent with his physical interpretation.

Our results for the UV divergent part of $\chi_a(k)$ simplify considerably in the limit $l_1 = l_2 = \bar{l}$ of equal statistical segment lengths. In this case, the coefficient A vanishes in Eq. (44) for χ_{eff} . In addition, we find that the coefficients H_i (in a binary blend) and H (in a diblock copolymer melt) also vanish in this limit, for all k . In this case, we thus obtain

$$\chi_a(\mathbf{k}) = \chi \left[1 - \frac{6}{\pi^3} l \Lambda \right] + \delta \chi^*(\mathbf{k}), \quad (54)$$

where $l = l_1 = l_2$. Here, $\delta \chi^*(\mathbf{k})$ is a UV convergent part. The term proportional to Λ is the UV divergent correction to χ

that was originally identified by de la Cruz *et al.* [5].

The corrections to SCFT that are of physical interest arise from the smaller UV convergent contribution $\delta\chi^*(k)$. The exact one-loop expression for this quantity is given by a UV convergent integral, that may be expressed, in either blends or diblock copolymer melts, in the nondimensional form

$$N\delta\chi_a^*(k) = \frac{1}{\bar{N}^{1/2}} \delta\hat{\chi}^*(kR, \chi N, \dots), \quad (55)$$

where $\delta\hat{\chi}^*$ is a dimensionless function of the same variables as those used in Eq. (51). The $k \rightarrow 0$ limit of our result for this quantity agrees with that obtained by examining the composition dependence of the free energy density.

D. End-effects and square-gradient terms

The UV divergent terms in Eqs. (52) and (53) that are of order Λ/N cannot be absorbed into the renormalized SCFT parameter χ_{eff} because they depend on molecular weight N , wave number k , and chain architecture. To explain the physical origin of these terms, we consider a slightly generalized form of SCFT in which we allow for two physical effects that are not included in the standard form of the theory. These are:

(1) Excess free energies associated with chain ends and junctions between blocks in block copolymers.

(2) A square-gradient contribution to the one-loop interaction free energy.

In Sec. XII, we thus compare our one-loop results for $\chi_a(k)$ to the predictions of a phenomenological model in which the UV divergent part of the one-loop contribution to F_{int} is assumed to be of the form

$$\delta F_{\text{int}} = \int d\mathbf{r} \left(\delta f_{\text{local}} + \sum_{\alpha} d_{\alpha} \psi_{\alpha} + \frac{1}{2} D (\nabla \phi_1)^2 \right), \quad (56)$$

where $\phi_1(\mathbf{r}) = v c_1(\mathbf{r})$ is a local volume fraction for one of the components in an incompressible liquid. Here, $\delta f_{\text{local}}(\mathbf{r})$ is a local free-energy density, $d_{\alpha}(\mathbf{r})$ is a local concentration of chain end or junction “defects,” and $\psi_{\alpha}(\mathbf{r})$ is an excess free energy arising from the presence of a “defect” of type α . In a binary homopolymer blend, $d_1(\mathbf{r})$ and $d_2(\mathbf{r})$ are the concentrations of chain ends for chains of type 1 and 2, respectively. In a diblock copolymer melt, the index α can take values 1, 2, or J , where $d_J(\mathbf{r})$ is the local concentration of junctions between the blocks. The free energy density $\delta f_{\text{local}}(\mathbf{r})$, the defect free energy $\psi_{\alpha}(\mathbf{r})$ for each type of defect, and the coefficient D are all assumed to be sensitive to local fluid structure, and so may depend upon the cutoff Λ , the statistical segment lengths, and the local composition $\phi_1(\mathbf{r})$.

Excess free energies for chain ends and junctions can arise in the one-loop approximation, even in a model in which the end and junction monomers are assumed to be identical to other monomers of the same type, simply because the local environment of a chain end or junction is different from that of a monomer in the middle of a long chain. This difference is captured at a crude level even by a one-loop theory. In any real polymer liquid, the excess free

energy associated with chain ends would also be sensitive to any differences between the actual chemical structure of the terminal units and the chemical repeat unit.

Previous analyses of the one-loop approximation have ignored these $O(\Lambda/N)$ contributions to $\chi_a(\mathbf{k})$. It was tempting for us to do the same, on the grounds that these terms are smaller by a factor of $1/N$ than those absorbed into χ_{eff} . Actually, however, these contributions are the same order in an expansion in $1/N$ as the term proportional to χ_0 , since χ_0 must be less than a binodal value of $O(1/N)$ in order for the homogeneous state of interest to remain stable. We also found that we needed to analyze and subtract these $O(\Lambda/N)$ divergences in order to carry out the numerical renormalization procedure that we are now using to calculate UV convergent predictions of the theory. This procedure is described briefly in Sec. XV.

We discuss contributions to $\delta\chi_a(k)$ that arise from a postulated square-gradient contribution to F_{int} simultaneously with those that arise from end and junction defects because we find that these contributions are otherwise difficult to disentangle. The square-gradient contribution to δF_{int} in the above model simply adds a contribution $\delta\chi_a(k) = -\frac{v}{2} D k^2$ to $\chi_a(k)$. This, however, can also be written as $\delta\chi_a(k) = -\frac{v}{2} D k^2 R^2 / N b^2$, where $R = \sqrt{N} b$, and so can be absorbed into a contribution of the more general functional form $H(kR)\Lambda/N$, if $D \propto \Lambda$. The only way for us to identify a squared-gradient contribution is thus to explicitly calculate the wave-number dependence that would be produced by end and junction defects alone, and then see if our one-loop results for $\delta\chi_a(k)$ can be expressed as the sum of this defect contribution plus an additional square-gradient contribution.

1. Free energy of homogeneous liquids

Expressions for δf_{local} and ψ_{α} in this generalized SCFT may be obtained by examining the one-loop contribution to the free-energy density of a homogeneous liquid.

The quantity δf_{local} may be obtained by considering the $N \rightarrow \infty$ limit of the UV divergent part of the free-energy density of either a homogeneous binary blend or a disordered diblock copolymer melt. In either case, we obtain

$$\delta f_{\text{local}} = \frac{1}{12\pi^3} \left[\ln \left(12 B_0 \frac{\bar{l}}{v \Lambda^2} \right) + \frac{2}{3} \right] \Lambda^3 - \frac{6}{\pi^2 v} \frac{l_1 l_2}{\bar{l}} \chi_0 \phi_1 \phi_2 \Lambda, \quad (57)$$

where ϕ_i is the macroscopic volume fraction of i monomers. The one-loop contribution to the parameter χ_{eff} defined in Eq. (44) is related to δf_{local} by a second derivative with respect to ϕ_1 , as in Eq. (38).

In a homogeneous binary blend, we find that the total UV divergent part of the one-loop free-energy density δf of a liquid of finite chains may be expressed as the sum

$$\delta f = \delta f_{\text{local}} + \frac{2\phi_1}{N_1 v} \psi_1 + \frac{2\phi_2}{N_2 v} \psi_2, \quad (58)$$

where $2\phi_{\alpha}/N_{\alpha}v$ is the concentration of chain ends for chains of type α and

$$\psi_\alpha = -\frac{3}{4\pi^2\bar{l}}l_\alpha^2\Lambda. \quad (59)$$

The quantity ψ_α is thus tentatively identified as the excess free energy of an α chain end.

The corresponding free energy for a disordered diblock copolymer melt can be written as a sum

$$\delta f = \delta f_{\text{local}} + \frac{1}{N\nu}(\psi_1 + \psi_2 + \psi_J), \quad (60)$$

where ψ_1 and ψ_2 are excess free energies for the ends of the 1 and 2 blocks, as given by Eq. (59). The remaining energy ψ_J is given by

$$\psi_J = -\frac{3}{4\pi^2\bar{l}}(l_1 - l_2)^2\Lambda. \quad (61)$$

This is assumed to be the excess free energy arising from the junction in a single diblock copolymer. The fact that this expression for ψ_J vanishes in the limit $l_1=l_2$ is consistent with the fact that in the limit $\chi_0=0$ and $l_1=l_2$ the two blocks of a diblock copolymer become indistinguishable, so that the excess free energy associated with the junction must thus vanish in this limit. (This argument would allow $\psi_J \neq 0$ for $l_1=l_2$ and $\chi_0 \neq 0$, but this does occur to first order in a loop expansion.)

2. Composition fluctuations

The main evidence for our interpretation of the $O(\Lambda/N)$ contributions to $S^{-1}(k)$ as a combination of end and junction effects and square-gradient contributions is a demonstration that the wave number and parameter dependence of these terms can be explained by this interpretation.

In Sec. XII we present an RPA calculation for $S^{-1}(k)$ in a system with an additional free energy of the form given in Eq. (56), using the explicit expressions for ψ_α given in Eqs. (59) and (61). For a binary blend, the required calculation is the same as the RPA calculation for a blend of polymers with chemically distinct end groups, or a mixture of CAC and DBD triblocks with very short C and D end groups. The calculation for diblock copolymers is similar to that for a pentablock copolymer with very short end and middle blocks. The inclusion of end effects in the RPA generally yields contributions to $S^{-1}(k)$ that are proportional to $1/N$, with a nontrivial k dependence that is different in binary blends and diblock copolymer melts.

The excess free energies associated with chain ends and junctions affect the collective correlation function $S(k)$ if and only if the defect free energies $\psi_1(\mathbf{r})$, $\psi_2(\mathbf{r})$, and $\psi_J(\mathbf{r})$ depend upon the local composition $\phi_1(\mathbf{r})$. If the free energy per defect depends upon the composition of its environment, defects will tend to cluster where their free energies are lowest, and to favor collective composition fluctuations that lower the total defect free energy. In systems with $l_1 \neq l_2$, the above expressions for $\psi_\alpha(\mathbf{r})$ generally do depend upon $\phi_1(\mathbf{r})$, because of the composition dependence of the average packing length $\bar{l}(\phi_1)$. Both end and junction defect free energies are independent of ϕ_1 when $l_1=l_2$, however, implying (correctly)

that we should find no ‘‘defect’’ corrections to $S^{-1}(k)$ in this special case.

We find that the results of this generalized RPA calculation exactly reproduce the structure of the UV divergent $O(1/N)$ terms obtained in our one-loop calculation of $S^{-1}(k)$, if we allow for both end effects and a square-gradient contribution to $F_{\text{int}}[\langle c \rangle]$. The contributions to $S^{-1}(k)$ that arise from the defects vanish in the limit $l_1=l_2$, for the reason discussed above. The value of the coefficient D that we infer by this method (which is the same in binary blend and diblock copolymer melts of the same composition) is given by

$$D = -\frac{(l_1 - l_2)^2}{3\pi^2\bar{l}^2}\Lambda. \quad (62)$$

Because both the defect contributions and this square-gradient coefficient vanish when $l_1=l_2$, the $O(\Lambda/N)$ contribution to $\delta S^{-1}(\mathbf{k})$ vanishes in this case.

The success of this approach strongly suggests that the UV divergent part of the one-loop contribution to the free-energy functional $F_{\text{int}}[\langle c \rangle]$ is of the form assumed in Eq. (56), even for strongly inhomogeneous liquids. We hope that this result will also provide a basis for removing the UV divergence of the one-loop approximation for the free energy of *ordered* phases of block copolymer melts.

IV. AUXILIARY FIELD METHOD

The Edwards’ functional integral representation of Z may be obtained from the identity

$$e^{-(1/2)c^*U^*c} = N^{-1} \int D[J] e^{-(1/2)J^*U^{-1}*J+iJ^*c}. \quad (63)$$

Here, $\int D[J]$ represents a functional integral with respect to an auxiliary chemical potential field, where $J_i(\mathbf{r})$ is a field component that couples to $c_i(\mathbf{r})$. The constant N is given by the integral

$$N \equiv \int D[J] e^{-(1/2)J^*U^{-1}*J}. \quad (64)$$

Substituting this representation of $e^{-U_{\text{int}}}$ into the definition of the grand-canonical partition function Z yields a functional integral

$$Z[h] = N^{-1} \int D[J] e^{L[h,J]}, \quad (65)$$

$$L[h,J] \equiv \ln \tilde{Z}[h+iJ] - \frac{1}{2}J^*U^{-1}*J. \quad (66)$$

Here, we have introduced the notation $\tilde{Z}[\tilde{h}]$ for the partition function of an ideal gas of molecules subjected to an applied field \tilde{h} , for which the total potential energy is $U_0 + U_{\text{ext}}[\tilde{h}]$. In Eq. (66), $\tilde{Z}[h+iJ]$ is the grand-canonical partition function for an ideal gas in which monomers of type i are subjected to a fluctuating complex field

$$\tilde{h}_i(\mathbf{r}) \equiv h_i(\mathbf{r}) + iJ_i(\mathbf{r}). \quad (67)$$

Hereafter, quantities such as \tilde{Z} and \tilde{h} that are defined in this ideal-gas reference state will be denoted with a tilde.

The functional derivative of $\ln \tilde{Z}[\tilde{h}]$ with respect to \tilde{h} is the average monomer concentration

$$\langle c_i(\mathbf{r}) \rangle = \frac{\delta \ln \tilde{Z}[\tilde{h}]}{\delta \tilde{h}_i(\mathbf{r})}. \quad (68)$$

Here, $\langle \cdots \rangle$ denotes an average taken in the ideal gas subjected to a field \tilde{h} . Higher derivatives yield

$$\tilde{\Omega}_{i_1 i_2 \dots i_n}^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{\delta^{(n)} \ln \tilde{Z}[\tilde{h}]}{\delta \tilde{h}_{i_1}(\mathbf{r}_1) \delta \tilde{h}_{i_2}(\mathbf{r}_2) \cdots \delta \tilde{h}_{i_n}(\mathbf{r}_n)}, \quad (69)$$

where

$$\tilde{\Omega}_{i_1 i_2 \dots i_n}^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \equiv \sum_{am} \sum_{s_1 \dots s_n} \langle c_{ami_1}(\mathbf{r}_1) \cdots c_{ami_n}(\mathbf{r}_n) \rangle \quad (70)$$

is an n -point intramolecular correlation function in the ideal gas reference state for monomers of types i_1, i_2, \dots, i_n on the same molecule.

A. Gaussian fluctuations

As already noted, a very simple form of mean-field theory is obtained by applying a saddle-point approximation to functional integral (65). Requiring that

$$\frac{\delta L[h, J]}{\delta J_i(\mathbf{r})} = 0 \quad (71)$$

and using Eq. (68) yields the saddle-point condition given in Eq. (40), in which $\tilde{h}_i(\mathbf{r})$ denotes the saddle-point value of the field $\tilde{h} = h + iJ$ defined in Eq. (67), and in which $\langle c_j(\mathbf{r}) \rangle$ is the corresponding ideal-gas monomer concentration.

A Gaussian approximation for Z is obtained by the approximating the deviation δL of L from its saddle point value by an expansion to second order in the deviation $\delta J_i(\mathbf{r}) \equiv J_i(\mathbf{r}) - J_i^s(\mathbf{r})$ of J from the saddle-point field J^s . We thus approximate

$$\delta L \approx -\frac{1}{2} \sum_{ij} \int d\mathbf{r} \int d\mathbf{r}' \tilde{G}_{ij}^{-1}(\mathbf{r}, \mathbf{r}') \delta J_i(\mathbf{r}) \delta J_j(\mathbf{r}') \quad (72)$$

where

$$\tilde{G}_{ij}^{-1}(\mathbf{r}, \mathbf{r}') = -\frac{\delta L[J, h]}{\delta J_i(\mathbf{r}) \delta J_j(\mathbf{r}')} = \tilde{\Omega}_{ij}(\mathbf{r}, \mathbf{r}') + U_{ij}^{-1}(\mathbf{r}, \mathbf{r}'). \quad (73)$$

In the Fourier space representation for a homogeneous fluid,

$$\tilde{G}_{ij}^{-1}(\mathbf{k}) = \tilde{\Omega}_{ij}(\mathbf{k}) + U_{ij}^{-1}(\mathbf{k}). \quad (74)$$

The ‘‘propagator’’ \tilde{G} obtained by inverting \tilde{G}^{-1} is the screened interaction potential identified by Edwards [11,12],

which is closely analogous to the electrostatic screened interaction in the Debye-Hückel theory of electrolytes. It was noted by Edwards that results of the one-loop theory could be obtained from a perturbation theory in which monomers interact via this screened interaction. It was shown more systematically by one of us [13] that the diagrammatic perturbation theory that arises naturally from the auxiliary field method is equivalent to a type of molecular cluster expansion in which interaction lines (or ‘‘bonds’’) represent factors of the screened interaction.

In the Gaussian approximation

$$Z \approx Z_s Z_G, \quad (75)$$

where $Z_s = e^{L[h, J^s]}$ is the saddle-point value, and Z_G is a factor arising from Gaussian fluctuations. The Gaussian contribution to the free energy in a homogeneous liquid is

$$\begin{aligned} -\ln Z_G &= \frac{1}{2} V \int_{\mathbf{k}} \ln \det[\tilde{\mathbf{G}}^{-1}(\mathbf{k}) \mathbf{U}(\mathbf{k})] \\ &= \frac{1}{2} V \int_{\mathbf{k}} \ln \det[\mathbf{I} + \tilde{\Omega}(\mathbf{k}) \mathbf{U}(\mathbf{k})], \end{aligned} \quad (76)$$

where $\det[\cdots]$ denotes the determinant of a 2×2 matrix.

B. Incompressibility and regularization

In the limit $k \ll \Lambda$, an explicit expression may be given for $\tilde{\mathbf{G}}(\mathbf{k})$ for a nearly incompressible homogeneous liquid. By taking the incompressible limit $B_0 \rightarrow \infty$, while approximating $\hat{F}(k/\Lambda) = 1$ for $k \ll \Lambda$, we obtain

$$G_{ij}(\mathbf{k}) = \frac{1 - 2\nu\chi_0 |\tilde{\Omega}(\mathbf{k})| \tilde{\Omega}_{ij}^{-1}(\mathbf{k})}{\tilde{\Omega}_+(\mathbf{k}) - 2\nu\chi_0 |\tilde{\Omega}(\mathbf{k})|}. \quad (77)$$

The ‘‘1’’ in the numerator denotes a contribution of unity to every matrix element.

In the opposite high-wave-number limit $k \gg \Lambda$, the bare potential $\mathbf{U}(\mathbf{k})$ in any liquid with a large but finite bare compression modulus B_0 is assumed to become vanishingly small, as a result of the decay of the crossover function $F(k/\Lambda)$. This decay of the bare potential will also cause the screened potential $\tilde{\mathbf{G}}(\mathbf{k})$ to become very small for $k \gg \Lambda$.

In Eq. (76), the Gaussian contribution to the free energy is expressed as a Fourier integral in which the integrand depends on $\tilde{\mathbf{G}}(\mathbf{k})$. This is a generic feature of the auxiliary field theory: Fluctuation corrections to mean-field results for all quantities of interest may be expressed as Fourier integrals involving factors of the screened interaction $\tilde{\mathbf{G}}(\mathbf{k})$. Because both $\mathbf{U}(\mathbf{k})$ and $\tilde{\mathbf{G}}(\mathbf{k})$ vanish for $k \gg \Lambda$, the use of any model with a nonzero range of interaction Λ^{-1} , rather than a point-like interaction, thus naturally introduces a cutoff length.

The effects of a nonzero range of interaction Λ^{-1} may thus be crudely mimicked by treating Λ as a cutoff wave number, and simply suppressing contributions from wave vectors $k \gg \Lambda$ in all Fourier integrals. This regularization scheme, which we will adopt, is equivalent to the use of a

model in which $\mathbf{U}(\mathbf{k})$ is independent of k for all $k < \Lambda$, and zero for all $k > \Lambda$. In what follows, we will also restrict ourselves to the nearly incompressible limit, in which $\tilde{\mathbf{G}}(\mathbf{k})$ is given for all $k < \Lambda$ by Eq. (77).

We consider a Gaussian approximation for the free energy density of a homogeneous liquid (i.e., either a binary homopolymer blend or a disordered diblock copolymer melt) in which the integral in Eq. (76) is restricted to $k < \Lambda$, and in which the integrand is evaluated for $k < \Lambda$ by considering the limit of large B_0 . This yields a one-loop correction to the free-energy density

$$\delta f \equiv -\ln Z_G/V \quad (78)$$

given by

$$\delta f = \frac{1}{2} \int_{|\mathbf{q}| < \Lambda} \ln\{[\tilde{\Omega}_+(\mathbf{q}) - 2v\chi_0|\tilde{\Omega}(\mathbf{q})|]B_0v\}. \quad (79)$$

Here, $\tilde{\Omega}_+(\mathbf{q})$ and $|\tilde{\Omega}(\mathbf{q})|$ are the sum of elements and determinant, respectively, of the ideal-gas correlation function matrix $\tilde{\Omega}_{ij}(\mathbf{q})$, defined by analogy to Eq. (35) for the related quantities $\Omega_+(\mathbf{q})$ and $|\Omega(\mathbf{q})|$.

V. FREE ENERGY IN BINARY BLENDS

Several authors [5–8] have obtained a UV divergent contribution to $\chi_a(\mathbf{k}=0)$ in a binary homopolymer blend by calculating the one-loop free energy δf for a homogeneous mixture, as a function of composition, and then using Eq. (38) to extract $\chi_a(\mathbf{k}=0)$. In this section, we review and extend this approach.

A. High- q behavior of $\tilde{\Omega}$ and \tilde{G}

To analyze the UV divergence of δf , we will need an asymptotic expansion of the high- q behavior of the intramolecular two-point function $\tilde{\Omega}_{ij}(\mathbf{q})$, as an expansion in increasing powers of $1/q$. In a binary blend of two Gaussian homopolymers, the function $\tilde{\Omega}_{ij}(\mathbf{q})$ is a diagonal matrix with elements

$$\tilde{\Omega}_{ij}(\mathbf{q}) = \delta_{ij}c_i D_i(\mathbf{q}) \quad (80)$$

with

$$D_i(\mathbf{q}) = N_i g(Q_i^2), \quad (81)$$

where $Q_i^2 \equiv q^2 N b_i^2 / 6$ and where

$$g(x) \equiv 2(e^{-x} - 1 + x)/x^2 \quad (82)$$

is the Debye function. The required high- q expansion of $D_i(\mathbf{q})$ may be obtained by simply dropping the exponentially decaying term in the Debye function (which is not an analytic function of $1/q$). This yields an approximation

$$D_i(\mathbf{q}) \approx D_i^{(0)}(\mathbf{q}) + D_i^{(1)}(\mathbf{q}), \quad (83)$$

$$D_i^{(0)}(\mathbf{q}) = \frac{2N_i}{Q_i^2} = \frac{12l_i}{v} \frac{1}{q^2}, \quad (84)$$

$$D_i^{(1)}(\mathbf{q}) = -\frac{2N_i}{Q_i^4} = -\frac{72l_i^2}{v^2 N_i} \frac{1}{q^4}, \quad (85)$$

where v is a monomer reference volume, and $l_i = v/b_i^2$.

A corresponding expansion of the screened interaction to the same order yields

$$\tilde{G}_{ij}(\mathbf{q}) \approx \tilde{G}^{(0)}(\mathbf{q}) + \tilde{G}^{(1)}(\mathbf{q}) + \tilde{G}_{ij}^{(X)}(\mathbf{q}) \quad (86)$$

where

$$\tilde{G}^{(0)}(\mathbf{q}) = \frac{v^2}{12\bar{l}} q^2,$$

$$\tilde{G}^{(1)}(\mathbf{q}) = \frac{v}{2\bar{l}^2} \left(\frac{\phi_1 l_1^2}{N_1} + \frac{\phi_2 l_2^2}{N_2} \right),$$

$$\tilde{G}_{ij}^{(X)}(\mathbf{q}) = \frac{2v}{\bar{l}^2} Z_{ij} \chi_0, \quad (87)$$

with $\bar{l} \equiv \phi_1 l_1 + \phi_2 l_2$ and

$$Z \equiv \begin{bmatrix} -\phi_2^2 l_2^2 & \phi_1 \phi_2 l_1 l_2 \\ \phi_1 \phi_2 l_1 l_2 & -\phi_1^2 l_1^2 \end{bmatrix}. \quad (88)$$

In Eqs. (86) and (87), the quantities $\tilde{G}^{(0)}(\mathbf{q})$ and $\tilde{G}^{(1)}(\mathbf{q})$ are written with no monomer type indices i and j to indicate that the values of these quantities are actually independent of i and j .

B. Free-energy density

In a binary homopolymer blend, Eq. (79) for δf reduces to

$$\delta f \approx \frac{1}{2} \int_{\mathbf{q}} \ln[(\tilde{\Omega}_1 + \tilde{\Omega}_2 - 2v\chi_0 \tilde{\Omega}_1 \tilde{\Omega}_2) B_0 v]. \quad (89)$$

The dominant contribution to the argument of the logarithm in Eq. (89) in the high- k limit arises from the leading order contribution to $\tilde{\Omega}_+ \equiv \tilde{\Omega}_1 + \tilde{\Omega}_2$, which is

$$\tilde{\Omega}_+^{(0)}(\mathbf{q}) \equiv \sum_i c_i D_i^{(0)}(\mathbf{q}) = \frac{12\bar{l}}{v^2} \frac{1}{q^2}. \quad (90)$$

Note that $\tilde{\Omega}_+^{(0)}(\mathbf{q}) = 1/G^{(0)}(\mathbf{q})$. Factoring $\tilde{\Omega}_+^{(0)} B_0$ out of the argument of the logarithm yields an expression

$$\delta f = \delta f^{(0)} + \frac{1}{2} \int_{\mathbf{q}} \ln\{1 + G^{(0)}[\Delta \tilde{\Omega}_+ - 2v\chi_0 |\tilde{\Omega}|]\} \quad (91)$$

in which $\Delta \tilde{\Omega}_+(\mathbf{q}) \equiv \tilde{\Omega}_+(\mathbf{k}) - \tilde{\Omega}_+^{(0)}(\mathbf{k})$, and in which

$$\delta f^{(0)} = \frac{1}{2} \int_{\mathbf{q}} \ln(\tilde{\Omega}_+^{(0)} B_0 v) = \frac{1}{12\pi^2} \left[\ln\left(12B_0 \frac{\bar{l}}{v\Lambda^2}\right) + \frac{2}{3} \right] \Lambda^3 \quad (92)$$

is the most strongly UV divergent contribution.

Upon expanding the integrand of the remaining integral in Eq. (91) in powers of $1/q$, we find that the leading-order

terms are of $1/q^2$, and yield UV divergent contributions of $O(\Lambda)$ to the integral, but that all subsequent terms in the expansion are UV convergent. The total UV divergent contribution to δf is given by a sum

$$\delta f \simeq \delta f^{(0)} + \delta f^{(\chi)} + \delta f^{(1)} \quad (93)$$

where

$$\delta f^{(\chi)} = -\chi_0 \int_{\mathbf{q}} G^{(0)} |\tilde{\Omega}^{(0)}|, \quad (94)$$

$$\delta f^{(1)} = \frac{1}{2} \int_{\mathbf{q}} G^{(0)} \tilde{\Omega}_+^{(1)}, \quad (95)$$

where $|\tilde{\Omega}^{(0)}(\mathbf{q})| = c_1 c_2 D_1^{(0)}(\mathbf{q}) D_2^{(0)}(\mathbf{q})$ and $\tilde{\Omega}_+^{(1)} = \sum_i c_i D_i^{(1)}(\mathbf{q})$. Completing the integrals yields

$$\delta f^{(\chi)} = -\frac{6\chi_0 l_1 l_2}{\pi^2 v \bar{l}} \phi_1 \phi_2 \Lambda, \quad (96)$$

$$\delta f^{(1)} = -\frac{3}{2\pi^2 v \bar{l}} \left(\frac{\phi_1 l_1^2}{N_1} + \frac{\phi_2 l_2^2}{N_2} \right) \Lambda. \quad (97)$$

The quantity $\delta f^{(0)}$, which is the one-loop contribution to the free energy density of a nearly incompressible blend of infinite chains with $\chi=0$, arises solely from the strong repulsive interactions that suppress overall concentration fluctuations. This quantity generally depends on composition, because of the composition dependence of \bar{l} , and thus can contribute to $\chi_a(0)$. It is independent of composition only in the special case $l_1=l_2=\bar{l}$. The contribution $\delta f^{(\chi)}$ is a negative contribution that reflects a reduction in the average interaction energy from its mean-field value by correlations. We show in Sec. XII that $\delta f^{(1)}$ arises from changes in packing near the chain ends.

C. Direct correlation function

Once the UV divergent contribution δf is known, the corresponding contribution $\delta C_{ij}(\mathbf{k}=0)$ to the direct correlation function may be obtained from the relation

$$\delta C_{ij}(0) = \frac{\delta^2(\delta f)}{\partial c_i \partial c_j}. \quad (98)$$

Differentiation of Eqs. (92), (96), and (97) yields a UV divergent contribution

$$\delta C_{ij}(0) \simeq \delta C_{ij}^{(0)} + \delta C_{ij}^{(\chi)} + \delta C_{ij}^{(1)},$$

$$\delta C_{ij}^{(0)}(0) = \frac{v^2 l_i l_j}{12\pi^2 \bar{l}^3} \Lambda^3, \quad (99)$$

$$\delta C_{ij}^{(\chi)}(0) = \frac{12v l_i l_j}{\pi^2 \bar{l}^3} Z_{ij} \chi_0 \Lambda, \quad (100)$$

$$\delta C_{ij}^{(1)}(0) = \frac{6v l_i l_j}{2\pi^2 \bar{l}^3} \left(\frac{\phi_1 l_1^2}{N_1} + \frac{\phi_2 l_2^2}{N_2} \right) \Lambda - \frac{6v l_i l_j}{4\pi^2 \bar{l}^2} \left(\frac{l_i}{N_i} + \frac{l_j}{N_j} \right) \Lambda. \quad (101)$$

By applying Eq. (36), we obtain a corresponding UV divergent contribution to $\chi_a(0)$,

$$\begin{aligned} \delta \chi_a(0) \simeq & \frac{(l_1 - l_2)^2 v}{24\pi^2 \bar{l}^2} \Lambda^3 - \frac{6l_1^2 l_2^2}{\pi^2 \bar{l}^3} \chi_0 \Lambda \\ & - \frac{3}{2\pi^2} \frac{l_1 l_2 (l_1 - l_2)}{\bar{l}^3} \left(\frac{l_1}{N_1} - \frac{l_2}{N_2} \right) \Lambda, \end{aligned} \quad (102)$$

of the form given in Eq. (41). Note that the coefficient A of the Λ^3 contribution and coefficients H_1 and H_2 of the terms linear in Λ/N_i all vanish in the case $l_1=l_2$ of two polymers with equal statistical segment lengths.

An alternative method of deriving $\delta C_{ij}(0)$, which is useful for comparison to the subsequent calculation of $\delta C_{ij}(\mathbf{q})$ at $\mathbf{q} \neq 0$, is to apply Eq. (32) to Eq. (76) before evaluating the Fourier integral. A straightforward differentiation yields an integral

$$\begin{aligned} \delta C_{ij}(0) &= -\frac{1}{2} \frac{\delta^2}{\partial c_i \partial c_j} \int_{\mathbf{q}} \ln \det[\tilde{\mathbf{G}}^{-1}(\mathbf{q}) \mathbf{U}(\mathbf{q})] \\ &= \frac{1}{2} \int_{\mathbf{q}} D_i(\mathbf{q}) \tilde{G}_{ij}(\mathbf{q}) \tilde{G}_{ij}(\mathbf{q}) D_j(\mathbf{q}). \end{aligned} \quad (103)$$

We show in what follows that this expression can be recovered by taking the $\mathbf{k} \rightarrow 0$ limit of our expression for $\delta C_{ij}(\mathbf{k})$.

VI. GAUSSIAN APPROXIMATION FOR $S(k)$

In this section, we derive an Gaussian approximation for the inverse correlation function $S_{ij}^{-1}(k)$ at $k \neq 0$. The derivation is based on a calculation of the second functional derivatives of $\ln Z_G[h]$ with respect to an external field h_i .

For this purpose, we now adopt a compact notation for position and monomer type indices in which $S(1,2)$ is used as shorthand for a function $S_{i_1 i_2}(\mathbf{r}_1, \mathbf{r}_2)$. In this notation, an integer label I is used as shorthand for a position r_I and a monomer type index i_I . For example, identity (18) becomes

$$S(1,2) = \frac{\delta^2 \ln Z}{\delta h(1) \delta h(2)}, \quad (104)$$

where $\delta/\delta h(2)$ denotes a functional derivative with respect to $h_{i_2}(\mathbf{r}_2)$.

The one-loop contribution to $S(1,2)$ is given by a derivative

$$\delta S(1,2) = \frac{\delta^2 \ln Z_G}{\delta h(1) \delta h(2)} \Big|_{\mu}, \quad (105)$$

in which Z_G is the Gaussian contribution to the partition function of a system in an applied field h . The Gaussian contribution to the free energy of a system that is subjected to an inhomogeneous field \tilde{h} is a functional

$$\ln Z_G = -\frac{1}{2} \text{Tr} \ln \tilde{G}^{-1} U. \quad (106)$$

Here, $\tilde{G}^{-1}(1,2)$ is an integral operator, which is generally not translationally invariant in a fluid that is subjected to an inhomogeneous external field h . The symbols \ln and Tr denote the generalized logarithm and trace for such an operator. The function

$$\tilde{G}^{-1}(1,2;[\tilde{h}]) \equiv \tilde{\Omega}^{(2)}(1,2;[\tilde{h}]) + U^{-1}(1,2) \quad (107)$$

is a functional of the field \tilde{h} , which is the saddle point of $h + iJ$ obtained in the presence of an external field h . The Gaussian integral Z_G is thus also a functional of \tilde{h} .

A straightforward differentiation of Eq. (106) twice with respect to the external field h yields

$$\begin{aligned} \delta S(1,2) &= \int_{1'} \int_{2'} \frac{\delta^2 \ln Z_G[\tilde{h}]}{\delta \tilde{h}(1') \delta \tilde{h}(2')} \frac{\delta \tilde{h}(1')}{\delta h(1)} \frac{\delta \tilde{h}(2')}{\delta h(2)} \\ &+ \int_{1'} \frac{\delta \ln Z_G[\tilde{h}]}{\delta \tilde{h}(1')} \frac{\delta \tilde{h}(1')}{\delta h(1) \delta h(2)}. \end{aligned} \quad (108)$$

Here, we have introduced the shorthand

$$\int_I \equiv \sum_{i_I} \int d\mathbf{r}_I \quad (109)$$

for integration over a position \mathbf{r}_I and summation over allowed values of a corresponding monomer type index i_I . To evaluate Eq. (108), we must evaluate both the first and second derivatives of $Z_G[\tilde{h}]$ with respect to the saddle-point field \tilde{h} , and the first and second derivatives of \tilde{h} with respect to the external field h .

To evaluate the required derivative of $Z_G[\tilde{h}]$, we apply the identities [13]

$$\frac{\delta \text{Tr} \ln \tilde{G}^{-1}}{\delta \tilde{h}(1)} = \int_2 \int_3 \tilde{G}(2,3) \frac{\delta \tilde{G}^{-1}(2,3)}{\delta \tilde{h}(1)},$$

$$\frac{\delta \tilde{\Omega}^{(n)}(1, \dots, n)}{\delta \tilde{h}(n+1)} = \tilde{\Omega}^{(n+1)}(1, \dots, n, n+1),$$

$$\frac{\delta \tilde{G}(1,2)}{\delta \tilde{h}(3)} = - \int_{1'} \int_{2'} \tilde{G}(1,1') \tilde{\Omega}^{(3)}(1',2',3) \tilde{G}(2',2) \quad (110)$$

to obtain

$$\frac{\delta \ln Z_G}{\delta \tilde{h}(1)} = -\frac{1}{2} \int_2 \int_3 \tilde{\Omega}^{(3)}(1,2,3) \tilde{G}(2,3) \quad (111)$$

and

$$\begin{aligned} \frac{\delta^2 \ln Z_G}{\delta \tilde{h}(1) \delta \tilde{h}(2)} &= -\frac{1}{2} \int_3 \int_4 \tilde{\Omega}^{(4)}(1,2,3,4) \tilde{G}(3,4) \\ &+ \frac{1}{2} \int_3 \int_4 \int_5 \int_6 \tilde{\Omega}^{(3)}(1,3,4) \tilde{G}(3,5) \\ &\times \tilde{\Omega}^{(3)}(2,5,6) \tilde{G}(6,4). \end{aligned} \quad (112)$$

To evaluate the derivatives of \tilde{h} with respect to the external field h , we differentiate the saddle-point condition

$$\tilde{h}(1) = h(1) - \int_2 U(1,2) \tilde{\Omega}^{(1)}(2), \quad (113)$$

with respect to h . Note that $\tilde{\Omega}^{(1)}(2)$ is a functional of $\tilde{h}(1)$, with derivatives given by Eq. (110). A single functional derivative yields

$$\int_2 \frac{\delta \tilde{h}(2)}{\delta h(1)} \left[\delta(2,4) + \int_3 \tilde{\Omega}^{(2)}(2,3) U(3,4) \right] = \delta(1,4). \quad (114)$$

Let

$$\tilde{S}^{-1}(1,2) \equiv \tilde{\Omega}^{-1}(1,2) + U(1,2) \quad (115)$$

denote the inverse correlation function obtained in the mean-field approximation, in which $C(1,2) = -U(1,2)$. Using this definition for \tilde{S}^{-1} and Eq. (73) for \tilde{G}^{-1} , we may rewrite Eq. (114) in either of the equivalent forms

$$\frac{\delta \tilde{h}(2)}{\delta h(1)} = \int_3 \tilde{S}(1,3) \tilde{\Omega}^{-1}(3,2) \quad (116)$$

$$= \int_3 U^{-1}(1,3) \tilde{G}(3,2). \quad (117)$$

A second functional derivative yields

$$\begin{aligned} \frac{\delta^2 \tilde{h}(3)}{\delta h(1) \delta h(2)} &= - \int_{1'} \int_{2'} \int_{3'} \int_{4'} \frac{\delta \tilde{h}(1')}{\delta h(1)} \frac{\delta \tilde{h}(2')}{\delta h(2)} \\ &\times \tilde{\Omega}^{(3)}(1',2',4') U(4',3') \frac{\delta \tilde{h}(3)}{\delta h(3')}. \end{aligned} \quad (118)$$

An explicit expression for $\delta S(1,2)$ may then be obtained by combining Eqs. (108), (111), (112), (116) or (117), and (118). We are more interested, however, in obtaining a one-loop contribution to the inverse correlation function $S^{-1}(1,2)$ that appears in the OZ relation. To the order required here, this is related to $\delta S(1,2)$ by

$$\delta S^{-1}(1,4) = - \int_2 \int_3 \tilde{S}(1,2) \delta S(2,3) \tilde{S}(3,4). \quad (119)$$

Combining Eq. (119) with our expression for $\delta S(1,2)$ yields a one-loop contribution

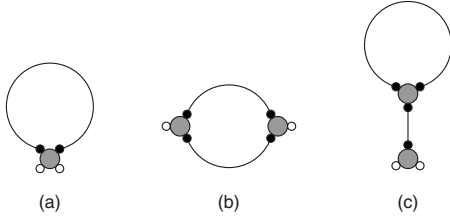


FIG. 1. The three one-loop diagrams of $\tilde{\Omega}$ vertices and $-\tilde{G}$ bonds that contribute to the expression for $\delta\Lambda(1,2)$ given in Eq. (121). Diagrams (a) and (b) represent cluster integrals arising from the first and second terms of the RHS of Eq. (112) for $\delta^2 \ln Z / \delta\tilde{h}(1)\delta\tilde{h}(2)$, respectively, in the first term of Eq. (121). Diagram (c) represents the second term of Eq. (121), in which $\delta \ln Z / \delta\tilde{h}(4)$ is given by Eq. (111).

$$\delta S^{-1}(1,2) = - \int_{1'} \int_{2'} \tilde{\Omega}^{-1}(1,1') \delta\Lambda(1',2') \tilde{\Omega}^{-1}(2',2) \quad (120)$$

in which

$$\delta\Lambda(1,2) \equiv \frac{\delta^2 \ln Z_G}{\delta\tilde{h}(1)\delta\tilde{h}(2)} - \int_3 \int_4 \tilde{\Omega}^{(3)}(1,2,3) \tilde{G}(3,4) \frac{\delta \ln Z_G}{\delta\tilde{h}(4)}. \quad (121)$$

The required functional derivatives of $\ln Z_G$ are given in Eqs. (111) and (112).

VII. DIAGRAMMATIC APPROACH

It is convenient to introduce a diagrammatic representation of cluster integrals such as those obtained in Eqs. (111), (112), and (121). We adopt the diagrammar used previously in Ref. [13]. Some examples of the type of diagrams used here are shown in Fig. 1. Each integral is represented as a diagram containing vertices and bonds. An n -point vertex, shown as a shaded circle with n smaller circles around its circumference, represents a function of n coordinates and type indices, such as $\tilde{\Omega}^{(n)}(1, \dots, n)$. Each of the small circles around the perimeter of a vertex is either a field circle (shown blackened), which represents an argument of the corresponding function that must be integrated over, or a root circle (white), which represents a fixed parameter, rather than an integration variable. Each bond represents a function of two coordinates and type indices, such as the bare interaction $U(1,2)$ or the screened interaction $\tilde{G}(1,2)$. Each bond must be connected at each end to either a vertex field site, or a free root site. (A free root site is the small white circle that is not associated with a vertex, which is used simply to indicate the arguments associated with the free end of a bond are known parameters.) The value of a diagram is the value of the integral obtained by integrating over the coordinates associated with all of the black circles, divided by a combinatorial prefactor that is given by the order of the group of permutational symmetries of the diagram. The diagrams discussed here are all diagrams of $\tilde{\Omega}$ vertices and $-\tilde{G}$ bonds, in which

a factor of $\tilde{\Omega}^{(n)}$ is associated with each n -point vertex and a factor of $-\tilde{G}$ is associated with each bond. In diagrams with $-\tilde{G}$ bonds, vertices with no white circles (i.e., with no root circles) must each have three or more black (field) circles, representing factors of $\tilde{\Omega}^{(n)}$ with $n \geq 3$.

Figure 1 shows a diagrammatic representation of Eq. (121), for $\delta\Lambda(1,2)$, in which we have used Eqs. (111) and (112) for the required functional derivatives of $\ln Z_G$. The correspondence between diagrams and integral expressions is discussed in the figure caption.

It was shown in Ref. [13] how $\ln Z$ and various correlation functions could be expressed to any order in perturbation theory as sums of well-defined infinite sets of such cluster diagrams. It was found that the two-point correlation function $S(1,2)$ can be expressed as an infinite sum

$$S(1,2) = \left\{ \begin{array}{l} \text{Sum of all connected diagrams} \\ \text{of } \tilde{\Omega} \text{ vertices and } -\tilde{G} \text{ bonds} \\ \text{with 2 roots circles labeled} \\ \text{1 and 2} \end{array} \right\}. \quad (122)$$

The intramolecular correlation function $\Omega(1,2)$ in an interacting fluid is given by the subset of these diagrams in which both of the root sites are one of the same vertex (the root vertex),

$$\Omega(1,2) = \left\{ \begin{array}{l} \text{Sum of connected diagrams} \\ \text{of } \tilde{\Omega} \text{ vertices and } -\tilde{G} \text{ bonds} \\ \text{with 2 roots circles labeled} \\ \text{1 and 2 on the same vertex} \end{array} \right\}. \quad (123)$$

Among the diagrams described in Eq. (123) is one consisting of a single two-point $\tilde{\Omega}$ vertex, with no bonds, which represents the ideal-gas contribution $\tilde{\Omega}(1,2)$. The corresponding expansion of the intramolecular correlation function $\Omega_a(1,2)$ for molecule of a specific type in a mixture may be obtained by replacing the $\tilde{\Omega}$ root vertex in each diagram of Eq. (123) (i.e., the vertex with two white circles) by a corresponding $\tilde{\Omega}_a$ vertex, representing a factor of the intramolecular correlation function $\tilde{\Omega}_a$ for the specified molecule type, while using $\tilde{\Omega}$ vertices for all other vertices in the diagram.

A. Diagrammatic resummations

The screened interaction $-\tilde{G}$ used in the cluster expansions described above can be expressed algebraically as an infinite geometrical series

$$-\tilde{G} = -[1 + U * \tilde{\Omega}]^{-1} * U = -U + U * \tilde{\Omega} * U - \dots, \quad (124)$$

where $\tilde{\Omega}$ denotes $\tilde{\Omega}^{(2)}$. This can also be expressed diagrammatically as the sum of an infinite series of all possible chain diagrams of alternating $-U$ bonds and $\tilde{\Omega}^{(2)}$ vertices. By substituting this diagrammatic expansion of $-\tilde{G}$ into the above expansions of S and Ω , we may obtain a formally equivalent expansions of these quantities in terms of diagrams of $\tilde{\Omega}$

vertices and $-U$ bonds. That is, the perturbation theory may be expressed in terms of either the screened interaction \tilde{G} or the underlying bare interaction U . The descriptions of the infinite sums of diagrams of $\tilde{\Omega}$ vertices and $-U$ bonds required to construct S and Ω are identical to those given in Eqs. (122) and (123) for diagrams of $\tilde{\Omega}$ vertices and $-\tilde{G}$ bonds, except for a replacement of $-\tilde{G}$ bonds by $-U$ bonds, and a change in the rule for the nature of the allowed Ω vertices: Two-point $\tilde{\Omega}^{(2)}$ vertices with two field circles and no root circles are allowed in diagrams of $-U$ bonds, but are prohibited in diagrams of $-\tilde{G}$ bonds.

A Dyson equation for $S(1,2)$ may be obtained by defining a function

$$\Lambda(1,2) = \left\{ \begin{array}{l} \text{Sum of bond irreducible diagrams} \\ \text{of } \tilde{\Omega} \text{ vertices and } -\tilde{G} \text{ bonds with} \\ \text{2 roots circles labeled 1 and 2} \end{array} \right\}. \quad (125)$$

A ‘‘bond irreducible’’ diagram is one that cannot be divided into two disconnected pieces that each contain one of the two root circles by cutting or removing only one bond. Equation (125) can also be expressed as a sum of all bond-irreducible diagrams of $\tilde{\Omega}$ diagrams and $-U$ bonds, if $\tilde{\Omega}^{(2)}$ vertices with two field sites and no root sites are allowed. This set of diagrams includes the trivial diagram consisting only of a $\tilde{\Omega}^{(2)}$ vertex with two root sites and no bonds, which represents the function $\tilde{\Omega}^{(2)}(1,2)$. Thus, to a first approximation (or ‘‘tree level’’), $\Lambda(1,2) \approx \tilde{\Omega}(1,2)$. The only one-loop diagrams that contribute to $\Lambda(1,2)$ are the three diagrams shown in Fig. 1. The expression for $\delta\Lambda(1,2)$ given explicitly in Eq. (121) is thus the one-loop contribution to the quantity $\Lambda(1,2)$ defined in Eq. (125).

The function S can be expressed in terms of Λ as a geometric series

$$S = \Lambda - \Lambda * U * \Lambda + \dots = \Lambda - \Lambda * U * S, \quad (126)$$

or diagrammatically as a sum of chain diagrams of Λ vertices connected by $-U$ bonds. Resumming this series, or solving the recursion relation, yields

$$S^{-1}(1,2) = \Lambda^{-1}(1,2) + U(1,2). \quad (127)$$

Approximating $\Lambda(1,2)$ by $\tilde{\Omega}^{(2)}(1,2)$ yields the mean-field approximation for S . Note that Eq. (127) for $S^{-1}(1,2)$ is *not* the same as the generalized OZ equation.

B. One-loop contributions

To calculate one-loop corrections to S^{-1} , it is useful to define

$$\Lambda(1,2) = \tilde{\Omega}(1,2) + \delta\Lambda(1,2), \quad (128)$$

where $\delta\Lambda(1,2)$ is a sum of all contributions to $\Lambda(1,2)$ other than the tree-level contribution $\tilde{\Omega}(1,2)$. To first order in a loop expansion $\delta\Lambda(1,2)$ is given by the sum of the three one-loop diagrams shown in Fig. 1. Substituting Eq. (128)

into Eq. (127) yields a geometrical series in which the first few terms are

$$S^{-1} = U + \tilde{\Omega}^{-1} - \tilde{\Omega}^{-1} * \delta\Lambda * \tilde{\Omega}^{-1} + \dots \quad (129)$$

The one-loop contribution to $S^{-1}(1,2)$ is thus given by

$$\delta S^{-1} = -\tilde{\Omega}^{-1} * \delta\Lambda * \tilde{\Omega}^{-1} \quad (130)$$

with $\delta\Lambda$ approximated by the sum of the three one-loop diagrams for Λ .

The one-loop contribution to the OZ expression for S^{-1} may also be expressed as a sum

$$\delta S^{-1} = \delta\Omega^{-1} - \delta C, \quad (131)$$

where $\delta\Omega^{-1}$ and δC represent one-loop contributions to Ω^{-1} and C , respectively. The one-loop correction to Ω^{-1} is given by the convolution

$$\delta\Omega^{-1} \simeq -\tilde{\Omega}^{-1} * \delta\Omega * \tilde{\Omega}^{-1} \quad (132)$$

where $\delta\Omega$ represents the one-loop correction to Ω . According to the diagrammatic rule given in Eq. (123), the one-loop contribution to $\Omega(1,2)$ is given by the sum of Figs. 1(a) and 1(c). It follows that we may identify $-\delta C$ with the remaining contribution to Eq. (130) that arises from the contribution of Fig. 1(b) to $\delta\Lambda$. That is, to first order in a loop expansion,

$$\delta C \simeq \tilde{\Omega}^{-1} * \Sigma * \tilde{\Omega}^{-1}, \quad (133)$$

where Σ is the value of Fig. 1(b). This expression was obtained previously [13] as the one-loop contribution to a general diagrammatic expansion of the direct correlation function.

1. Intramolecular correlations

The quantity $\delta\Omega_{ij}(\mathbf{k})$ may be expressed as a sum

$$\delta\Omega_{ij}(\mathbf{k}) = \sum_a \delta\Omega_{a,ij}(\mathbf{k}), \quad (134)$$

where $\delta\Omega_{a,ij}(\mathbf{k})$ is a one-loop correction to the intramolecular correlation function $\Omega_{a,ij}(\mathbf{k})$ for molecules of species a . Using the diagrammatic rules discussed above, the one-loop contribution $\delta\Omega_{a,ij}(\mathbf{k})$ may be expressed as a Fourier integral

$$\delta\Omega_{a,ij}(\mathbf{k}) = \tilde{\rho}_{al}[I_{a,ij}^{(2)}(\mathbf{k}) - \tilde{\omega}_{a,ij}(\mathbf{k})\tilde{G}_{ab}\tilde{\rho}_b^{(0)}]. \quad (135)$$

Here,

$$I_a^{(0)} \equiv -\frac{1}{2} \int_{\mathbf{q}} \tilde{\omega}_{a,ij}(\mathbf{q})\tilde{G}_{ij}(\mathbf{q}),$$

$$I_{a,ij}^{(2)}(\mathbf{k}) \equiv -\frac{1}{2} \int_{\mathbf{q}} \tilde{\omega}_{a,ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q})\tilde{G}_{kl}(\mathbf{q}), \quad (136)$$

where $\tilde{\omega}_{a,ij}(\mathbf{k}) \equiv \tilde{\omega}_{a,ij}^{(2)}(\mathbf{k}, -\mathbf{k})$ and

$$\tilde{G}_{ab} \equiv \sum_{kl} N_{ak} G_{kl}(\mathbf{k}=0) N_{bl}, \quad (137)$$

where N_{ak} is the number of monomers of type k on a molecule of type a . Here and in what follows, we use the notation

$$\int_{\mathbf{q}} \equiv \int \frac{d^3q}{(2\pi)^3} \quad (138)$$

for Fourier integrals. To obtain the above expression, we have used the identity $\tilde{\omega}_{a,ijk}^{(3)}(\mathbf{k}, -\mathbf{k}, 0) = N_{ak} \tilde{\omega}^{(2)}(\mathbf{k})$. The first term in square brackets in Eq. (135) corresponds to Fig. 1(a), while the second corresponds to Fig. 1(c). To obtain the above expressions for $\delta\tilde{\Omega}_{a,ij}(\mathbf{k})$, the root vertices in these diagrams must be taken to be $\tilde{\Omega}_a$ vertices. A corresponding contribution for the sum $\delta\tilde{\Omega}_{ij}(\mathbf{k})$ may be obtained either by adding the results for $\delta\tilde{\Omega}_{a,ij}$ for different species in a mixture, or by taking the root vertices in these diagrams to be $\tilde{\Omega}$ vertices (with no species index).

2. Direct correlation function

Equation (133) for δC may be expressed more explicitly in Fourier space as a product,

$$\delta C_{ij}(\mathbf{k}) \approx \tilde{\Omega}_{ik}^{-1}(\mathbf{k}) \Sigma_{kl}(\mathbf{k}) \tilde{\Omega}_{lj}^{-1}(\mathbf{k}), \quad (139)$$

in which

$$\begin{aligned} \Sigma_{ij}(\mathbf{k}) &= \frac{1}{2} \int_{\mathbf{q}} \tilde{\Omega}_{ikm}^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+) \tilde{G}_{kl}(\mathbf{q}_+) \\ &\times \tilde{\Omega}_{jln}^{(3)}(-\mathbf{k}, -\mathbf{q}_-, \mathbf{q}_+) \tilde{G}_{ln}(\mathbf{q}_-) \end{aligned} \quad (140)$$

is the Fourier transform of Fig. 1(a), where $\mathbf{q}_{\pm} \equiv \mathbf{q} \pm \frac{\mathbf{k}}{2}$.

VIII. CANONICAL VS GRAND-CANONICAL ENSEMBLE

Because we have worked thus far in grand-canonical ensemble, the one-loop contribution to S^{-1} derived above is a correction to the mean-field result for a system with a fixed set of chemical potentials, rather than a fixed set of molecular concentrations. In grand-canonical ensemble, a one-loop approximation for the free energy will generally yield a slightly different concentration for each type of molecule than that obtained at the same chemical potentials from the saddle-point approximation. In this section, we first calculate the difference between the molecular concentrations obtained in the mean-field and one-loop approximation at equal chemical potentials, and then use this to obtain a one-loop approximation for S^{-1} for a system with fixed molecular concentrations.

A. Concentration at fixed chemical potential

In grand-canonical ensemble, molecular concentration is given by a derivative

$$\rho_a = \frac{1}{V} \frac{\partial \ln Z}{\partial \mu_a}. \quad (141)$$

The concentration obtained in a Gaussian or one-loop approximation thus differs from that obtained in mean-field theory at equal chemical potential by an amount

$$\delta\rho_a = \frac{1}{V} \frac{\partial \ln Z_G}{\partial \mu_a}. \quad (142)$$

Here, the derivative is evaluated at fixed temperature and fixed values of the chemical potentials of species other than

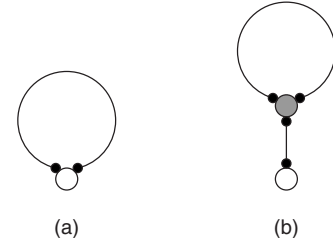


FIG. 2. The two one-loop diagrams of $\tilde{\Omega}$ vertices and $-\tilde{G}$ bonds that contribute to the molecular number density ρ_a . Diagrams (a) and (b) correspond to the first and second lines of Eq. (147), respectively. Here, whitened vertices (larger circles) are used to represent factors of the ideal-gas intramolecular correlation function $\tilde{\Omega}_a$ for a specific molecular species a , while the gray vertex in diagram (b) represents a factor of $\tilde{\Omega}$, as defined in Eq. (22).

a . Because the saddle-point field \tilde{h} will shift in response to changes in chemical potential, however, and $\ln Z_G$ is expressed as a functional of the saddle-point field, this derivative is a sum

$$V\delta\rho_a = \left. \frac{\partial \ln Z_G}{\partial \mu_a} \right|_{\tilde{h}} + \int_1 \frac{\partial \tilde{h}(1)}{\partial \mu_a} \left. \frac{\delta \ln Z_G}{\delta \tilde{h}(1)} \right|_{\mu}, \quad (143)$$

where $\delta \ln Z_G / \delta \tilde{h}(1)$ is given in Eq. (111), and where

$$\left. \frac{\partial \ln Z_G}{\partial \mu_a} \right|_{\tilde{h}} = -\frac{1}{2} \int_1 \int_2 \tilde{\Omega}_a(1,2) \tilde{G}(2,1). \quad (144)$$

A straightforward functional derivative yields the identity

$$\frac{\partial \tilde{h}(1)}{\partial \mu_a} = \int_2 \tilde{G}(1,2) \tilde{\Omega}_a^{(1)}(2), \quad (145)$$

where $\tilde{\Omega}_{ai}^{(1)}(\mathbf{r})$ is the contribution of molecules of type a to the concentration of monomers of type i in the reference ideal gas. This is given in a homogeneous fluid by a constant

$$\tilde{\Omega}_{ai}^{(1)}(\mathbf{r}) = N_{ai} \tilde{\rho}_a \quad (146)$$

for all \mathbf{r} , where N_{ai} is the number of monomers of type i on a molecule of type a . By combining Eqs. (143) and (144), we obtain

$$\begin{aligned} V\delta\rho_a &= -\frac{1}{2} \int_1 \int_2 \tilde{\Omega}_a(1,2) \tilde{G}(2,1) \\ &+ \frac{1}{2} \int_1 \int_2 \int_3 \int_4 \tilde{\Omega}_a^{(1)}(1) \tilde{G}(1,2) \tilde{\Omega}(2,3,4) \tilde{G}(3,4). \end{aligned} \quad (147)$$

This expression is shown diagrammatically in Fig. 2. Evaluating the Fourier representation of these diagrams yields

$$\delta\rho_a = \tilde{\rho}_a [I_a^{(0)} - \bar{G}_{ab} \tilde{\rho}_b I_b^{(0)}] \quad (148)$$

where $I_a^{(0)}$ and \bar{G}_{ab} are defined in Eqs. (136) and (137).

B. $S(k)$ at fixed concentration

We would like to obtain an expression for the one-loop correction to $S(k)$ in an interacting liquid with a fixed concentration ρ_a for each species of molecules. To do so, we consider a one-loop approximation in which each chemical potential is shifted by an amount $\delta\mu_a$ from the value used in the mean-field calculation, where $\delta\mu_a$ is chosen so as to produce a shift $-\delta\rho_a$ that exactly cancels the the one-loop contributions to ρ_a at fixed chemical potential. To first order in a loop expansion, the only effect of this shift in chemical potentials is to shift the intramolecular correlation function by an amount

$$\delta\Omega_{a,ij}(\mathbf{k}) = -\delta\rho_a \tilde{\omega}_{a,ij}(\mathbf{k}) \quad (149)$$

where $\delta\rho_a$ is the one-loop contribution to ρ_a at fixed chemical potential. There is no corresponding correction to $C_{ij}(\mathbf{k})$, because this is given to zeroth order by a quantity $-U_{ij}(\mathbf{k})$ that is independent of μ .

Upon combining Eq. (149) with Eq. (148) for $\delta\rho_a$, we find that the contribution of Fig. 1(c) to $\delta\Omega_a$ is precisely cancelled by the contribution of Fig. 2(b) to $\delta\rho_a$. The contributions arising from Fig. 1(a) and Fig. 2(a) yield a correction $\delta\Omega_{a,ij}(\mathbf{k}) = \rho_a \delta\omega_{a,ij}(\mathbf{k})$, where

$$\delta\omega_{a,ij}(\mathbf{k}) = I_{a,ij}^{(2)}(\mathbf{k}) - \tilde{\omega}_{a,ij}(\mathbf{k}) I_a^{(0)}. \quad (150)$$

This one-loop contribution to $\omega_{a,ij}(\mathbf{k})$ at fixed molecular concentration may also be expressed as an integral

$$\delta\omega_{a,ij}^{(2)}(\mathbf{k}) \simeq -\frac{1}{2} \sum_{ij} \int_{\mathbf{q}} \tilde{\psi}_{a,ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}) \tilde{G}_{kl}(\mathbf{q}), \quad (151)$$

where

$$\tilde{\psi}_{a,ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}) \equiv \tilde{\omega}_{a,ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}) - \tilde{\omega}_{a,ij}^{(2)}(\mathbf{k}) \tilde{\omega}_{a,kl}^{(2)}(\mathbf{q}). \quad (152)$$

This expression for $\delta\omega_{a,ij}^{(2)}(\mathbf{k})$ was obtained in Ref. [13] by similar reasoning. It was obtained previously by Barrat and Fredrickson by calculating a one-loop correction to $\omega_{ij}(\mathbf{k})$ in canonical, rather than grand-canonical, ensemble.

IX. ASYMPTOTIC ANALYSIS OF SINGLE-CHAIN CORRELATIONS

To show that the one-loop approximation for $\Omega_{ij}^{-1}(\mathbf{k})$ is renormalizable, we must show that the UV divergent parts of the one-loop contributions to $\omega_{ij}(\mathbf{k})$ and $C_{ij}(\mathbf{k})$ each have a specific wave-number dependence. In both cases, the proof relies critically upon an analysis of the dominant asymptotic high- q behavior of a three- or four-point intramolecular correlation function. To show that dominant UV divergent part of Eq. (139) for $\delta C_{ij}(\mathbf{k})$ is independent of \mathbf{k} , as required by our criteria for renormalizability, we must examine the asymptotic high- q behavior of the three-point function $\tilde{\Omega}_{ijk}^{(3)} \times (\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)$ that appears in Eq. (140). Similarly, to show that the UV divergent part of Eq. (151) for $\delta\omega_{a,ij}(\mathbf{k})$ has the

nontrivial wave-number dependence implied by Eq. (48), we must examine the asymptotic behavior of the four-point function $\tilde{\psi}_{ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q})$. In both cases, we need the asymptotic behavior of a multipoint correlation function in the limit of large integration wave-vector \mathbf{q} , for arbitrary \mathbf{k} . The correlation functions required here are closely related to, but distinct from, the three- and four-point vertex functions introduced by Leibler [27], which are defined as the third and fourth functional derivatives of the SCFT free-energy $F[\langle c \rangle]$. For simplicity, we limit ourselves in this section to the identification of the dominant high- q behavior for homopolymers. A more systematic asymptotic expansion for homopolymers and the generalization to diblock copolymers are given in the Appendix.

A. Multipoint correlations

To begin, we consider some general features of the n -point intramolecular correlation function $\tilde{\omega}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n)$ for a Gaussian homopolymer. This quantity is given by an integral

$$\tilde{\omega}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \int_0^N d^n s \langle e^{i\mathbf{k}_j \cdot \mathbf{R}(s_j)} \rangle, \quad (153)$$

where $\langle \dots \rangle$ indicates an average over conformations of a single Gaussian chain. Here, we have introduced the notation

$$\int_0^N d^n s \equiv \int_0^N ds_n \cdots \int_0^N ds_2 \int_0^N ds_1 \quad (154)$$

for an integral over n contour variables. Because we consider only homopolymers in this section, no monomer species indices are needed, or used.

To calculate $\tilde{\omega}^{(n)}(\{\mathbf{k}\})$, we divide the integral over $0 < s_1, s_2, \dots, s_n < N$ into $n!$ contributions arising from different ways of ordering the values of s_1, s_2, \dots, s_n , each corresponding to a different way of ordering labeled monomers along a chain. We first consider a restricted n -dimensional integral in which the variables s_1, \dots, s_n are restricted to the ordered subspace $s_1 < s_2 < \dots < s_n$, and then reconstruct the original integral by summing over all $n!$ permutations of the index labels $i=1, \dots, n$. By this method, Eq. (153) may be rewritten as a sum

$$\tilde{\omega}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \sum_{\{P\}} \omega_i^{(n)}(\mathbf{k}_1^P, \dots, \mathbf{k}_n^P) \quad (155)$$

in which the list $\mathbf{k}_1^P, \dots, \mathbf{k}_n^P$ is a permutation P of the original list of wave vectors $\mathbf{k}_1, \dots, \mathbf{k}_n$, and $\sum_{\{P\}}$ denotes a sum over all possible permutations of the n wave vectors. Here,

$$\omega^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n) \equiv \int_0^N d^n \underline{s} \langle e^{i\sum_j \mathbf{k}_j \cdot \mathbf{R}(s_j)} \rangle \quad (156)$$

is an ordered integral, in which we introduce the notation

$$\int_0^N d^n \underline{s} \equiv \int_0^N ds_n \cdots \int_0^{s_3} ds_2 \int_0^{s_2} ds_1, \quad (157)$$

to indicate an ordered integral over the space $0 < s_1 < s_2 < s_3 < \dots < s_n < N$.

To obtain an expression for the ordered integral $\hat{\omega}_i^{(n)}$, we first rewrite the sum of dot products that appears in the exponential in Eq. (156) as sum

$$\sum_{j=1}^n \mathbf{k}_j \cdot \mathbf{R}(s_j) = \mathbf{e}_n \cdot \mathbf{R}(s_n) - \sum_{j=1}^{n-1} \mathbf{e} \cdot \Delta \mathbf{R}_{j+1,j} \quad (158)$$

in which

$$\Delta \mathbf{R}_{ij} \equiv \mathbf{R}(s_i) - \mathbf{R}(s_j) \quad (159)$$

and in which

$$\mathbf{e}_i \equiv \sum_{j=1}^i \mathbf{k}_j, \quad (160)$$

where $\mathbf{k}_1, \dots, \mathbf{k}_n$ denotes the ordered list of arguments of the ordered integral $\hat{\omega}_i^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n)$. Using the property

$$\langle e^{i\mathbf{e} \cdot [\mathbf{R}(s) - \mathbf{R}(s')]} \rangle = e^{-e^2 b^2 |s-s'|/6} \quad (161)$$

of a Gaussian chain, where $e^2 \equiv |\mathbf{e}|^2$, we then obtain an explicit expression,

$$\hat{\omega}_i^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \int_0^N d^n \underline{s} e^{-\sum_{j=1}^{n-1} |\mathbf{e}_j|^2 b^2 s_{j+1,j}/6}, \quad (162)$$

where

$$s_{ij} \equiv s_i - s_j \quad (163)$$

is a difference in monomer contour variables, for any set of wave-vectors $\mathbf{k}_1, \dots, \mathbf{k}_n$ for which $\mathbf{e}_n = \sum_{i=1}^n \mathbf{k}_i = 0$, as required by translational invariance.

By changing variables in the above integrals to contour variables $\hat{s}_i \equiv s_i/N$, for which $0 < \hat{s}_i < 1$, we find that

$$\begin{aligned} \tilde{\omega}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n; N, b) &= N^n \hat{\omega}^{(n)}(\mathbf{K}_1, \dots, \mathbf{K}_n), \\ \underline{\omega}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n; N, b) &= N^n \hat{\omega}^{(n)}(\mathbf{K}_1, \dots, \mathbf{K}_n), \end{aligned} \quad (164)$$

where the functions $\hat{\omega}^{(n)}$ and $\underline{\omega}^{(n)}$ depend only upon the rescaled wave-vectors $\mathbf{K}_j \equiv \mathbf{k}_j \sqrt{N} b/6$, and

$$\hat{\omega}_i^{(n)}(\mathbf{K}_1, \dots, \mathbf{K}_n) = \int_0^1 d^n \hat{s} e^{-\sum_{j=1}^{n-1} E_j^2 \hat{s}_{j+1,j}}. \quad (165)$$

Here, $E_j^2 \equiv |\mathbf{K}_1 + \dots + \mathbf{K}_j|^2$, and the integral in Eq. (165) is taken over $0 < \hat{s}_1 < \hat{s}_2 < \dots < \hat{s}_n < 1$. The function $\hat{\omega}^{(n)}$ is an n -point generalization of the Debye function, which is related to $\underline{\omega}^{(n)}$ by a sum over permutations analogous to Eq. (155).

B. Three point function

Consider the asymptotic high- q behavior of the function $\hat{\omega}^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+)$, which is needed in Eq. (140) to calculate $\delta C_{ij}(\mathbf{K})$. Adding the $3! = 6$ permutations of the monomers or wave-vector labels yields

$$\begin{aligned} \hat{\omega}^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+) &= 2\hat{\omega}^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+) + 2\hat{\omega}^{(3)}(\mathbf{K}, -\mathbf{Q}_+, \mathbf{Q}_-) \\ &\quad + 2\hat{\omega}^{(3)}(\mathbf{Q}_-, \mathbf{K}, -\mathbf{Q}_+), \end{aligned} \quad (166)$$

where $\mathbf{Q}_\pm \equiv \mathbf{Q} \pm \mathbf{K}/2$. Equal contributions to this sum are

made by permutations that are related by a reversal of the order of the wave-vector arguments, so that, e.g., $\hat{\omega}^{(3)} \times (\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+) = \hat{\omega}^{(3)}(-\mathbf{Q}_+, \mathbf{Q}_-, \mathbf{K})$.

We are interested here in the asymptotic behavior of $\hat{\omega}^{(3)} \times (\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+)$ in the limit $Q^2 \gg 1$ and $Q^2 \gg K^2$, for otherwise arbitrary K . First, consider the first two ordered integrals in Eq. (166), in which \mathbf{K} is the first of the three arguments. These may be related by taking $\mathbf{Q} \rightarrow -\mathbf{Q}$, so we need consider only $\hat{\omega}^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+)$. This is given by an integral

$$\hat{\omega}^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+) = \int_0^1 d^3 \hat{s} e^{-Q_+^2 \hat{s}_{32} - K^2 \hat{s}_{21}}. \quad (167)$$

In the limit $Q^2 \gg 1$ of interest, this integral is dominated by contributions in which the separation \hat{s}_{32} is of order $1/Q^2$, yielding $\hat{s}_{32} \ll 1$. The dominant asymptotic behavior in this limit may thus be obtained by replacing the integral with respect to \hat{s}_3 over the domain $\hat{s}_2 < \hat{s}_3 < 1$ by an integral over the seminfinite domain $\hat{s}_2 < \hat{s}_3 < \infty$, while still requiring that $0 < \hat{s}_1 < \hat{s}_2 < 1$. To leading order in an expansion in powers of $1/Q$, this approximation yields

$$\hat{\omega}^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+) \approx \frac{1}{2Q^2} g(K^2) + O(Q^{-4}), \quad (168)$$

where

$$g(K^2) = 2 \int_0^1 ds_2 \int_0^{s_2} ds_1 e^{-K^2 s_{21}} \quad (169)$$

is the Debye function. Because the result is invariant under $\mathbf{Q} \rightarrow -\mathbf{Q}$, this approximation yields $\hat{\omega}^{(3)}(\mathbf{K}, -\mathbf{Q}_+, \mathbf{Q}_-) \approx \hat{\omega}^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+)$. Next, we consider the remaining ordered integral,

$$\hat{\omega}^{(3)}(\mathbf{Q}_-, \mathbf{K}, -\mathbf{Q}_+) = \int_0^1 d^3 \hat{s} e^{-Q_+^2 \hat{s}_{32} - Q_-^2 \hat{s}_{21}}. \quad (170)$$

By reasoning similar to that discussed above, we may approximate this integral in the limit $Q_\pm^2 \gg 1$ by an integral over a domain $-\infty < \hat{s}_1 < \hat{s}_2$, $\hat{s}_2 < \hat{s}_3 < \infty$ and $0 < \hat{s}_2 < 1$. This yields a leading order approximation

$$\hat{\omega}^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+) \approx \frac{1}{Q^4} + O(Q^{-6}), \quad (171)$$

which does not contribute to the leading order $O(Q^{-2})$ term in $\hat{\omega}^{(3)}$. The leading order contribution to $\hat{\omega}^{(3)}$ thus arises from the four permutations in which \mathbf{K} is either the first or last argument of $\hat{\omega}^{(3)}$, and is equal to four times the RHS of Eq. (168).

A more systematic asymptotic expansion, which is outlined in the Appendix, yields

$$\hat{\omega}^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+) = \hat{\omega}^{(3,0)} + \hat{\omega}^{(3,1)} + \dots \quad (172)$$

with

$$\hat{\omega}^{(3,0)} = \frac{2}{Q^2} g(K^2), \quad (173)$$

$$\hat{\omega}^{(3,1)} = \frac{1}{2Q^4} [K^2(3 + 4\alpha^2)g(K^2) - 4], \quad (174)$$

where $\alpha \equiv \mathbf{Q} \cdot \mathbf{K} / QK$. Further terms in the expansion are not needed to analyze the UV divergence of $\delta C_{ij}(\mathbf{k})$. The observation that the leading-order contribution $\hat{\omega}^{(3,0)}$ has the same K dependence as the two-point function $\hat{\omega}^{(2)} = g(K^2)$ plays an essential role in our analysis of $\delta C_{ij}(\mathbf{k})$.

C. Four-point function

The function $\psi^{(4)} \equiv \psi^{(4)}(-\mathbf{k}, \mathbf{k}, -\mathbf{q}, \mathbf{q})$ may be expressed as an integral

$$\psi^{(4)} = \int_0^N d^n s (\langle e^{i\mathbf{k} \cdot \Delta \mathbf{R}_{21}} e^{i\mathbf{q} \cdot \Delta \mathbf{R}_{43}} \rangle - \langle e^{i\mathbf{k} \cdot \Delta \mathbf{R}_{21}} \rangle \langle e^{i\mathbf{q} \cdot \Delta \mathbf{R}_{43}} \rangle) \quad (175)$$

in which the integral ranges over $0 < s_i < N$ for all $i = 1, \dots, 4$. Like the integral for $\hat{\omega}^{(4)}$, this integral may be divided into contributions arising from each of the $4! = 24$ different possible permutations of the contour variables $\hat{s}_1, \dots, \hat{s}_4$. We thus define functions $\underline{\psi}$ analogous to the ordered integrals $\omega^{(4)}$, in which arguments $\pm \mathbf{k}$ and $\pm \mathbf{q}$ are listed in the same order as order of the values of the associated contour variables. For example,

$$\underline{\psi}^{(4)}(-\mathbf{k}, -\mathbf{q}, \mathbf{q}, \mathbf{k}) \equiv \int_0^N d^n \underline{s} (\langle e^{i\mathbf{k} \cdot \Delta \mathbf{R}_{41}} e^{i\mathbf{q} \cdot \Delta \mathbf{R}_{32}} \rangle - \langle e^{i\mathbf{k} \cdot \Delta \mathbf{R}_{41}} \rangle \langle e^{i\mathbf{q} \cdot \Delta \mathbf{R}_{32}} \rangle),$$

where the integration is over a subspace $0 < s_1 < s_2 < s_3 < s_4 < N$. We also define functions

$$\hat{\psi}^{(4)}(\mathbf{K}, -\mathbf{K}, \mathbf{Q}, -\mathbf{Q}) \equiv N^{-4} \psi^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}),$$

$$\hat{\underline{\psi}}^{(4)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3, \mathbf{K}_4) \equiv N^{-4} \underline{\psi}^{(4)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4), \quad (176)$$

analogous to $\hat{\omega}$ and $\hat{\underline{\omega}}$, which depend only upon the dimensionless wave-vectors $\mathbf{K} \equiv \mathbf{k} \sqrt{Nb^2/6}$ and $\mathbf{Q} \equiv \mathbf{q} \sqrt{Nb^2/6}$.

The function $\hat{\underline{\psi}}^{(4)}$ is unchanged by permutations of its arguments that reverse the order (i.e., $\mathbf{K}_1, \dots, \mathbf{K}_4 \rightarrow \mathbf{K}_4, \dots, \mathbf{K}_1$) or that reverse all of their signs (i.e., $\mathbf{K}_1, \dots, \mathbf{K}_4 \rightarrow -\mathbf{K}_1, \dots, -\mathbf{K}_4$). Using these symmetries, we find that

$$\begin{aligned} \hat{\psi}^{(4)} &= 4\hat{\underline{\psi}}(\mathbf{K}, \mathbf{Q}, -\mathbf{K}, -\mathbf{Q}) + 4\hat{\underline{\psi}}(\mathbf{K}, -\mathbf{Q}, -\mathbf{K}, \mathbf{Q}) \\ &+ 2\hat{\underline{\psi}}(\mathbf{K}, \mathbf{Q}, -\mathbf{Q}, -\mathbf{K}) + 2\hat{\underline{\psi}}(\mathbf{K}, -\mathbf{Q}, \mathbf{Q}, -\mathbf{K}) \\ &+ 2\hat{\underline{\psi}}(\mathbf{Q}, \mathbf{K}, -\mathbf{K}, -\mathbf{Q}) + 2\hat{\underline{\psi}}(-\mathbf{Q}, \mathbf{K}, -\mathbf{K}, \mathbf{Q}). \end{aligned} \quad (177)$$

The values of $\hat{\underline{\psi}}^{(4)}$ arising from the eight permutations in which $\pm \mathbf{K}$ are the first two or the last two arguments, such as $\hat{\underline{\psi}}^{(4)}(\mathbf{K}, -\mathbf{K}, \mathbf{Q}, -\mathbf{Q})$, vanish because of a cancellation of the first and second terms in the integrand of Eq. (175).

In the limit $Q^2 \gg 1$ and $Q^2 \gg K^2$ of interest, the dominant contributions to $\hat{\psi}^{(4)}$ arise from the four permutations in

which $\pm \mathbf{K}$ are the first and last arguments of $\hat{\underline{\psi}}$. (The analysis required to show this is given in the Appendix.) The sum of these permutations yields a dominant contribution of $O(Q^{-4})$ in an expansion in powers of $1/Q$. For example, the function $\hat{\underline{\psi}}^{(4)}(\mathbf{k}, \mathbf{q}, -\mathbf{q}, -\mathbf{k})$ is given by an integral

$$\begin{aligned} \hat{\underline{\psi}}^{(4)}(\mathbf{K}, \mathbf{Q}, -\mathbf{Q}, -\mathbf{K}) &= \int_0^1 d^4 \hat{s} (e^{-K^2 \hat{s}_{43} - Q^2 \hat{s}_{32} - K^2 \hat{s}_{21}} \\ &- e^{-K^2 \hat{s}_{41} - Q^2 \hat{s}_{32}}). \end{aligned} \quad (178)$$

Throughout this section, $Q_{\pm}^2 \equiv |\mathbf{Q} \pm \mathbf{K}|^2$. In the limit $Q^2 \gg 1$ of interest, the dominant behavior of this integral is

$$\begin{aligned} \hat{\underline{\psi}}^{(4)}(\mathbf{K}, \mathbf{Q}, -\mathbf{Q}, -\mathbf{K}) &\simeq \left[\frac{-2K\alpha}{Q^3} + \frac{4(K\alpha)^2}{Q^4} \dots \right] \\ &\times \int_0^1 d\hat{s}_4 \int_0^{\hat{s}_4} d\hat{s}_1 \hat{s}_{41} e^{-K^2 \hat{s}_{41}}, \end{aligned} \quad (179)$$

where $\alpha \equiv \mathbf{K} \cdot \mathbf{Q} / QK$. The integral in the second line may be expressed as a derivative of Eq. (169) for the Debye function since

$$\frac{dg(K^2)}{d(K^2)} = -2 \int_0^1 d\hat{s}_2 \int_0^{\hat{s}_2} d\hat{s}_1 \hat{s}_{21} e^{-K^2 \hat{s}_{21}}. \quad (180)$$

Upon adding the four permutations in which $\pm \mathbf{K}$ are the first and last arguments of $\hat{\underline{\psi}}^{(4)}$, the terms linear in α cancel. This yields a leading-order contribution

$$\hat{\psi}^{(4)}(\mathbf{K}, -\mathbf{K}, \mathbf{Q}, -\mathbf{Q}) \simeq -\frac{8K^2 \alpha^2}{Q^4} \frac{dg(K^2)}{d(K^2)}. \quad (181)$$

The dominant contribution to the function $\psi^{(4)} = N^4 \hat{\psi}^{(4)}$ may be expressed in terms of a partial derivative

$$\psi^{(4,0)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}) = -\frac{288\alpha^2}{q^4 b^2} \frac{\partial \hat{\omega}^{(2)}(\mathbf{k})}{\partial(b^2)} \quad (182)$$

of $\hat{\omega}^{(2)}$ with respect to b^2 . Here, we have introduced the notation $\psi^{(4,0)}$ to denote the leading order term in an expansion of $\psi^{(4)}$ in powers of $1/q$. This asymptotic expression is used in Sec. X to relate the one-loop correction to $\hat{\omega}^{(2)}$ to a renormalization of the statistical segment length.

X. CORRELATIONS IN BINARY BLENDS

We can now analyze the UV divergent contributions to $S_{ij}^{-1}(\mathbf{k})$ in a binary homopolymer blend. We consider the intramolecular and direct correlation functions separately.

A. Intramolecular correlations

The one-loop contribution to $\omega_{a,ij}^{(2)}(\mathbf{k})$ in either a blend or a copolymer melt is given by Eq. (151). In the case of a binary homopolymer blend this simplifies to

$$\delta\omega_i^{(2)}(\mathbf{k}) = -\frac{1}{2} \int_{\mathbf{q}} \psi_i^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}) \tilde{G}_{ii}(\mathbf{q}), \quad (183)$$

where the integral is constrained to $|\mathbf{q}| < \Lambda$, and where we have introduced the notation $\omega_i^{(2)} \equiv \omega_{ii}^{(2)}$ and $\psi_i^{(4)} \equiv \psi_{iiii}^{(4)}$ appropriate for a homopolymer mixture.

To determine the order of the dominant ultraviolet divergence of $\delta\omega_i^{(2)}(\mathbf{k})$, we note that Eq. (87) yields $\tilde{G}(\mathbf{q}) \propto q^2$ and that Eq. (182) yields $\psi^{(4)} \propto q^{-4}$ for large q . We thus expect

$$\int_{q < \Lambda} d^3q \psi_i^{(4)} \tilde{G}_{ii} \sim \Lambda. \quad (184)$$

All subdominant terms in an expansion of the integrand in powers of $1/q^2$ yield contributions to the integrand that are smaller by factors of $O(1/q^2)$, which lead to UV convergent contributions to the integral.

The ultraviolet divergent part of the one-loop approximation for $\delta\omega_i^{(2)}$ is thus given by a cutoff integral,

$$\delta\omega_i^{(2)}(\mathbf{k}) = -\frac{1}{2} \int_{\mathbf{q}} \psi_i^{(4,0)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}) \tilde{G}^{(0)}(\mathbf{q}), \quad (185)$$

in which $\psi^{(4,0)}$ denotes the leading-order approximation for $\psi^{(4)}$ given in Eq. (182) and $\tilde{G}^{(0)}(\mathbf{q})$ denotes the leading-order asymptotic approximations to $G_{ij}(\mathbf{q})$ given in Eq. (87) (which is the same for all i and j). A straightforward integration yields

$$\delta\omega_i^{(2)}(\mathbf{k}) \approx \frac{\partial \tilde{\omega}_i^{(2)}(\mathbf{k})}{\partial (b_i^2)} \delta(b_i^2) \quad (186)$$

where

$$\delta(b_i^2) = b_i^2 \frac{2l_i^2}{\pi^2 l} \Lambda \quad (187)$$

is a shift in the value of b_i^2 .

The UV convergent correction to $\omega(\mathbf{k})$ is given by the difference

$$\delta\omega_i^*(\mathbf{k}) = -\frac{1}{2} \int_{\mathbf{q}} [\psi_i^{(4)} \tilde{G}_{ii} - \psi_i^{(4,0)} \tilde{G}^{(0)}] \quad (188)$$

between the one-loop integral expression and the UV divergent part. Here, $\psi^{(4)}$ and $\psi^{(4,0)}$ represent the exact and leading asymptotic expression for $\psi^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q})$, respectively, while \tilde{G}_{ii} and $G^{(0)}$ represent the exact and leading asymptotic expressions for $\tilde{G}_{ii}(\mathbf{q})$. This is a convergent integral, which we evaluate by taking $\Lambda \rightarrow \infty$. It is straightforward to show that both terms in this integrand may be expressed as vN^3 (where N is N_1 or N_2) times a function of a dimensionless wave-number qR (where $R = \sqrt{Nb}$ and b is b_1 or b_2) and of the dimensionless parameters $\chi_0 N$, N_1/N_2 , and b_1/b_2 . By nondimensionalizing the measure in the wave-vector integral by length scale R , we may express $\delta\omega^*$ as a convergent dimensionless integral times a prefactor of $vN^3/R^3 = N^2/\bar{N}^{1/2}$. The corresponding nondimensional form of $\delta\Omega_i^*$ is given in Eq. (51).

B. Direct correlation function

The one-loop contribution to the direct correlation function is given by Eqs. (139) and (140). In case of a binary homopolymer blend, for which all of the monomer type indices of the functions $\tilde{\Omega}_{ij}^{(2)}$ or $\tilde{\Omega}_{ijk}^{(3)}$ must be the same, Eqs. (139) and (140) may be combined and simplified to obtain

$$\delta C_{ij}(\mathbf{k}) \approx \frac{1}{2} \int_{\mathbf{q}} D_i(\mathbf{k}, \mathbf{q}) \tilde{G}_{ij}(\mathbf{q}_+) D_j(-\mathbf{k}, -\mathbf{q}) \tilde{G}_{ij}(\mathbf{q}_-), \quad (189)$$

where

$$D_i(\mathbf{k}, \mathbf{q}) \equiv \frac{\tilde{\Omega}_i^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)}{\tilde{\Omega}_i(\mathbf{k})}. \quad (190)$$

Here, $\tilde{\Omega}_i \equiv \tilde{\Omega}_{ii}^{(2)}$ and $\tilde{\Omega}_i^{(3)} \equiv \tilde{\Omega}_{iii}^{(3)}$ are the intramolecular two- and three-point functions for homopolymers of type i , respectively.

Consider the $\mathbf{k} \rightarrow 0$ limit of Eq. (189). By using the long-wavelength limits

$$\tilde{\Omega}_i^{(2)}(0) = N_i c_i,$$

$$\tilde{\Omega}_i^{(3)}(0, \mathbf{q}, -\mathbf{q}) = N_i \tilde{\Omega}_i(\mathbf{q}), \quad (191)$$

we find that

$$\lim_{\mathbf{k} \rightarrow 0} D_i(\mathbf{k}, \mathbf{q}) \equiv \frac{\tilde{\Omega}_i(\mathbf{q})}{c_i}. \quad (192)$$

By substituting this into Eq. (189), we may immediately confirm that $\mathbf{k} \rightarrow 0$ limit of Eq. (189) for $\delta C_{ij}(\mathbf{k})$ is equivalent to Eq. (103) for $\delta C_{ij}(\mathbf{k}=0)$, which was obtained by considering the composition dependence of the free-energy density.

To find the divergent part of Eq. (189) for $C_{ij}(\mathbf{k})$, we will need high- q asymptotic expansions for the screened interaction $\tilde{G}_{ij}(\mathbf{q}_\pm)$, and the function $D_i(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)$. To the required order in an expansion in powers of $1/q$,

$$G_{ij}(\mathbf{q}_\pm) = G^{(0)} + G^{(\pm)} + G^{(1)} + G_{ij}^{(x)},$$

$$G^{(0)} = \frac{v^2}{12l} q^2,$$

$$G^{(\pm)} = \pm \frac{v^2}{12l} \mathbf{k} \cdot \mathbf{q},$$

$$G^{(1)} = \frac{v}{2l^2} \left(\frac{\phi_1 l_1^2}{N_1} + \frac{\phi_2 l_2^2}{N_2} \right) + \frac{k^2 v^2}{48l},$$

$$G_{ij}^{(x)} = \frac{2v}{l^2} Z_{ij} \chi_0. \quad (193)$$

To obtain a corresponding asymptotic expansion of D_i in the high- q limit, for fixed \mathbf{k} , we note that

$$D_i(\mathbf{k}, \mathbf{q}) = \frac{N_i \hat{\omega}_i^{(3)}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+)}{g(K_i^2)} \quad (194)$$

and use expansion (172) of $\hat{\omega}^{(3)}$. This yields

$$D_i(\mathbf{k}, \mathbf{q}) \simeq D_i^{(0)} + D_i^{(1)} + \dots,$$

$$D_i^{(0)} = \frac{12l_i}{vq^2},$$

$$D_i^{(1)} = \left[\frac{3l_i}{v} k^2 (3 + 4\alpha^2) - \frac{72l_i^2}{v^2 N_i g(K_i^2)} \right] \frac{1}{q^4}, \quad (195)$$

where $K_i^2 = k^2 N_i b_i^2 / 6 = k^2 N_i v / (6l_i)$. The key simplifying feature of this expansion is the fact that the leading-order contribution $D_i^{(0)}$ to $D_i(\mathbf{k}, \mathbf{q})$ is independent of \mathbf{k} .

By substituting these expressions into Eq. (189), and keeping only the terms of $O(1)$ and $O(1/q^2)$ in the integrand that lead to UV divergent integrals, we obtain a UV divergent contribution to $\delta C_{ij}(\mathbf{k})$ as a sum:

$$\delta C_{ij}(\mathbf{k}) \simeq \delta C_{ij}^{(0)} + \delta C_{ij}^{(\chi)} + \delta C_{ij}^{(1)}, \quad (196)$$

where

$$\delta C_{ij}^{(0)} \simeq \frac{1}{2} \int_{\mathbf{q}} D_i^{(0)} D_j^{(0)} \tilde{G}^{(0)} \tilde{G}^{(0)},$$

$$\delta C_{ij}^{(\chi)} \simeq \int_{\mathbf{q}} D_i^{(0)} D_j^{(0)} \tilde{G}_{ij}^{(\chi)} \tilde{G}^{(0)},$$

$$\begin{aligned} \delta C_{ij}^{(1)} \simeq & \frac{1}{2} \int_{\mathbf{q}} D_i^{(0)} D_j^{(0)} [\tilde{G}^{(+)} \tilde{G}^{(-)} + 2\tilde{G}^{(1)} \tilde{G}^{(0)}] \\ & + \frac{1}{2} \int_{\mathbf{q}} [D_i^{(1)} D_j^{(0)} + D_i^{(0)} D_j^{(1)}] \tilde{G}^{(0)} \tilde{G}^{(0)}. \end{aligned} \quad (197)$$

Evaluating the integrals with respect to \mathbf{q} yields

$$\delta C_{ij}^{(0)} = \frac{l_i l_j v^2}{12\pi^2 \bar{l}^2} \Lambda^3$$

$$\delta C_{ij}^{(\chi)} = \frac{12v}{\pi^2} \frac{l_i l_j}{\bar{l}^3} Z_{ij} \chi_0 \Lambda,$$

$$\begin{aligned} \delta C_{ij}^{(1)} = & \frac{7k^2 l_i l_j v^2}{12\pi^2 \bar{l}^2} \Lambda + \frac{3l_i l_j v}{\pi^2 \bar{l}^3} \left(\frac{\phi_1 l_1^2}{N_1} + \frac{\phi_2 l_2^2}{N_2} \right) \Lambda \\ & - \frac{3l_i l_j v}{2\pi^2 \bar{l}^2} \left(\frac{l_i}{N_i g(K_i^2)} + \frac{l_j}{N_j g(K_j^2)} \right) \Lambda. \end{aligned} \quad (198)$$

The divergent part of the corresponding apparent χ parameter is a sum of the three terms

$$\delta \chi^{(0)} = \frac{(l_1 - l_2)^2 v \Lambda^3}{8\pi^2 \bar{l}^2 3},$$

$$\delta \chi^{(\chi)} = -\frac{6l_1^2 l_2^2}{\pi^2 \bar{l}^3} \chi_0 \Lambda,$$

$$\begin{aligned} \delta \chi^{(1)} = & \frac{7k^2 (l_1 - l_2)^2 v}{24\pi^2 \bar{l}^2} \Lambda + \frac{3(l_1 - l_2)^2}{2\pi^2 \bar{l}^3} \left(\frac{\phi_1 l_1^2}{N_1} + \frac{\phi_2 l_2^2}{N_2} \right) \Lambda \\ & + \frac{3(l_1 - l_2)}{2\pi^2 \bar{l}^2} \left(\frac{l_2^2}{N_2 g(K_2^2)} - \frac{l_1^2}{N_1 g(K_1^2)} \right) \Lambda. \end{aligned} \quad (199)$$

Note that both $\chi^{(0)}$ and $\chi^{(1)}$ vanish in the case $l_1 = l_2$ of equal statistical segment lengths.

The UV convergent contribution $\delta C_{ij}^*(\mathbf{k})$ is given by the difference between the exact integral expression of Eq. (189) and the sum of the UV divergent integrals given in Eqs. (196) and (197). The resulting UV convergent integral can be nondimensionalized by arguments similar to those used to nondimensionalize $\delta \Omega_{ij}^*(k)$, which in this case yield a nondimensional integral times a prefactor of $v/(N\bar{N}^{1/2})$. The corresponding nondimensional form of $\delta \chi_a^*(k)$ is given in Eq. (55).

XI. CORRELATIONS IN DIBLOCK COPOLYMER MELTS

We now consider the calculation of $\delta S_{ij}(q)$ for a diblock copolymer melt. The calculation is closely analogous to that given above for a blend.

A. Two-point functions

The two-point intramolecular function $\tilde{\Omega}_{ij}(\mathbf{q})$ for a Gaussian diblock copolymer of length N with blocks of length $f_1 N$ and $f_2 N$ is a matrix

$$\tilde{\Omega}_{ij}(\mathbf{q}) = \frac{N}{v} g_{ij}(\mathbf{q}) \quad (200)$$

where

$$g_{ij} = \begin{bmatrix} g_1 & e_1 e_2 \\ e_1 e_2 & g_2 \end{bmatrix},$$

$$g_i \equiv 2(e^{-f_i Q_i^2} - 1 + f_i Q_i^2) / Q_i^4,$$

$$e_i \equiv (1 - e^{-f_i Q_i^2}) / Q_i^2, \quad (201)$$

with $Q_i^2 \equiv q^2 N b_i^2 / 6$. The high- q asymptotic behavior of these function may be obtained by dropping all terms that contain factors of $e^{-f_i Q_i^2}$.

The high- q behavior of the propagator $\tilde{G}_{ij}(\mathbf{q})$ may be approximated to the required accuracy by an expansion

$$\tilde{G}_{ij}(\mathbf{q}) \simeq \frac{v^2}{12l} |\mathbf{q}|^2 + \frac{(l_1^2 - l_1 l_2 + l_2^2)v}{2\bar{l}^2 N} + \frac{2v}{\bar{l}^2} \chi_0 Z_{ij}.$$

Here, \bar{l} and Z_{ij} have the same values as in a homopolymer blend of the same composition, with $\phi_i = f_i$. That is,

$$\bar{l} \equiv f_1 l_1 + f_2 l_2,$$

$$Z \equiv \begin{bmatrix} -f_2^2 l_2^2 & f_1 f_2 l_1 l_2 \\ f_1 f_2 l_1 l_2 & -f_1^2 l_1^2 \end{bmatrix}. \quad (202)$$

The only difference between this expansion and the corresponding expansion of $\tilde{G}_{ij}(\mathbf{q})$ in a homopolymer blend of equal composition is the nature of the term $\tilde{G}_{ij}^{(1)}(\mathbf{k})$ that is proportional to $1/N$ and independent of χ , which is the first term in the second line of Eq. (202).

B. Free-energy density

The one-loop contribution δf to the free-energy density of a homogeneous diblock copolymer melt can be calculated by a procedure closely analogous to that given in Sec. V B for a binary homopolymer blend. The UV divergent contribution is of the form

$$\delta f \simeq \delta f^{(0)} + \delta f^{(\chi)} + \delta f^{(1)}. \quad (203)$$

The expressions for $\delta f^{(0)}$ and $\delta f^{(\chi)}$ are identical to those given in Eqs. (92) and (96), respectively, for a blend of the same composition. As for a homopolymer blend, the sum of these two terms yields the quantity $\delta f_{\text{local}} = \delta f^{(0)} + \delta f^{(\chi)}$. The remaining $O(1/N)$ contribution is given in a diblock melt by

$$\delta f^{(1)} = \frac{1}{2} \int_{\mathbf{q}} G^{(0)} \tilde{\Omega}_+^{(1)} = -\frac{3}{2\pi^2 v \bar{l}} \frac{l_1^2 - l_1 l_2 + l_2^2}{N} \Lambda. \quad (204)$$

Here, $\tilde{\Omega}_+^{(1)} = \sum_{ij} \tilde{\Omega}_{ij}^{(2,1)}$, where $\tilde{\Omega}_{ij}^{(2,1)}$ is the $O(N/Q^4)$ contribution to $\tilde{\Omega}_{ij}^{(2)}(\mathbf{q})$.

C. Intramolecular correlations

In the diblock case, we calculate $\delta \omega_{ij}^{(2)}(\mathbf{k})$ using Eq. (151). To analyze the divergence of this expression we need to identify the high- \mathbf{q} behavior of its components. As in the blend case, this integral has a divergent part proportional to Λ , which may be obtained by using the dominant contributions to $\psi_{ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q})$ and $\tilde{G}_{kl}^{(2)}(\mathbf{k})$. As in a blend, the dominant contribution to $\tilde{G}_{kl}^{(2)}(\mathbf{k})$ is independent of the values of the indices, and is given by Eq. (87).

The high- q behavior of $\psi_{ijkl}^{(4)}$ is analyzed in the Appendix. As for the case of the blend, we find a simple expression for the dominant asymptotic behavior $\psi^{(4)}$ which largely determines the form of the result: The dominant contribution to the function $\psi_{ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q})$ arises only for elements with $k=l$, and is given by

$$\psi_{ijkk}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}) \simeq -\frac{288\alpha^2}{q^4 b_k^2} \frac{\partial \tilde{\omega}_{ij}^{(2)}(\mathbf{k})}{\partial (b_k^2)}. \quad (205)$$

For $i=j$, the derivative with respect to b_k^2 is nonzero only for $i=j=k$, while for $i \neq j$, the derivative is nonzero for both $k=1$ and $k=2$. The dominant contributions to elements of $\psi_{ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q})$ with $k \neq l$ are all found to be $O(1/q^6)$ or smaller, and thus do not contribute to the divergent part of Eq. (151) for $\delta \tilde{\omega}_{ij}^{(2)}(\mathbf{k})$.

Using this asymptotic result for $\psi^{(4)}$, the UV divergent contribution to Eq. (151) can be written as a sum

$$\delta \omega_{ij}^{(2)}(\mathbf{k}) \simeq \sum_k \frac{\partial \tilde{\omega}_{ij}^{(2)}(\mathbf{k})}{\partial (b_k^2)} \delta (b_k^2) \quad (206)$$

where $\delta (b_k^2)$ is again given by Eq. (187). For the diblock melt, as for the blend, we thus find that the divergent contributions to $\delta \omega_{ij}^{(2)}(\mathbf{k})$ can be absorbed into a renormalization of statistical segment lengths.

D. Direct correlation function

The one-loop contribution to the direct correlation function in a diblock copolymer melt can be written as

$$\delta C_{ij}(\mathbf{k}) \simeq \frac{1}{2} \int_{\mathbf{q}} D_{ikm}(\mathbf{k}, \mathbf{q}) \tilde{G}_{kl}(\mathbf{q}_+) D_{jln}^{(3)}(\mathbf{k}, \mathbf{q}) \tilde{G}_{mn}(\mathbf{q}_-), \quad (207)$$

where, in this context, we define

$$D_{ikl}(\mathbf{k}, \mathbf{q}) \equiv \tilde{\Omega}_{ij}^{-1} \tilde{\Omega}_{jkl}^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+), \quad (208)$$

with $D_{ikl}(\mathbf{k}, \mathbf{q}) = D_{ikl}(-\mathbf{k}, -\mathbf{q})$. As for the binary blend, we expand the three-point function $\tilde{\Omega}_{jkl}^{(3)} = \tilde{\Omega}_{jkl}^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)$ in the high- q limit as a sum

$$\tilde{\Omega}_{jkl}^{(3)} = \tilde{\Omega}_{jkl}^{(3,0)} + \tilde{\Omega}_{jkl}^{(3,1)} \quad (209)$$

and $D_{ikl}(\mathbf{k}, \mathbf{q})$ as a corresponding sum

$$D_{ikl} \simeq D_{ikl}^{(0)} + D_{ikl}^{(1)} \quad (210)$$

where $\tilde{\Omega}_{jkl}^{(3,0)}$ and $D_{ikl}^{(0)}$ are $O(1/q^2)$ and $\tilde{\Omega}_{jkl}^{(3,1)}$ and $D_{ikl}^{(1)}$ are $O(1/q^4)$.

A detailed analysis of the high- q behavior of $\tilde{\Omega}_{jkl}^{(3)}$, which is outlined in the Appendix, shows that the leading-order contribution $\tilde{\Omega}_{jkl}^{(3,0)}$, which is of $O(1/q^2)$, is nonzero only for $k=l$, and has four elements $\tilde{\Omega}_{jkk}^{(3,0)}$ that are all of the form

$$\tilde{\Omega}_{jkk}^{(3,0)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+) = \tilde{\Omega}_{jk}^{(2)}(\mathbf{k}) \frac{12l_k}{vq^2}. \quad (211)$$

It follows from Eq. (208) and this expression that the corresponding leading-order contribution to D_{ikl} is

$$D_{ikl}^{(0)}(\mathbf{k}, \mathbf{q}) = \delta_{ik} \delta_{kl} D_i^{(0)}(\mathbf{q}) \quad (212)$$

where

$$D_i^{(0)}(\mathbf{q}) \equiv \frac{12l_i}{vq^2} \quad (213)$$

is independent of \mathbf{k} , and is the same function as that found in the binary blend.

The only nonzero elements of the subdominant contribution $\tilde{\Omega}_{jkl}^{(3,1)} = \tilde{\Omega}_{jkl}^{(3,1)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)$ are

$$\tilde{\Omega}_{jjj}^{(3,1)} = \frac{18l_j^2}{v^3} [K_j^2(3 + 4\alpha^2)g_j - 4f_j] \frac{1}{q^4},$$

$$\tilde{\Omega}_{jkk}^{(3,1)} = \frac{18l_j^2}{v^3} e_j [K_k^2(3 + 4\alpha^2)e_k - 4] \frac{1}{q^4},$$

$$\tilde{\Omega}_{jjk}^{(3,1)} = \frac{36l_j l_k e_j}{v^3} \frac{1}{q^4},$$

where $k \neq j$. In order to calculate the one-loop contribution to $\delta C_{ij}(\mathbf{k})$, we will need a quantity

$$D_i^{(1)}(\mathbf{k}, \mathbf{q}) \equiv \sum_{kl} D_{ikl}^{(1)}(\mathbf{k}, \mathbf{q}). \quad (214)$$

This is given by

$$D_i^{(1)} = \left[\frac{3l_i}{v} k^2(3 + 4\alpha^2) - \frac{72}{Nv^2} g_{ij}^{-1} L_j \right] \frac{1}{q^4} \quad (215)$$

where we have defined a vector L_i with components

$$\begin{aligned} L_1 &\equiv f_1 l_1^2 + e_1 l_2^2 - e_1 l_1 l_2, \\ L_2 &\equiv f_2 l_2^2 + e_2 l_1^2 - e_2 l_1 l_2. \end{aligned} \quad (216)$$

The expression for $D_i^{(1)}$ in a homopolymer blend given in Eq. (85) may be recovered by the replacements $L_i \rightarrow l_i^2$ and $g_{ij}^{-1}/N \rightarrow \delta_{ij}/(g_i N_i)$.

When expressed in terms of G_{ij} and the quantity D_i defined above, the integral expression for the divergent part of $\delta C_{ij}(\mathbf{k})$ in a diblock copolymer melt is identical to that given in Eq. (197) for a homopolymer blend. The only differences between the expressions obtained for δC_{ij} in a diblock copolymer melt and that in a homopolymer blend of the same composition arise from the use of different expressions for the k -independent part of $G_{ij}^{(1)}$ [given for a diblock by the first term of the second line of Eq. (202)], and for $D_i^{(1)}$ [given by Eq. (215)]. Moreover, the integral expressions for $\delta C_{ij}^{(0)} \times(\mathbf{k})$ and $\delta C_{ij}^{(x)}(\mathbf{k})$ are identical to those obtained for a homopolymer blend of the same composition. Only the contribution $\delta C_{ij}^{(1)}(\mathbf{k})$ differs from that obtained for a corresponding blend. This is given by

$$\begin{aligned} \delta C_{ij}^{(1)} &= \frac{7k^2 l_i l_j v^2}{12\pi^2 \bar{l}^2} \Lambda + \frac{3v l_i l_j (l_1^2 - l_1 l_2 + l_2^2)}{\pi^2 N \bar{l}^3} \Lambda \\ &- \frac{3v}{2N\pi^2 \bar{l}^2} (g_{ik}^{-1} L_k l_j + l_i L_k g_{kj}^{-1}) \Lambda. \end{aligned} \quad (217)$$

The first line, the term proportional to k^2 , is identical to the corresponding expression for a blend of the same composition. The second line, which arises from the integral involving the k -independent part of $\tilde{G}^{(1)}$, is different because of the use of different expression for $\tilde{G}^{(1)}$. The third line is different because of the use of a different expression for $D_i^{(1)}$.

The corresponding expression for the UV divergent contribution to $\delta\chi(\mathbf{k})$ is similar to that obtained for a blend of the same composition. The expressions for $\delta\chi^{(0)}$ and $\delta\chi^{(x)}$

terms are identical to those obtained in a homopolymer blend. The expression for $\delta\chi^{(1)}(\mathbf{k})$ is different, but retains the property that $\delta\chi^{(1)}=0$ in the limit $l_1=l_2$ of equal statistical segment lengths.

XII. END EFFECTS

We show in this section that the form of our results for the UV divergent part of $\delta C_{ij}(k)$ are consistent with the existence of a UV divergent one-loop contribution to the free energy of the form proposed in Eq. (56). Here, it is convenient to start from the more general expression

$$\delta F_{\text{int}} = \int d\mathbf{r} \left[\delta f_{\text{local}} + \sum_{\alpha} d_{\alpha} \psi_{\alpha} + \frac{1}{2} D_{ij} \nabla c_i \nabla c_j \right], \quad (218)$$

in which the gradient-squared term is expressed in terms of monomer concentrations, as would be required to describe a slightly compressible liquid. The postulated free energy is the sum of a Ginzburg-Landau-like functional of the monomer concentrations plus additional free energies arising from chain ends and (for a diblock) from the junction that connects the two blocks.

The excess free energies arising from chain ends and junctions are assumed to depend linearly on the concentrations of these defects because the defect concentrations are dilute. Direct defect-defect interactions, which would yield contributions to $S^{-1}(k)$ of $O(1/N^2)$, could become important in systems of relatively short chains with strongly interacting end groups, but do not appear in our model within the one-loop approximation.

A. Monomer and defect chemical potentials

We compare our one-loop results to a form of SCFT in which the average monomer concentrations are calculated from those of ideal-gas reference system with a self-consistent field Hamiltonian

$$\tilde{U} = U_{\text{chain}} - \sum_i \tilde{h}_i * c_i + \sum_{\alpha} d_{\alpha} * \psi_{\alpha}, \quad (219)$$

in which a chain end of type $\alpha=1$ or $\alpha=2$, or a junction ($\alpha=J$) at position \mathbf{r} is penalized by a free energy $\psi_{\alpha}(\mathbf{r})$. In the absence of any external field, monomers of type i are subjected to a field

$$-\tilde{h}_i = U_{ij} * c_j + \frac{\delta(\delta F_{\text{int}})}{\delta c_i}, \quad (220)$$

in which δF_{int} is given by Eq. (218), and $\delta/\delta c_i$ represents a functional derivative.

To construct an RPA calculation of $S(k)$, we consider the deviations from a homogeneous reference state induced by a small external field h_i that couples only to the monomer density. This external perturbation will induce deviations δc_i and δd_{α} in monomer and defect concentrations, respectively, and deviations $\delta \tilde{h}_i$ and $\delta \psi_{\alpha}$ in the conjugate fields. These devia-

tions in chemical potential fields are given, to linear order in the deviations in the concentrations, by

$$-\delta\tilde{h}_i = U'_{ij} * \delta c_j + V_{i\alpha} * \delta d_\alpha - h_i, \\ \delta\psi_\alpha = V_{\alpha i}^T * \delta c_i, \quad (221)$$

where

$$U'_{ij} \equiv -\frac{\delta\tilde{h}_j}{\delta c_i} = U_{ij} + \frac{\delta^2(\delta F_{\text{int}})}{\delta c_i \delta c_j}, \\ V_{i\alpha} \equiv \frac{\delta\psi_\alpha}{\delta c_i}. \quad (222)$$

Here, U'_{ij} is an effective monomer-monomer interaction and $V_{i\alpha}$ is an effective monomer-defect interaction. Here, and throughout this section, we use “*” to represent spatial convolution only, and display the monomer- and defect-type indices explicitly.

In Fourier space, the effective interaction $U'_{ij}(\mathbf{k})$ is given by

$$U'_{ij}(\mathbf{k}) = U_{ij}(\mathbf{k}) + \frac{\partial^2(\delta f_{\text{local}})}{\partial c_i \partial c_j} + W_{ij} + D_{ij}k^2 \quad (223)$$

where

$$W_{ij} \equiv \sum_\alpha d_\alpha \frac{\partial^2 \psi_\alpha}{\partial c_i \partial c_j}. \quad (224)$$

Here d_α is the defect density in the homogeneous reference state: For hopolymers, the ends densities are $d_\alpha = 2\phi_\alpha/(vN_\alpha)$; for diblock copolymers, both ends and junction densities are $d_\alpha = 1/(vN)$. All derivatives are evaluated in this homogeneous reference state. Note that our definition of U'_{ij} as a second functional derivative of the interaction free energy yields a contribution $D_{ij}k^2$ that arises from the (postulated) gradient-squared contribution to δF_{int} .

B. Generalized RPA

To complete the RPA linear response calculation, we must combine the above with a description of the linear response of an ideal gas of polymers. The linear response of the monomer and defect concentrations to deviations in the above combination of fields is given by

$$\delta c_i = \tilde{\Omega}_{ij} * \delta\tilde{h}_j - \tilde{R}_{i\beta} * \delta\psi_\beta, \\ \delta d_\alpha = \tilde{R}_{\alpha j}^T * \delta\tilde{h}_j - \tilde{E}_{\alpha\beta} * \delta\psi_\beta. \quad (225)$$

Here, $\tilde{\Omega}_{ij}$ is the ideal-gas intramolecular correlation between monomers of types i and j , $\tilde{R}_{j\alpha}$ is the intramolecular correlation between α defects and j monomers, and $\tilde{E}_{\alpha\beta}$ is the intramolecular correlation between defects of type α and β . All of these functions are diagonal in a homopolymer blend (i.e., are nonzero only for $i=j$, $i=\alpha$, or $\alpha=\beta$), and all become nondiagonal in a diblock copolymer melt.

By combining linear-response equations (225) with self-consistency conditions (221), it is straightforward to show

that, in a Fourier representation, $\delta c_i(\mathbf{k})$ is given by

$$\delta c_i = A_{ij}[-B_{jk}\delta c_k + h_j] \quad (226)$$

where all quantities are implicitly functions of a wave-number \mathbf{k} and

$$A_{ij} \equiv P_{ik}^{-1} \tilde{\Omega}_{kl} [P^T]_{lj}^{-1}, \\ P_{ij} \equiv \delta_{ij} + \tilde{R}_{i\alpha} V_{\alpha j}^T, \\ B_{jk} \equiv U'_{jk} - V_{j\alpha} \tilde{E}_{\alpha\beta} V_{\beta k}^T. \quad (227)$$

Solving for the inverse response and/or correlation function $S_{ij}^{-1}(\mathbf{k}) = \delta h_j(\mathbf{k}) / \delta c_i(\mathbf{k})$ yields

$$S_{ij}^{-1} = A_{ij}^{-1} + B_{ij} = \tilde{\Omega}_{ij}^{-1} + U_{ij} + \delta S_{ij}^{-1} \quad (228)$$

in which

$$\delta S_{ij}^{-1} = \frac{\partial(\delta f_{\text{local}})}{\partial c_i \partial c_j} + D_{ij}k^2 - \delta C_{ij}^{(d)} \quad (229)$$

is the correction to mean-field theory, and where $\delta C_{ij}^{(d)}$ is a contribution arising from the interaction of the end and junction “defects” with the monomer concentration. This quantity is given by a sum

$$-\delta C_{ij}^{(d)} \equiv -\delta C_{ij}^{(d1)} - \delta C_{ij}^{(d2)}, \\ -\delta C_{ij}^{(d1)} \equiv W_{ij} + V_{i\alpha} \tilde{R}_{\alpha k}^T \tilde{\Omega}_{kj}^{-1} + \tilde{\Omega}_{ik}^{-1} \tilde{R}_{k\alpha} V_{\alpha j}^T, \\ -\delta C_{ij}^{(d2)} \equiv V_{i\alpha} [\tilde{R}_{\alpha k}^T \tilde{\Omega}_{ki}^{-1} \tilde{R}_{i\beta} - \tilde{E}_{\alpha\beta}] V_{\beta j}^T. \quad (230)$$

Note that the quantity $\delta C_{ij}^{(d1)}$ depends linearly upon the effective interaction $V_{i\alpha}$, while $\delta C_{ij}^{(d2)}$ is second order in $V_{i\alpha}$.

C. Comparison to one-loop results

To test our phenomenological model, we compare our explicit one-loop calculations for the $\delta C_{ij}^{(1)}(\mathbf{k})$ to the results of the above generalized RPA calculation, while using the explicit expressions for ψ_α given in Eqs. (59) and (61), and treating D_{ij} as a free parameter. We find that, in both blends and diblock copolymer melts, the quantity $\delta C_{ij}^{(1)}$ obtained in the one-loop approximation for $\delta C_{ij}(\mathbf{k})$ can be written as a sum of the form

$$-\delta C_{ij}^{(1)}(\mathbf{k}) = D_{ij}k^2 - \delta C_{ij}^{(d1)}(\mathbf{k}) \quad (231)$$

where $\delta C_{ij}^{(d1)}$ is the first-order defect contribution given in Eq. (230), and

$$D_{ij} = -\frac{v^2 l_j}{3\pi^2 \bar{l}^2} \Lambda. \quad (232)$$

The same value is obtained for D_{ij} in blends and diblock copolymer melts of the same composition. The scalar coefficient given in Eq. (62) is obtained by requiring that $\nabla c_1 = -\nabla c_2$ in an incompressible liquid.

In both blends and diblock copolymer melts, the result from the one-loop approximation is thus identical to that

obtained from the generalized RPA, *except* for the absence in our one-loop results of the contribution $\delta C_{ij}^{(d2)}$ predicted by RPA result. Note that the contribution $\delta C_{ij}^{(d2)}$ that is “missing” from the results of the one-loop approximation has a qualitatively different dependence on both $V_{i\alpha}$ and Λ than terms that are found in the one-loop calculation: The quantity $\delta C_{ij}^{(2d)}$ is second order in the strength of the coupling $V_{i\alpha}$, and so would yield a contribution $\delta C_{ij}^{(2d)} \propto \Lambda^2$ in a theory in which $V_{i\alpha} \propto \Lambda$, while the terms that *do* appear in our one-loop results are linear in $V_{i\alpha}$, and proportional to Λ . The one-loop calculation of δC_{ij} yields only terms proportional to Λ and Λ^3 , so it appears that the missing contribution predicted by the RPA could not possibly be generated by a one-loop approximation. We assume that the discrepancy occurs because terms that are quadratic in the magnitude of the one-loop contributions to $V_{i\alpha}$ appear only at second order in a loop expansion of $S^{-1}(k)$. The Λ dependence of the missing contribution appears to be consistent with this conjecture: The power counting analysis of the loop expansion given in Sec. XIII and in Ref. [13] indicates that the dominant UV divergence of the two-loop contribution to δC will be $O(\Lambda^4)$, to which we expect to find subdominant corrections of $O(\Lambda^2)$ and $O(\ln \Lambda)$. While this conjecture could be proved only by analyzing the two-loop theory, it seems clear that the missing terms cannot be produced by a one-loop approximation, and so may be neglected when making this comparison.

Below, we present some details of the application of the generalized RPA to binary blends and diblock copolymer melts, respectively.

1. Binary blends

For a binary blend of homopolymers,

$$\begin{aligned} V_{i\alpha} &= \frac{3vl_i}{4\pi^2\bar{l}^2} l_\alpha^2 \Lambda, \\ W_{ij} &= -\frac{3vl_i l_j}{\pi^2\bar{l}^3} \left[\frac{\phi_1 l_1^2}{N_1} + \frac{\phi_2 l_2^2}{N_2} \right] \Lambda, \\ \tilde{\Omega}_{ij} &= \delta_{ij} v^{-1} \phi_i N_i g_i, \\ \tilde{R}_{i\alpha} &= \delta_{i\alpha} 2v^{-1} \phi_i e_i, \end{aligned} \quad (233)$$

where $g_i \equiv g(K_i^2)$ is the Debye function, and where $e_i \equiv (1 - e^{-K_i^2})/K_i^2$ for a homopolymer. This yields

$$-\delta C_{ij}^{(d1)} \equiv W_{ij} + \frac{3vl_i l_j}{2\pi^2\bar{l}^2} \left[\frac{l_i e_i}{N_i g_i} + \frac{l_j e_j}{N_j g_j} \right] \Lambda. \quad (234)$$

By using the identity $e_i = 1 - g_i K_i^2/2$ and the definition of $K_i^2 = k^2 v / (6l_i)$, we obtain the alternative expression

$$-\delta C_{ij}^{(d1)} \equiv W_{ij} + \frac{3vl_i l_j}{2\pi^2\bar{l}^2} \left[\frac{l_i}{N_i g_i} + \frac{l_j}{N_j g_j} \right] \Lambda - \frac{v^2 l_i l_j}{4\pi^2\bar{l}^2} \Lambda. \quad (235)$$

By substituting this expression for $\delta C_{ij}^{(d1)}$ into Eq. (231), and using Eq. (232) for D_{ij} , we reproduce the one-loop result for $\delta C_{ij}^{(1)}$ given in Eq. (198)

2. Diblock copolymer melts

For a diblock copolymer melt, we obtain

$$\begin{aligned} V_{ij} &= \frac{3vl_i}{4\pi^2\bar{l}^2} (l_1 - l_2)^2 \Lambda, \\ W_{ij} &= -\frac{3vl_i l_j (l_1^2 - l_1 l_2 + l_2^2)}{\pi^2 N \bar{l}^3} \Lambda, \end{aligned} \quad (236)$$

and

$$\begin{aligned} \tilde{\Omega}_{ij} &= \delta_{ij} v^{-1} N g_{ij}, \\ \tilde{R}_{i\alpha} &= v^{-1} e_i, \quad (\alpha = i), \\ \tilde{R}_{i\alpha} &= v^{-1} e_i e^{-f_\alpha K_\alpha^2}, \quad (\alpha \neq i, j), \\ \tilde{R}_{ij} &= v^{-1} e_i, \end{aligned} \quad (237)$$

where g_{ij} , g_i , e_i are defined for a diblock copolymer by Eq. (201). This yields

$$-\delta C_{ij}^{(d1)} \equiv W_{ij} + \frac{3vl_i l_j}{2\pi^2 N \bar{l}^2} [g_{ik}^{-1} e_i l_j + l_i e_k g_{kj}^{-1}] \Lambda. \quad (238)$$

By using the identity $e_i = f_i - g_i K_i^2/2$, we obtain the alternative expression

$$-\delta C_{ij}^{(d1)} \equiv W_{ij} + \frac{3vl_i l_j}{2\pi^2 N \bar{l}^2} [g_{ik}^{-1} L_k l_j + l_i L_k g_{kj}^{-1}] \Lambda - \frac{v^2 l_i l_j}{4\pi^2\bar{l}^2} \Lambda \quad (239)$$

where L_k is given by Eq. (216). By using this expression for $\delta C_{ij}^{(d1)}$ and Eq. (232) for D_{ij} in Eq. (231), we reproduce Eq. (217).

XIII. BEYOND ONE LOOP

In this section, we briefly look beyond the one-loop theory. We consider the structure of UV divergences of an arbitrary diagram in the unrenormalized diagrammatic perturbation theory, at the level of naive power counting. We also consider the structure of a renormalized loop expansion, and argue that this should yield an asymptotic expansion of corrections to SCFT in powers of $1/\sqrt{N}$.

For this purpose, we use the diagrammatic formalism presented in Ref. [13]. There, it was shown that corrections to the Gaussian or one-loop approximation for the grand-

potential $\ln Z$ for a polymer liquid could be expressed as an infinite sum of connected diagrams of $-\tilde{G}$ bonds and $\tilde{\Omega}$ vertices, with no root sites. Here, we consider the dominant UV divergence of an arbitrary diagram in the expansion of the free-energy density $\ln Z/V$ for a model with a wave-number cutoff Λ . For generality, we consider a model of continuous Gaussian polymers in a space of arbitrary spatial dimension d . We consider a generic connected diagram with B bonds, each representing a factor of $-\tilde{G}$, connecting V vertices, each representing a factor of $\tilde{\Omega}^{(n)}$, where n is the number of attached bonds. The number L of loops, or independent wavevector integrals, in such a diagram is $L=B-V+1$. For simplicity, we consider only the dominant UV divergent to the free-energy density of a one-component liquid (or of a blend with $\chi=0$ and $b_1=b_2$), without attempting to analyze the dependence of the free-energy density on χ , or on the composition of a blend.

To analyze the UV divergence of an arbitrary diagram, we must characterize the asymptotic high- q behavior of $\tilde{G}(q)$, and of $\tilde{\Omega}^{(n)}(\mathbf{q}_1, \dots, \mathbf{q}_n)$ for arbitrary n . The dominant q dependence of the screened interaction $\tilde{G}(q)$, given in Eq. (87), is

$$\tilde{G}(q) \sim (qb)^2/c, \quad (240)$$

where $c=1/v$ is the monomer concentration. The function $\tilde{\Omega}^{(n)}$ can be expressed, for a Gaussian homopolymer in any spatial dimension d , as a product of the form $\tilde{\Omega}^{(n)}(\mathbf{q}_1, \dots, \mathbf{q}_n) = cN^{n-1} \hat{\omega}^{(n)}(\mathbf{Q}_1, \dots, \mathbf{Q}_n)$, where c/N is the number concentration of polymers, $\mathbf{Q}_i \equiv \mathbf{q}_i R$, and $R = b\sqrt{N}/6$. To characterize the high- q limit, it is useful to consider the limit of infinitely long chains, $N \rightarrow \infty$, at constant monomer concentration c . In this limit, all nonzero wave vectors become “large” compared to $1/R$. The function $\tilde{\Omega}^{(n)}(\mathbf{q}_1, \dots, \mathbf{q}_n)$ generally approaches a nonzero limit as $N \rightarrow \infty$. For $\tilde{\Omega}^{(n)}$ to approach a value that is independent of N in this limit, $\hat{\omega}^{(n)}(\mathbf{Q}_1, \dots, \mathbf{Q}_n)$ must approach a homogeneous scaling function

$$\lim_{N \rightarrow \infty} \hat{\omega}^{(n)}(\lambda \mathbf{Q}_1, \dots, \lambda \mathbf{Q}_n) = \lambda^{2(n-1)} \hat{\omega}^{(n)}(\mathbf{Q}_1, \dots, \mathbf{Q}_n) \quad (241)$$

when $|\mathbf{Q}_i| \gg 1$ for all n arguments. At a power counting level, this implies that the function $\hat{\omega}^{(n)}$ is of order $Q^{2(n-1)}$ when all of its arguments are of order Q . Corresponding, $\tilde{\Omega}^{(n)}$ must be of order

$$\tilde{\Omega}^{(n)} \sim \frac{c(qb)^2}{(qb)^{2n}} \quad (242)$$

when all of its arguments are of order $q \gg 1/R$.

To count powers of q in the Fourier integral associated with an arbitrary diagram in the expansion of $\ln Z/V$, it is useful to associate one of the n factors of $(qb)^2$ in the denominator of Eq. (242) for $\tilde{\Omega}^{(n)}$ with one end of one of the n bonds that must be attached to the associated vertex. This method of counting leaves an overall factor of $c(qb)^2$ for

each vertex, and a factor of $c^{-1}(qb)^{-2}$ for each bond in an incompressible liquid. In a diagram with L loops, in d dimensions, we obtain an additional factor of order q^{dL} from the integration over L wave vectors. By combining these factors, we find that the contribution to $\ln Z/V$ from a generic connected L -loop diagram with a cutoff wave number Λ is of order

$$\Lambda^d (\Lambda^{d-2} c/b^2)^{L-1}. \quad (243)$$

In the physically relevant case $d=3$ we may define a packing length $p=1/(cb^2)$ to rewrite this as

$$\Lambda^3 (\Lambda p)^{L-1}. \quad (244)$$

The order of UV divergence is thus expected to increase by one factor of Λp at each order in the loop expansion.

In the one-loop theory considered here, with $d=3$ and $L=1$, this argument yields a UV divergent contribution of order Λ^3 . This agrees with the results of our explicit one-loop calculation of free-energy density of an incompressible liquid. Corresponding L -loop contributions to the functional derivatives of $F[\langle c \rangle]$, such as the second derivative $S^{-1}(k)$, are expected to have the same dependence on Λ as the underlying free-energy contributions, at each order in the loop expansion. Thus, for example, the dominant UV divergent one-loop contribution to $S^{-1}(k)$ in our explicit one-loop calculation is also of order Λ^3 .

We have shown that this UV divergence of the one-loop theory can be removed by renormalization. Let us assume, for the moment, that this procedure can be extended to arbitrary order in a loop expansion. We imagine that the contribution of an L -loop diagram to the renormalized perturbation theory can be obtained by subtracting an asymptotic approximation for the integrand of the corresponding Fourier integral that is accurate at high wave numbers, $q \gg 1/R$. This will generally leave a UV convergent contribution that arises primarily from wave numbers of order $1/R$, due to deviations of the integrand from the asymptotic approximation at low wave numbers. The resulting contribution to the renormalized perturbation theory is expected to be similar in magnitude to the value of the unrenormalized integral evaluated with a cutoff $\Lambda \sim 1/R$. This suggests that the renormalized perturbation theory (if one exists) will yield a loop expansion in which the L -loop correction to the SCFT free-energy functional will have a prefactor of order

$$\frac{1}{R^3} \left(\frac{p}{R} \right)^{L-1} \sim \frac{1}{vN\bar{N}^{L/2}}. \quad (245)$$

We have used the fact that $R/p = N^{1/2} b^3/v = \bar{N}^{1/2}$ to obtain the second expression in the above. The value of each diagram will be given by this prefactor times a nondimensionalized convergent integral whose value is a dimensionless function of χN and the other SCFT dimensionless parameters. If our renormalization procedure can be extended beyond the one-loop level, the resulting renormalized loop expansion is thus expected to yield an asymptotic expansion of the free energy in powers of $1/\sqrt{\bar{N}}$.

Equation (245) may also be obtained by dimensional analysis: If we nondimensionalize all lengths in units of $R = \sqrt{Nb}$ in the functional Taylor expansion of the statistical weight L that appears in the Edwards functional integral, we obtain an expression for L as the product of a nondimensionalized functional times a large parameter \sqrt{N} . The existence of such a large prefactor is known to imply [21] that the loop expansion (or, more precisely, the renormalized-loop expansion) will yield an expansion in powers of $\bar{N}^{-1/2}$.

XIV. POLYMER SOLUTIONS

UV divergences also appear in the excluded volume problem for polymers in good solvent. The diagrammatic formalism and power counting arguments given above for an incompressible liquid can also be applied to the excluded volume problem. A comparison of the two problems in the same language is instructive.

In the standard Edwards model [11,12] of a polymer in good solvent, the two-body interaction is approximated by a pointlike effective interaction $U(\mathbf{r}) = a\delta(\mathbf{r})$, or $U(q) = a$, where a is an effective excluded volume. The one-loop theory given here for incompressible liquids is closely analogous to Edwards' one-loop theory of solutions. The screened interaction in the original Edwards theory is given, in the limit $N \rightarrow \infty$, by

$$G^{-1}(q) = \frac{12c}{q^2 b^2} + a^{-1}, \quad (246)$$

where the first term is the limit $qR \gg 1$ of $\tilde{\Omega}(q)$. In this theory, we thus obtain an essentially unscreened interaction $\tilde{G}(q) \sim a$ for $k\xi \gg 1$, and a screened interaction identical to that given in Eq. (240) for $k\xi \ll 1$, where $\xi \sim b/\sqrt{ca}$ is the Edwards screening length.

The one-loop theory for a nominally incompressible liquid is thus very similar to the Edwards theory with a cutoff wave number $\Lambda \ll \xi^{-1}$. In studies of nondilute polymer solutions one is generally interested in the dependence of the radius of gyration, osmotic pressure etc. upon contributions from wavelengths less than ξ , which determine the concentration dependence of these quantities. To retain this information, one must use a cutoff $\Lambda \gg \xi^{-1}$.

The UV divergence contributions from the regime $q\xi \gg 1$ may be analyzed by repeating the power counting arguments given above for an incompressible liquid, while using the unscreened interaction $\tilde{G}(q) = a$, rather than the screened interaction $\tilde{G}(q) \propto q^2$. By this method, we find that the contribution to the free-energy density of an L -loop diagram with V vertices is of order

$$\Lambda^d (\Lambda b)^{(L-1)(d-4)-2V} (a/b^d)^{L-1} (ac)^V. \quad (247)$$

In the infinite dilution limit, in which one considers only the interaction among monomers of a single chain, the only relevant diagrams have only one vertex, $V=1$. In this limit, the above expression becomes equivalent to the known result [28] for the naive degree of divergence of diagrams in the perturbation theory for swelling of a single self-avoiding chain.

In the physically relevant case $d=3$, the only UV divergent diagrams in the expansion of the free-energy density for a solution are the one loop diagram with one-vertex ($L=V=1$), which diverges as Λ , and the two-loop contribution with one vertex ($L=2$ and $V=1$), which exhibits a logarithmic divergence in $d=3$. The strongly divergent one-loop diagram was correctly identified by Edwards as a divergence in the free energy per monomer due to interactions between pairs of nearby monomers on the same chain. Edwards removed this divergence by subtracting the free energy per monomer of a single isolated chain from the total free energy. All of the diagrams involving more than one vertex, which are necessary to calculate, e.g., the second virial coefficient, are UV convergent in $d=3$.

Alexander-Katz *et al.* [29] have recently considered the UV divergence of the chemical potential in a stochastic field-theoretic simulation of a polymer solution. In this context, the UV divergence shows up as a dependence of the polymer chemical potential μ upon a spatial discretization length Δx . They found that the UV divergence of μ found in their simulation could be removed by subtracting a one-loop approximation for the free energy per monomer of a system of non-interacting chains from their simulation results. (The above analysis suggests that a logarithmic divergence should have remained, but they reported no evidence that suggests this.) Our analysis of the incompressible liquid model indicates that this simple subtraction will not be sufficient to remove the UV divergences from analogous simulations of dense polymer mixtures, in which the divergence appears at all orders in the loop expansion.

The appearance of negative exponents of Λ in all but a few diagrams in the expansion of the dilute solution free energy in $d=3$ is a symptom of the fact that most diagrams in this theory are infrared (IR) rather than UV divergent. In the infinite dilution limit, in which only diagrams with $V=1$ are relevant, the IR divergence is cutoff at a wavelength of order $R \sim \sqrt{Nb}$. In this limit, a generic diagram diverges with increasing chain length N as $N^{d/2} N^{(4-d)(L-1)/2}$ for all d less than the upper critical dimension $d_c=4$. In a semidilute or concentrated solution, this IR divergence is cutoff at the screening length ξ . The quantities that we calculate in this paper, other than the free-energy density (i.e., the direct correlation function, which is analogous to the second virial coefficient, and the interaction-induced change in the single-chain correlation function) are actually UV convergent and IR divergent in the dilute solution problem. It is, of course, the IR divergence of the excluded volume problem that makes the problem interesting, and that leads to nontrivial scaling behavior for a self-avoiding walk.

The above analysis makes it clear that the excluded volume problem is "renormalizable" in the sense that this word is normally used in quantum or statistical field theory, and that the theory of incompressible liquids considered here is not. A field theory is normally said to have a renormalizable UV divergence if the divergence can be absorbed into a finite number of measurable parameters, such as the mass and charge in quantum electrodynamics. More precisely, it is usually required that only a finite number of vertex functions contain a primitive UV divergence in spatial dimensions d less than or equal to an upper critical dimension d_c [21]. For

this to be true, it must generally be the case that the degree of UV divergence of all vertex functions decrease with increasing order in a loop expansion for all $d < d_c$. For any $d < d_c$ only a few low order diagrams thus remain UV divergent, but the theory instead becomes susceptible to the appearance of IR divergences in (in different contexts) the limit $T \rightarrow T_c$ or $N \rightarrow \infty$, leading to nontrivial critical phenomena. The Edwards model for polymers in good solvent fits this description, with an upper critical dimension $d_c=4$. In the model of incompressible liquids considered here, however, we see from Eq. (244) that the degree of UV divergence increases with increasing order in a loop expansion for all $d > 2$, implying that $d_c=2$. This model would thus normally be said to be unrenormalizable in $d=3$. The difference between the upper critical dimensions of the two theories is a result of the replacement of the unscreened pointlike interaction, which is independent of wave number, by a strongly wave-number dependent screened interaction, $\tilde{G}(q) \propto q^2$.

The notion of “renormalizability” used in this paper is thus different from its usual meaning in field theory, and is specific to the physics of dense polymer mixtures. In either context, a theory is said to be renormalizable if all of its UV divergences can be absorbed into the parameters of an appropriate phenomenological model. In addition, for renormalization to be useful, it is required in both contexts that the functional form of a phenomenological model that is sufficiently flexible to absorb all UV divergences also be sufficiently constrained to allow nontrivial predictions to be made. A theory is properly described as unrenormalizable if the functional form of the theory required to absorb all UV divergent parts of the free-energy functional is so flexible that it could describe all conceivable behavior. In the present context, the appropriate phenomenological model is a SCFT of Gaussian chains. The only constraint that we place on the functional form of this theory is that interaction free-energy functional (excluding the contributions of chain ends and junctions) be independent of chain length N and chain architecture. We show here that, to first order in a loop expansion, a SCFT of this form is recovered as the $N \rightarrow \infty$ limit of the true free-energy functional, and that the sensitivity of the theory to the cutoff (or more generally, to monomer scale chemical details) can be absorbed into this $N \rightarrow \infty$ limit. The renormalized perturbation theory makes nontrivial predictions about N -dependent, UV convergent corrections to this theory. If the same ideas were applied to a liquid of point particles, there would be no constraint on the functional form of the free energy, and so the theory would have no predictive power. It is thus the appearance of $1/\bar{N}$ as a small parameter that makes it possible to extract useful information from a theory that would be considered unrenormalizable by the usual rules of field theory.

XV. CONCLUSIONS

Several previous calculations have shown that predictions of a coarse-grained model of polymer liquids, when extended beyond the mean-field level, depend very sensitively on the value chosen for an arbitrary coarse-graining length. In light of this, it is reasonable to ask whether such models can make

any unambiguous physical predictions. We know how to extract physical predictions from a UV divergent theory only if we can absorb all UV divergences into the values of a finite number of phenomenological coefficients. The question of whether such coarse-grained theories can predict anything thus inevitably boils down to the question of whether they are, in some sense, renormalizable. The definition of “renormalizability” that we introduce here (as discussed above) is based upon the assumption that a renormalized SCFT with an interaction free energy that is independent of N is obtained as the limit $N \rightarrow \infty$ of the true free energy, and that all UV divergences can be absorbed into this asymptotic theory.

In this paper, we have explicitly demonstrated the renormalizability of the one-loop approximation for $S^{-1}(k)$ in the auxiliary field approach, for arbitrary k , for both polymer blends and diblock copolymer melts. We showed that all UV divergent contributions to $S^{-1}(k)$ can be absorbed into changes in the values of the parameters of an appropriate form of SCFT. To make this work, it was necessary to allow for renormalization of all of the parameters of the standard SCFT, i.e., of the statistical segment lengths as well as the local interaction free energy. We also found that it was necessary to allow for some free energy contributions that are plausible on physical grounds, but not usually considered, i.e., a square-gradient interaction free energy and excess energies for chain end and for junctions in block copolymers.

At a conceptual level, this analysis is important because it provides evidence for the logical consistency of the study of coarse-grained models, and for our assumption that some form of SCFT is exact in the limit $N \rightarrow \infty$. Because we have analyzed only one vertex function, $S^{-1}(k)$, only to first order in a loop expansion, our calculation provides a consistency check, but not a proof of renormalizability. This is quite different from the situation in quantum and statistical field theory, in which methods were developed long ago to prove renormalizability to all orders in perturbation theory. An analogous proof would require an enormous generalization of the explicit analysis given here.

At a practical level, our analysis is important as a necessary step in the development of a rigorous renormalized perturbation theory of corrections to SCFT: Identification and removal of all UV divergences is a prerequisite to the systematic study of the long wavelength physics that coarse-grained models are intended to describe. In subsequent work on this subject, we will focus on an examination of physical predictions of the renormalized one-loop theory for corrections to SCFT, and on extending the theory beyond the one-loop level.

Our procedure for extracting the UV convergent contributions of physical interest is, for the moment, to simply subtract the results of our analytic calculation of the UV divergent contribution to each quantity from the results of a numerical evaluation of the underlying Fourier integral, using the same finite cutoff wave-number Λ in both calculations. To make this procedure work, we must identify and subtract all UV divergent contributions to the unrenormalized integrals, including the $O(\Lambda/N)$ divergences discussed in Sec. XII. We have confirmed numerically that this procedure yields results that are nearly independent of Λ for large values of Λ , and that converge in the limit $\Lambda \rightarrow \infty$. It is worth

noting that this numerical procedure provides a very stringent test of the correctness of our results: Any error in either our analytic calculation of UV divergent contributions or in our numerical integration would destroy the required cancellation of UV divergent terms.

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APPENDIX: SINGLE-CHAIN CORRELATIONS

In this appendix, we provide further details of the derivation of asymptotic high- q expansions of the three- and four-point correlation functions for both homopolymers and diblock copolymers. The leading order terms in the required expansions were obtained for homopolymers in Sec. IX.

1. Generalization to block copolymers

To begin, we generalize to block copolymers the discussion of multipoint correlations for a Gaussian homopolymer that was given in Sec. IX A. We consider an n -point correlation function

$$\tilde{\omega}_{i_1 \dots i_n}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n) = \int_0^N d^n s \langle e^{i\mathbf{k}_j \cdot \mathbf{R}(s_j)} \rangle. \quad (\text{A1})$$

Here, $d^n s$ should be understood to indicate an integral over all values of s_1, \dots, s_n , subject only to the constraint that, in a block copolymer, the integral over s_j must be taken over only the block of the polymer that contains monomers of type i_j . (For simplicity, we will only discuss situations in which each block is chemically distinct.) For example, in a diblock copolymer for which monomers with $0 < s < fN$ are of type 1,

$$\tilde{\omega}_{122}^{(3)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = \int_{fN}^N ds_3 \int_{fN}^N ds_2 \int_0^{fN} ds_1 \langle e^{i\mathbf{k}_j \cdot \mathbf{R}(s_j)} \rangle. \quad (\text{A2})$$

We may also write $\tilde{\omega}^{(n)}$ as sum of ordered integrals involving different permutations of the wave-vector arguments, of the form given in Eq. (155), if it is understood that (i) the sum over permutations must be restricted to permutations that do not change any monomer types, but only that exchange the identities of monomers of the same type, and (ii) the ordered integral $\tilde{\omega}_{i_1 \dots i_n}^{(n)}$ is defined by integrating over a subspace defined by the requirement that $s_1 < s_2 < \dots < s_n$ and that the integral with respect to monomer index s_j may not extend beyond the block containing monomers of type i_j . For example,

$$\tilde{\omega}_{122}^{(3)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = \omega_{122}^{(3)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) + \omega_{122}^{(3)}(\mathbf{k}_1, \mathbf{k}_3, \mathbf{k}_2), \quad (\text{A3})$$

where

$$\omega_{122}^{(3)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = \int_{fN}^N ds_3 \int_{fN}^{s_3} ds_2 \int_0^{fN} ds_1 \langle e^{i\mathbf{k}_j \cdot \mathbf{R}(s_j)} \rangle. \quad (\text{A4})$$

The value of an ordered integral $\omega_{i_1 \dots i_n}^{(n)}$ can be evaluated using a slight generalization of Eq. (162), in which the limits of integration in the ordered integral are interpreted in this manner, and in which the integrand is generalized to allow for the existence of different statistical segment lengths in different blocks.

We also define functions

$$\hat{\omega}_{i_1 \dots i_n}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n) \equiv N^{-n} \tilde{\omega}_{i_1 \dots i_n}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n), \quad (\text{A5})$$

$$\hat{\omega}_{i_1 \dots i_n}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n) \equiv N^{-n} \omega_{i_1 \dots i_n}^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n). \quad (\text{A6})$$

Explicit expressions for these quantities may be written as functions of the $2n$ dimensionless wave-vectors $\mathbf{K}_{ai} = \mathbf{k}_a b_i \sqrt{N}/6$, and of f_1 and f_2 . Because the existence of two statistical segment lengths b_1 and b_2 provides two ways to nondimensionalize each wave vector, we will write $\hat{\omega}_{i_1 \dots i_n}^{(n)}$ and $\hat{\omega}_{i_1 \dots i_n}^{(n)}$ for diblock copolymers as functions of $\mathbf{k}_1, \dots, \mathbf{k}_n$, rather than as functions of dimensionless wave vectors.

2. Three-point correlations

a. Homopolymer

The dimensionless ordered integral $\hat{\omega}^{(3)}$ for a homopolymer is given exactly, for arbitrary wave-vector arguments, by

$$\hat{\omega}^{(3)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3) = \frac{1}{2} \frac{g(K_1^2) - g(K_3^2)}{K_3^2 - K_1^2}. \quad (\text{A7})$$

Each of the ordered integrals required in Eq. (166) may be evaluated using this general result. To obtain an asymptotic expansion of each of the resulting integrals, we drop all terms that are proportional to e^{-Q^2} (which are not analytic functions of $1/Q$ in the limit $1/Q \rightarrow 0$), and expand the remaining terms in powers of $1/Q$. To $O(Q^{-4})$, this yields

$$\begin{aligned} \hat{\omega}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+) &\simeq g(K^2) \left[\frac{1}{2Q^2} - \frac{\alpha K}{2Q^3} \right] \\ &+ \left[\frac{1}{2} K^2 (3 + 4\alpha^2) g(K^2) - 4 \right] \frac{1}{4Q^4}, \\ \hat{\omega}(\mathbf{Q}_-, \mathbf{K}, -\mathbf{Q}_+) &\simeq \frac{1}{Q^4}. \end{aligned} \quad (\text{A8})$$

An expression for $\hat{\omega}(\mathbf{K}, -\mathbf{Q}_+, \mathbf{Q}_-)$ may be obtained by taking $\mathbf{Q} \rightarrow -\mathbf{Q}$, and $\alpha \rightarrow -\alpha$, in the expression for $\hat{\omega}(\mathbf{K}, \mathbf{Q}_-, -\mathbf{Q}_+)$. Terms linear in α cancel upon adding permutations, giving Eqs. (173) and (174).

b. Diblock copolymers

For a diblock copolymer, we need the four functions $\hat{\omega}_{ii}^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)$, $\hat{\omega}_{ij}^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)$, $\hat{\omega}_{ij}^{(3)}(\mathbf{k}, \mathbf{q}_+, -\mathbf{q}_+)$, and

$\hat{\omega}_{ij}^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)$ for $i \neq j$. The function $\hat{\omega}_{ij}^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)$ may be obtained by taking $\mathbf{q} \rightarrow -\mathbf{q}$ in our result for $\hat{\omega}_{ij}^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+)$. The function $\hat{\omega}_{ii}^{(3)}$ for a diblock copolymer with an i block of length $f_i N$ is simply equal to the corresponding function for a homopolymer of type i and length $f_i N$.

To calculate the remaining two functions, in which one of the species indices is different from the other two, we may start from the general result

$$\hat{\omega}_{ij}^{(3)}(\mathbf{k}_a, \mathbf{k}_b, \mathbf{k}_c) = e_i(K_{ai}^2) \frac{e_j(K_{aj}^2) - e_j(K_{ci}^2)}{K_{cj}^2 - K_{aj}^2}, \quad (\text{A9})$$

where $K_{ai}^2 \equiv |\mathbf{k}_a|^2 b_i^2 N/6$ and $K_{ci}^2 \equiv |\mathbf{k}_c|^2 b_i^2 N/6$. To calculate $\hat{\omega}_{jji}^{(3)}$, we note the symmetry $\hat{\omega}_{jji}^{(3)}(\mathbf{k}_c, \mathbf{k}_b, \mathbf{k}_a) = \hat{\omega}_{ijj}^{(3)}(\mathbf{k}_a, \mathbf{k}_b, \mathbf{k}_c)$. Evaluating and expanding the required integrals yields

$$\begin{aligned} \hat{\omega}_{ijj}^{(3)}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+) &\approx e_i(K_i^2) e_j(K_j^2) \left[\frac{1}{Q_j^2} - \frac{\alpha K}{Q_j^3} \right] \\ &\quad + [e_j(K_j^2) K_j^2 (3 + 4\alpha^2) - 4] \frac{e_i(K_i^2)}{4Q_j^4}, \\ \hat{\omega}_{ijj}(\mathbf{k}, \mathbf{q}_-, -\mathbf{q}_+) &\approx e_i(K_i^2) \frac{1}{Q_j^4}. \end{aligned} \quad (\text{A10})$$

Expressions for $\hat{\omega}_{ijj}^{(3)}(\mathbf{k}, -\mathbf{q}_+, \mathbf{q}_-)$ and $\hat{\omega}_{ijj}^{(3)}(\mathbf{k}, -\mathbf{q}_+, \mathbf{q}_-)$ may be obtained by taking $\mathbf{q} \rightarrow -\mathbf{q}$ in the above to integrals. The quantities $\hat{\omega}_{ijj}(\mathbf{q}_-, \mathbf{k}, -\mathbf{q}_+)$ and $\hat{\omega}_{ijj}(-\mathbf{q}_+, \mathbf{k}, \mathbf{q}_-)$ are $O(Q^{-6})$, and so may be neglected.

3. Four-point correlations

a. Homopolymers

The ordered integrals required to calculate the four-point function $\hat{\psi}^{(4)}(\mathbf{K}, -\mathbf{K}, \mathbf{Q}, -\mathbf{Q})$ may be expressed as

$$\hat{\psi}^{(4)}(\mathbf{K}, \pm \mathbf{Q}, \mp \mathbf{Q}, -\mathbf{K}) = \int_0^1 d\hat{s} e^{-K^2 \hat{s}_{43}} H_{\pm}(\hat{s}_{32}) e^{-K^2 \hat{s}_{21}},$$

$$\hat{\psi}^{(4)}(\mathbf{K}, \pm \mathbf{Q}, -\mathbf{K}, \mp \mathbf{Q}) = \int_0^1 d\hat{s} e^{-K^2 \hat{s}_{43}} H_{\pm}(\hat{s}_{32}) e^{-Q^2 \hat{s}_{21}},$$

$$\hat{\psi}^{(4)}(\pm \mathbf{Q}, \mathbf{K}, -\mathbf{K}, \mp \mathbf{Q}) = \int_0^1 d\hat{s} e^{-Q^2 \hat{s}_{43}} H_{\pm}(\hat{s}_{32}) e^{-Q^2 \hat{s}_{21}},$$

where

$$H_{\pm}(\hat{s}_{32}) \equiv e^{-Q_{\pm}^2 \hat{s}_{32}} - e^{-(Q^2 + K^2) \hat{s}_{32}} \quad (\text{A11})$$

and $\mathbf{Q}_{\pm} \equiv \mathbf{Q} \pm \mathbf{K}$. The dominant behavior of each of these integrals can be obtained by noting that \hat{s}_{32} is confined to very small values by the exponential factors in $H(\hat{s}_{32})$, and that we may thus approximate the integral with respect to \hat{s}_3 over the domain $\hat{s}_2 < \hat{s}_3 < \hat{s}_4$ to a first approximation by an integral over $\hat{s}_2 < \hat{s}_3 < \infty$. This approximation yields a common factor

$$\int_0^{\infty} d\hat{s}_{32} H_{\pm}(\hat{s}_{32}) = \frac{1}{Q_{\pm}^2} - \frac{1}{Q^2 + K^2} \approx \frac{\mp 2K\alpha}{Q^3} + \frac{4(K\alpha)^2}{Q^4} + \dots \quad (\text{A12})$$

in the integrals

$$\hat{\psi}^{(4)}(\mathbf{K}, \pm \mathbf{Q}, \mp \mathbf{Q}, -\mathbf{K}) \approx -\frac{1}{2} \frac{\partial g(K^2)}{\partial (K^2)} \int_0^{\infty} ds H_{\pm}(s),$$

$$\hat{\psi}^{(4)}(\mathbf{K}, \pm \mathbf{Q}, -\mathbf{K}, \mp \mathbf{Q}) \approx \frac{1}{2Q^2} g(K^2) \int_0^{\infty} ds H_{\pm}(s),$$

$$\hat{\psi}^{(4)}(\pm \mathbf{Q}, \mathbf{K}, -\mathbf{K}, \mp \mathbf{Q}) \approx \frac{1}{Q^4} \int_0^{\infty} ds H_{\pm}(s). \quad (\text{A13})$$

Upon adding the four permutations in which $\pm \mathbf{K}$ are the first and last arguments, and using the expansion given in Eq. (A12) for the remaining integral, terms that are proportional to α and $O(Q^{-3})$ cancel. This leaves a leading order contribution of $O(Q^{-4})$. All other permutations lead to contributions of $O(Q^{-6})$ or higher, which do not lead to UV divergent contributions to $\delta\omega^{(2)}$ in the one-loop approximation.

b. Diblock copolymers

Consider a diblock in which block 1 extends from $0 < s < f_1 N$ and block 2 is $f_1 N < s < N$, and let $\hat{\psi}_{ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}) \equiv N^{-4} \hat{\psi}_{ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q})$. As for homopolymers, we may express $\hat{\psi}_{ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q})$ as a sum of ordered integrals. To calculate an ordered integral $\hat{\psi}_{i_1 \dots i_4}^{(4)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4)$ for a diblock, we require that the integrals over each monomer index s_i be constrained to the block specified by the corresponding monomer type index, as well as $s_1 < s_2 < s_3 < s_4$, and thus that $i_1 \leq i_2 \leq i_3 \leq i_4$. As for homopolymers, we find that $\hat{\psi}_{ijkl}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}, -\mathbf{q}) = 0$ for ordered integrals in which $\pm \mathbf{k}$ are the first two or the last two wave-vector arguments.

As found for homopolymers, we find that the dominant contributions to $\hat{\psi}_{ijkl}^{(4)}$ are $O(Q^{-4})$, and arise from ordered integrals in which $\pm \mathbf{k}$ are the first and last arguments of $\hat{\psi}_{ijkl}^{(4)}$. For diblock copolymers, the $O(Q^{-4})$ contributions are obtained only from ordered integrals of the form $\hat{\psi}_{ikkj}(\pm \mathbf{k}, \pm \mathbf{q}, \mp \mathbf{q}, \pm \mathbf{k})$, where $\pm \mathbf{q}$ are associated with monomers in the same block. The sum of the four ordered integrals of the form $\hat{\psi}_{1111}^{(4)}(\pm \mathbf{k}, \pm \mathbf{q}, \mp \mathbf{q}, \pm \mathbf{k})$ yield a contribution to $\hat{\psi}_{1111}^{(4)}(\mathbf{k}, \mathbf{q}, -\mathbf{q}, -\mathbf{k})$ equal to that obtained from for homopolymer of length $f_1 N$. The resulting contribution to $\hat{\psi}_{1111}^{(4)}(\mathbf{k}, \mathbf{q}, -\mathbf{q}, -\mathbf{k})$ is

$$\hat{\psi}_{1111}^{(4)} \approx \frac{16K_1^2 \alpha^2}{Q_1^4} \int_0^{f_1} d\hat{s}_2 \int_0^{\hat{s}_2} d\hat{s}_1 \hat{s}_{21} e^{-K_1^2 \hat{s}_{21}} \approx -\frac{8K^2 \alpha^2}{Q^4} \frac{\partial g_{11}}{\partial (K^2)}. \quad (\text{A14})$$

The dominant contributions to $\hat{\psi}_{1112}(\mathbf{k}, \mathbf{q}, -\mathbf{q}, -\mathbf{k})$ arise from the ordered integrals $\hat{\psi}_{1112}(\pm \mathbf{k}, \pm \mathbf{q}, \mp \mathbf{q}, -\mathbf{k})$, which yield

$$\begin{aligned}\hat{\psi}_{1112}^{(4)} &\approx \frac{16K_1^2\alpha^2}{Q_1^4} \int_0^{f_2} d\hat{s}'_2 e^{-K_2^2\hat{s}'_2} \int_0^{f_1} d\hat{s}'_1 \hat{s}'_1 e^{-K_1^2\hat{s}'_1} \\ &\approx -\frac{8K_1^2\alpha^2}{Q_1^4} \frac{\partial g_{12}}{\partial(K_1^2)},\end{aligned}\quad (\text{A15})$$

where $\hat{s}'_2 = \hat{s}_2 - f_1$ and $\hat{s}'_1 = f_1 - \hat{s}_2$. Corresponding approxima-

tions for $\hat{\psi}_{2222}^{(4)}(\pm\mathbf{k}, \pm\mathbf{q}, \mp\mathbf{q}, -\mathbf{k})$, $\hat{\psi}_{1222}^{(4)}(\pm\mathbf{k}, \pm\mathbf{q}, \mp\mathbf{q}, -\mathbf{k})$ can be obtained by analogy, by switching the labeling of blocks 1 and 2. The dominant contributions are thus all of the form

$$\hat{\psi}_{ikkj}^{(4)} \approx \frac{8K_k^2\alpha^2}{Q_k^4} \frac{\partial g_{ij}}{\partial(K_k^2)}. \quad (\text{A16})$$

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