

## Gaussian field model of fluids with an application to polymeric fluids

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This paper extends the Gaussian model of Li and Kardar [Phys. Rev. Lett. **67**, 3275 (1991)]. When applied self-consistently to density fluctuations of a hard-sphere fluid, it is shown that the model gives the Percus-Yevick theory. With the addition of an attractive tail potential, the mean spherical approximation is obtained. Unlike the random-phase approximation, this approach determines the normal modes of the model consistent with the presence of an excluding manifold. The resulting fluid response in the presence of such an object is derived. For a  $D = 1$  manifold, the self-consistent approach is a theory of polymeric fluids. Here, with an averaging approximation, the reference-interaction-site-model (RISM) equation in the thread limit is obtained. For polymer blends, the analysis yields a seemingly exact formula for a demixing critical temperature. It scales linearly with polymer mass, as in Flory's theory, but with an effective  $\chi$  parameter smaller than that in Flory's theory. The analysis sheds light on an erroneous prediction of different scaling made by others applying the RISM theory.

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### I. INTRODUCTION

This paper is concerned with a simple model of fluids, the Gaussian field model. It is often used in the development of theories for fluctuations over large length scales. Examples include its application to critical phenomena [1], to complex fluids [2], and to visualization of bicontinuous phases [3]. In each of these cases, one is concerned with spatial variations over distances far larger than the molecular species that make up the fluid. It may seem remarkable, therefore, that the Gaussian model can also prove useful at microscopic length scales. Indeed, the model is related to Percus-Yevick theory, the mean spherical approximation, and many other long-standing molecular theories of liquid matter. This relationship is derived in this paper.

The development is motivated by Li and Kardar's recent application of the Gaussian model [4]. They considered the effects of excluding a Gaussian field from a rigid manifold. They showed that the entropic effects of this exclusion lead to interactions such as the Casimir force. To the extent that fluctuations are Gaussian, Li and Kardar's method of analysis is very general. In Sec. II, it is applied in a self-consistent way to density fluctuations, and it is shown that the Percus-Yevick theory and related approximations result. This derivation places these theories into the context of a well defined, though admittedly simplistic, Hamiltonian. While it contrasts with arbitrary truncations of perturbation series, one might have anticipated this alternative derivation from older work [5,6], especially Ref. [5].

It is interesting to understand that the Li-Kardar approach is equivalent to older and well tested theories. The primary utility of the Li-Kardar perspective, however, is that one can foresee applications beyond those

of pair correlations in simple liquids. In Sec. III, the Li-Kardar method is applied to  $D = 1$  manifolds. Here, the physical system under consideration could be an electron in a disordered system, or a polymer in a liquid. In this case, it is shown that the Gaussian field theory in its simplest form coincides with the reference interaction site model (RISM) for these systems [7-9]. Schweizer and co-workers [10,11] have argued that this theory applied to polymer blends predicts a massive renormalization of Flory's  $\chi$  parameter [12], and that this prediction is undoubtedly incorrect. Our analysis of the RISM theory provides some understanding of the origins of this prediction.

It is the nature of a Gaussian model that the Fourier components of the dynamical fields, in this case the particle densities, are the normal modes of the homogeneous fluid. These are the normal modes of the random-phase approximation (RPA). Nevertheless, the Li-Kardar treatment of the inhomogeneous fluid, i.e., the fluid in the presence of an excluding manifold, is different than the RPA. The nonlinearities of excluded volume alter the normal modes. Physical manifestations of this alteration include vanishing distributions in regions of excluded-volume overlap and the screening or diminution of perturbation potential fluctuations by the packing or confinement of excluded volume forces. Neither of these effects is described by the RPA. Their significance has been sorted out and well understood long ago in the context of simple liquids [13,14]. The issues are pertinent to the physics of polymeric liquids as discussed in Sec. III. This paper is concluded with a brief discussion in Sec. IV.

### II. SPHERICAL MANIFOLD

Consider the solvation of a spherical object immersed in a fluid. The object is the solute, and the fluid is the

solvent. In the absence of the object, the Hamiltonian of the pure fluid is assumed to be

$$H_B = (k_B T/2) \int d\mathbf{r} \int d\mathbf{r}' \delta\rho(\mathbf{r}) \chi^{-1}(\mathbf{r}, \mathbf{r}') \delta\rho(\mathbf{r}'), \quad (2.1)$$

where  $\delta\rho(\mathbf{r})$  is the deviation of the fluid density from its mean,  $\rho$ ,  $\chi^{-1}(\mathbf{r}, \mathbf{r}')$  is the functional inverse of its variance,

$$\chi(\mathbf{r} - \mathbf{r}') = \langle \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \rangle, \quad (2.2)$$

and  $k_B T = \beta^{-1}$  is Boltzmann's constant times temperature.

In the presence of the object, two things happen. First, the solute excludes fluid density from the volume it occupies; i.e.,

$$\rho(\mathbf{r}) = 0, \quad \mathbf{r} \text{ inside.} \quad (2.3)$$

Here, "r inside" means  $\mathbf{r}$  at a point enveloped by the spherical solute. Second, outside that region, the solute interacts with the fluid with a spherically symmetric potential,  $-k_B T u(r) = w(r)$ . The resulting partition function is

$$Z[\phi] = \int \mathcal{D}\rho(\mathbf{r}) \left\{ \prod_{\mathbf{r} \text{ inside}} \delta[\rho(\mathbf{r})] \right\} \times \exp \left\{ -\beta H_B + \int d\mathbf{r} \rho(\mathbf{r}) [u(r) + \phi(\mathbf{r})] \right\}, \quad (2.4)$$

where we have introduced the usual auxiliary field  $\phi(\mathbf{r})$  as an aid to subsequent computation. The symbol  $\mathcal{D}$  indicates functional integration.

The product of  $\delta$  functions in Eq. (2.4) enforces the exclusion, (2.3). This exclusion is a nonlinear effect which cannot be incorporated into a Gaussian model by simply adding an expelling potential field to the Hamiltonian. That simple approach would lead to the unphysical  $\rho(\mathbf{r}) \rightarrow -\infty$ .

Following Li and Kardar [4], the Fourier representation is exploited:

$$Z[\phi] = \int \mathcal{D}\psi(\mathbf{r}) \int \mathcal{D}\rho(\mathbf{r}) \exp\{S[\rho(\mathbf{r}), \psi(\mathbf{r})]\}, \quad (2.5)$$

with

$$S[\rho(\mathbf{r}), \psi(\mathbf{r})] = -\beta H_B + i \int_{\text{in}} d\mathbf{r} \psi(\mathbf{r}) \rho(\mathbf{r}) + \int d\mathbf{r} \rho(\mathbf{r}) [u(r) + \phi(\mathbf{r})], \quad (2.6)$$

where the subscript "in" indicates that the integration so labeled is over the interior of the excluded spherical volume. The field  $\psi(\mathbf{r})$  is defined in this volume only. Cast in this form,  $Z[\phi]$  is easily evaluated in terms of Gaussian averages. The result is

$$\begin{aligned} Z[\phi] = & c [\det \chi_{\text{in}}]^{-1/2} \exp \left( \rho \int d\mathbf{r} [u(r) + \phi(\mathbf{r})] \right. \\ & + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \chi(|\mathbf{r} - \mathbf{r}'|) [u(r) + \phi(\mathbf{r})] [u(r') + \phi(\mathbf{r}')] \\ & - \frac{1}{2} \int_{\text{in}} d\mathbf{r} \int_{\text{in}} d\mathbf{r}' \chi_{\text{in}}^{-1}(\mathbf{r}, \mathbf{r}') \left\{ \rho + \int d\mathbf{r}'' [u(r'') + \phi(\mathbf{r}'')] \chi(|\mathbf{r} - \mathbf{r}''|) \right\} \\ & \left. \times \left\{ \rho + \int d\mathbf{r}''' [u(r''') + \phi(\mathbf{r}''')] \chi(|\mathbf{r}' - \mathbf{r}'''|) \right\} \right). \quad (2.7) \end{aligned}$$

The value of the constant  $c$  depends upon the metric convention for the functional integration; it is proportional to the partition function of the pure unperturbed solvent. The matrix  $\chi_{\text{in}}$  has elements  $\chi(|\mathbf{r} - \mathbf{r}'|)$  for  $\mathbf{r}$  and  $\mathbf{r}'$  both within the excluded manifold; its eigenvectors span the Hilbert space of functions defined within the manifold.

Equation (2.7) is a generalization of Li and Kardar's formula, e.g., Eq. (5) of Ref. [4(a)]. Through differentiation with respect to  $\phi(\mathbf{r})$ , one may compute average densities and correlation functions in the presence of the solute. Notice that  $\ln Z[\phi]$  is quadratic in  $\phi(\mathbf{r})$  and thus  $\langle \rho(\mathbf{r}) \rangle_\phi$  is linear in  $\phi(\mathbf{r})$ . Even in the presence of the excluding manifold, therefore, the statistics of the solvent remains Gaussian. Its normal modes and response function are altered by the manifold, but there are no nonlinear responses to an external disturbance.

Performing the differentiation and then setting  $\phi(\mathbf{r})$  to zero, one finds

$$\begin{aligned} \langle \rho(\mathbf{r}) \rangle_0 = & \rho + \int d\mathbf{r}' \chi(|\mathbf{r} - \mathbf{r}'|) u(r') \\ & - \int_{\text{in}} d\mathbf{r}' \int_{\text{in}} d\mathbf{r}'' \chi_{\text{in}}^{-1}(\mathbf{r}', \mathbf{r}'') \left[ \rho \chi(|\mathbf{r}' - \mathbf{r}|) \right. \\ & \left. + \int d\mathbf{r}''' \chi(|\mathbf{r}' - \mathbf{r}|) \chi(|\mathbf{r}'' - \mathbf{r}'''|) u(r''') \right], \quad (2.8) \end{aligned}$$

where the origin is the center of the spherical object. For  $\mathbf{r}$  inside that sphere, one may verify that the right-hand side of (2.8) is indeed zero. This is done by noting that

$$\int_{\text{in}} d\mathbf{r}'' \chi_{\text{in}}^{-1}(\mathbf{r}', \mathbf{r}'') \chi(|\mathbf{r}'' - \mathbf{r}|) = \delta(\mathbf{r}' - \mathbf{r}),$$

$\mathbf{r}'$  and  $\mathbf{r}$  inside. (2.9)

The solute-solvent radial distribution function is

$$\begin{aligned} c(r) &= u(r) - \int_{\text{in}} d\mathbf{r}' \chi_{\text{in}}^{-1}(\mathbf{r}, \mathbf{r}') \left[ \rho + \int d\mathbf{r}'' \chi(|\mathbf{r}' - \mathbf{r}''|) u(r'') \right] \\ &= - \int_{\text{in}} d\mathbf{r}' \chi_{\text{in}}^{-1}(\mathbf{r}, \mathbf{r}') \left[ \rho + \int_{\text{out}} d\mathbf{r}'' \chi(|\mathbf{r}' - \mathbf{r}''|) u(r'') \right], \quad \mathbf{r} \text{ inside,} \end{aligned} \quad (2.11)$$

and

$$c(r) = u(r), \quad \mathbf{r} \text{ outside.} \quad (2.12)$$

Equation (2.10) is recognized as the Ornstein-Zernike relationship, where  $c(r)$  is the direct-correlation function between solute and solvent [14]. Equations (2.11) and (2.12) are the closure relations, in this case the mean spherical approximation (MSA) [13–15]. In particular, outside the excluded volume,  $c(r)$  is the actual pair potential between solute and solvent (in units of  $-k_B T$ ), and inside the excluded region it is that function which makes  $g(r) = 0$  for  $r$  inside.

There are special cases worthy of note. First, when the solvent is in fact composed of the same species as the solute, self-consistency demands

$$\chi(|\mathbf{r} - \mathbf{r}'|) = \rho \delta(\mathbf{r} - \mathbf{r}') + \rho^2 [g(|\mathbf{r} - \mathbf{r}'|) - 1]. \quad (2.13)$$

Equations (2.10)–(2.13) are the self-consistent MSA equations. Second, if  $u(r) = 0$ , then  $c(r) = 0$  for  $r$  outside. In that case, Eqs. (2.10)–(2.13) are the Percus-Yevick (PY) equation for a hard-sphere fluid [6,14].

Alternatively, if  $\chi(|\mathbf{r} - \mathbf{r}'|)$  is provided as input, the theory is then a *linear* integral equation for  $g(r)$ , the solution of which is provided by Eqs. (2.10)–(2.12). In practice, implementation requires a choice of basis functions to span the interior manifold. Inversion of  $\chi_{\text{in}}$  can then be carried out in the representation prescribed by that basis.

The Pratt-Chandler theory of the hydrophobicity [16] is precisely this type of theory. There,  $\chi(|\mathbf{r} - \mathbf{r}'|)$  is the pair-correlation function between oxygen atoms in liquid water (as measured by, say, x-ray scattering). The expelling spherical object is the hydrophobic solute. The theory makes no explicit assumptions concerning the orientational structure of water. In effect, it computes the entropic consequences of permitting only those fluctuations for which no water exists in the excluded manifold. To the extent that the statistics of these fluctuations and

$g(r) = \langle \rho(\mathbf{r}) \rangle_0 / \rho$ . Accordingly, Eq. (2.8) is

$$\rho [g(r) - 1] = \int d\mathbf{r}' c(r') \chi(|\mathbf{r}' - \mathbf{r}|), \quad (2.10)$$

with

water reorganization can be regarded as Gaussian, the theory is exact.

### III. $D = 1$ MANIFOLD

Here, as a second example, the Li-Kardar approach is applied to a fluid with polymeric species. Again, we consider density as the pertinent field. In the process of solvating a polymer, the field is excluded from a chain of sites located on the path  $\mathbf{r}(t)$ ,  $0 \leq t \leq N$ . For simplicity, assume that the polymer is a chain with self-avoidance. In this case, the excluding manifold is the path  $\mathbf{r}(t)$ . [Without self-avoidance, it is possible to have redundancy in this characterization of the manifold, i.e.,  $\mathbf{r}(t) = \mathbf{r}(t')$ ,  $t \neq t'$ . Such redundancy must (and always can) be removed when formulating the model in order that  $\chi_{\text{in}}$  be invertible.] Finally, assume that  $N$  is sufficiently large that end effects are negligible. In that case, all segments on the chain are statistically equivalent. Further,  $N$  is large enough that the segment label  $t$  can be regarded as a continuous variable.

In the presence of the chain, the partition function of the fluid is now

$$Z[\phi] = \int \mathcal{D}\eta(t) \int \mathcal{D}\rho(\mathbf{r}) \exp\{S[\rho(\mathbf{r}), \eta(t)]\}, \quad (3.1)$$

where

$$\begin{aligned} S[\rho(\mathbf{r}), \eta(t)] &= -\beta H_B + i \int_0^N dt \eta(t) \rho[\mathbf{r}(t)] \\ &\quad + \int_0^N dt \int d\mathbf{r} \rho(\mathbf{r}) u[|\mathbf{r} - \mathbf{r}(t)|] \\ &\quad + \int d\mathbf{r} \rho(\mathbf{r}) \phi(\mathbf{r}). \end{aligned} \quad (3.2)$$

$\eta(t)$  is the Fourier variable analogous to  $\psi(\mathbf{r})$  in Sec. II;  $u(r)$  is the potential tail (in addition to the excluding core) that couples a segment of the chain to the fluid. The functional integrations and differentiations of Eq. (3.1) are carried out as in Sec. II, this time yielding

$$\begin{aligned} \langle \rho(\mathbf{r}) \rangle_{[\mathbf{r}(t)]} &= \rho + \int_0^N dt \int d\mathbf{r}' \chi(|\mathbf{r} - \mathbf{r}'|) \left\{ u(|\mathbf{r}' - \mathbf{r}(t)|) \right. \\ &\quad \left. - \int_0^N dt' \chi_{\text{in}}^{-1}(t, t') \delta[\mathbf{r}(t') - \mathbf{r}'] \left( \rho + \int_0^N dt'' \int d\mathbf{r}'' u(|\mathbf{r}'' - \mathbf{r}(t'')|) \chi[|\mathbf{r}'' - \mathbf{r}(t)|] \right) \right\}. \end{aligned} \quad (3.3)$$

The subscript  $[\mathbf{r}(t)]$  indicates that the labeled average is performed with the chain's path fixed, and it is understood that the auxiliary field  $\phi(\mathbf{r})$ , has been set to zero. The function  $\chi_{\text{in}}^{-1}(t, t')$  is the matrix inverse of

$$\chi_{\text{in}}(t, t') = \chi[|\mathbf{r}(t) - \mathbf{r}(t')|]. \quad (3.4)$$

When averaged over paths of the chain, it is

$$\langle \chi_{\text{in}}(t, t') \rangle = (2\pi)^{-3} \int d\mathbf{k} \rho S(k) \hat{\omega}(k, t - t'), \quad (3.5)$$

where  $S(k)$  is the structure factor of the fluid [i.e., the Fourier transform of  $\chi(|\mathbf{r} - \mathbf{r}'|)/\rho$ ], and

$$\hat{\omega}(k, t - t') = \langle \exp\{i\mathbf{k} \cdot [\mathbf{r}(t) - \mathbf{r}(t')]\} \rangle \quad (3.6)$$

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$$\begin{aligned} \rho g(r) &= \langle \rho(\mathbf{r}) \rangle_0 \\ &= \rho - \rho \int d\mathbf{r}' \chi(|\mathbf{r} - \mathbf{r}'|) \int_0^N dt \int_0^N dt' \langle \delta[\mathbf{r}' - \mathbf{r}(t')] \chi_{\text{in}}^{-1}(t', t) \rangle_0, \end{aligned} \quad (3.7)$$

where the subscript zero indicates that  $\mathbf{r}(0)$  is fixed at the origin during the averaging. A simplification is obtained by replacing  $\chi_{\text{in}}$  with its path average in Eq. (3.7). This yields

$$g(r) - 1 \approx c_0 \int d\mathbf{r}' \bar{\omega}(r') \chi(|\mathbf{r}' - \mathbf{r}|) / \rho, \quad (3.8)$$

with

$$\bar{\omega}(r) = \int_0^N dt \omega(r, t) \quad (3.9)$$

and

$$c_0 = - \left[ (2\pi)^{-3} \int d\mathbf{k} S(k) \hat{\omega}(k) \right]^{-1}, \quad (3.10)$$

where

$$\begin{aligned} \hat{\omega}(k) &= \int_0^N dt \hat{\omega}(k, t) \\ &= \int d\mathbf{r} \bar{\omega}(r) e^{-i\mathbf{k} \cdot \mathbf{r}}. \end{aligned} \quad (3.11)$$

To arrive at (3.8) from (3.7) with  $\chi_{\text{in}} = \langle \chi_{\text{in}} \rangle$ , it is useful to note that  $\omega(r, t) = \langle \delta[\mathbf{r} - \mathbf{r}(t) + \mathbf{r}(0)] \rangle = \langle \delta[\mathbf{r} - \mathbf{r}(t)] \rangle_0$ .

Equation (3.8) is the polymer reference interaction site model (RISM) equation for an excluding chain in the thread limit,  $d \rightarrow 0^+$  [7–9]. (The parameter  $d$  is the radius of the excluded sphere surrounding the center of a polymer segment. For  $d$  finite, these centers can be spaced at discrete intervals. In the thread limit, they form a continuum.) The analytical solution in the thread limit, Eq. (3.10), was derived by Schweizer and Curro [10(b)]. For the polymer melt, Eq. (3.10) is a self-consistent relationship for  $c_0$ . This is true since  $\rho(\mathbf{r})$  refers to the density of polymer segments in the fluid. As such,

is the Fourier transform of the pair distribution function of the chain,  $\omega(r, t - t')$ .

One may verify that  $\langle \rho(\mathbf{r}) \rangle_{[\mathbf{r}(t)]}$  given by Eq. (3.3) is indeed zero on the manifold. This is done by setting  $\mathbf{r}$  equal to some point on the path, say  $\mathbf{r}(t)$ . In that case, on the right hand side, the first and third terms cancel, and the second and fourth terms cancel.

#### A. Pair correlations with exclusion forces only

The pair distribution function between the chain and the fluid is obtained by averaging Eq. (3.3) over configurations of the chain keeping one segment of the chain, say  $\mathbf{r}(0)$ , fixed at the origin. For the situation in which  $u(r) = 0$  (i.e., exclusion interactions only), this averaging gives

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$$\chi(|\mathbf{r} - \mathbf{r}'|) = \rho \bar{\omega}(r) + \rho^2 [g(|\mathbf{r} - \mathbf{r}'|) - 1]. \quad (3.12)$$

Equations (3.12) and (3.8) give

$$\rho^{-1} \hat{\chi}(k) = S(k) = \hat{\omega}(k) / [1 - \rho c_0 \hat{\omega}(k)], \quad (3.13)$$

which is the RISM equation with direct correlation function

$$c(r) = c_0 \delta(\mathbf{r}). \quad (3.14)$$

Substitution of Eq. (3.13) into (3.10) yields Schweizer and Curro's self-consistent equation for the athermal polymer melt in the thread limit.

The solution of the Schweizer-Curro self-consistent equation gives  $-c_0$  as a positive quantity which, except for very low concentrations, is independent of chain length  $N$ . As such, while the range of  $\bar{\omega}(r)$  is  $R \sim N^{1/2}$ , one may show that Eq. (3.13) predicts the correlation length of  $\chi(r)$  to be independent of  $N$ . This analysis of the standard result for the correlation length of net density fluctuations (it is independent of  $N$ ) [2(b)] bears a close resemblance to that of the RPA. Indeed, Eq. (3.13) is the RPA for the effects of the repulsive potential  $-k_B T c_0 \delta(\mathbf{r})$ . One distinction of the current theory is that  $c_0$  is not simply a parameter; it is determined self-consistently by the conditions of geometry. More important distinctions will be discussed shortly, after we analyze the role of a potential tail,  $u(r)$ , in the model.

Before turning attention in that direction, note that this derivation of the RISM equation highlights the two essential and not unrelated ingredients in that theory of polymers: (1) a Gaussian or linear response model of solvation, and (2) the replacement of the instantaneous polymer configuration with its averaged pair distributions. These ingredients have been discussed before [7,9], but not perhaps as explicitly as we see them here. Both are justified provided fluctuations are not large. For in-

stance, the preaveraging approximation,  $\chi_{\text{in}} \approx \langle \chi_{\text{in}} \rangle$  in Eq. (3.7), breaks down when the polymer chain fluctuates between two distinct structures. This lack of monostability occurs, for example, in the vicinity of an intrachain transition between collapsed and swollen states. Similarly, the Gaussian approximation is not appropriate for a system undergoing clustering or bulk phase transitions. These effects will not be present in a melt with only excluded volume interactions. Rather, they will occur as a result of competition between, say, excluded volume interactions and a perturbation,  $u(r)$ .

### B. Exclusion forces plus perturbation tails

We consider now the case in which  $u(r)$  is not zero, assuming it is integrable and short ranged. As with

Eq. (3.7), we begin by averaging Eq. (3.3) to obtain an integral equation for  $\rho g(r)$ . The result looks much like (3.7), but with additional terms on the right-hand side involving the attractive tail. These terms are

$$\int d\mathbf{r}' \chi(|\mathbf{r} - \mathbf{r}'|) [t_1(r') + t_2(r')], \quad (3.15a)$$

where

$$t_1(r) = \int_0^N dt \langle u(|\mathbf{r} - \mathbf{r}(t)|) \rangle_0, \quad (3.15b)$$

and

$$t_2(r) = - \int_0^N dt \int_0^N dt' \int_0^N dt'' \int d\mathbf{r}' \langle u(|\mathbf{r}' - \mathbf{r}(t'')|) \chi(|\mathbf{r}' - \mathbf{r}(t)|) \chi_{\text{in}}^{-1}(t, t') \delta[\mathbf{r}(t') - \mathbf{r}] \rangle_0. \quad (3.15c)$$

The first can be expressed as

$$\begin{aligned} t_1(r) &= \int_0^N dt \int d\mathbf{r}' u(|\mathbf{r} - \mathbf{r}'|) \langle \delta[\mathbf{r}' - \mathbf{r}(t)] \rangle_0 \\ &= \int d\mathbf{r}' u(r') \bar{\omega}(|\mathbf{r} - \mathbf{r}'|). \end{aligned} \quad (3.16)$$

Similarly, the second term can be expressed as

$$t_2(r) = -(2\pi)^{-3} \int d\mathbf{k} \hat{u}(k) \hat{\chi}(k) \left\{ \int_0^N dt \int_0^N dt' \int_0^N dt'' \langle \exp\{i\mathbf{k} \cdot [\mathbf{r}(t) - \mathbf{r}(t'')]\} \chi_{\text{in}}^{-1}(t, t') \delta[\mathbf{r}(t') - \mathbf{r}] \rangle_0 \right\}. \quad (3.17)$$

Notice that if  $\mathbf{r}$  lies on any point of the manifold, say  $\mathbf{r}(t_0)$ , then the right side of (3.7) is zero, and similarly

$$\int d\mathbf{r}' \chi(|\mathbf{r}(t_0) - \mathbf{r}'|) [t_1(r') + t_2(r')] = 0. \quad (3.18)$$

This cancellation is the excluded volume condition enforced by the Li-Kardar technique. It persists in the right-hand side of (3.7) even when  $\chi_{\text{in}}^{-1}$  is replaced by  $\langle \chi_{\text{in}} \rangle^{-1}$ . In contrast, with this replacement alone made in Eq. (3.17), Eq. (3.18) no longer holds in general. If, however, one additionally assumes that the Fourier densities of the chain,  $\hat{\rho}(\mathbf{k}, t) = \exp[i\mathbf{k} \cdot \mathbf{r}(t)]$ , are Gaussian variables, the intrachain average in Eq. (3.17) can be performed in the thermodynamic limit yielding

$$t_2(r) \approx -\bar{\omega}(r) \int d\mathbf{k}' \hat{\omega}(k') \hat{u}(k') \hat{\chi}(k') / \int d\mathbf{k}'' \hat{\omega}(k'') \hat{\chi}(k''). \quad (3.19)$$

This approximation satisfies Eq. (3.18).

By adding (3.15a) to the right hand side of (3.7) with (3.16),  $\chi_{\text{in}}^{-1} \approx \langle \chi_{\text{in}} \rangle^{-1}$  and (3.19), one therefore obtains

$$\begin{aligned} \hat{h}(k) &= \frac{\hat{\omega}(k) \hat{c}(k) \hat{\chi}(k)}{\rho} \\ &= \frac{\hat{\omega}^2(k) \hat{c}(k)}{[1 - \rho \hat{\omega}(k) \hat{c}(k)]}, \end{aligned} \quad (3.20)$$

where  $\hat{h}(k)$  is the Fourier transform of  $g(r) - 1$ ,

$$\hat{c}(k) = c_0 + \hat{u}(k) + c_0 \int \frac{[d\mathbf{k}' / (2\pi)^3] \hat{u}(k') \hat{\omega}(k') \hat{\chi}(k')}{\rho}, \quad (3.21)$$

and  $c_0$  is the constant given by Eq. (3.10). Equations (3.20) and (3.21) are the RISM equation with the MSA-like closure,

$$c(r) = c \delta(\mathbf{r}) + u(r), \quad (3.22)$$

where  $c$  is the constant determined such that  $h(r) = -1$  at  $r = 0$ .

The steps leading to this result can be generalized to a two-component system yielding the RISM-MSA equations for a polymer bend. That is,

$$\rho \hat{\mathbf{h}}(k) \rho = \rho \hat{\omega}(k) \hat{\mathbf{c}}(k) \chi(k), \quad (3.23)$$

$$\hat{c}_{ij}(k) = c_{ij} \delta(\mathbf{r}) + u_{ij}(r). \quad (3.24)$$

Here,  $\rho$  and  $\hat{\omega}(k)$  are diagonal matrices with eigenvalues  $\rho_i$  and  $\hat{\omega}_i(k)$  giving the density and intrachain structure, respectively, for species  $i$  ( $= A$  or  $B$ );  $\hat{\chi}(k)$  has elements  $\rho_i \hat{\omega}_i(k) \delta_{ij} + \rho_i \rho_j \hat{h}_{ij}(k)$ ; and the constants  $c_{ij} = c_{ji}$  have values such that  $h_{ij}(r) + 1 \equiv g(r) = 0$  at  $r = 0$ . The solutions correspond to multicomponent generalizations of the algebraic relation (3.21).

### C. Stability and demixing

Schweizer and Curro [10(b)] have studied solutions of these equations analytically. Their analysis shows that the model has a low-temperature limit of stability,  $T_s(\rho_A, \rho_B)$ . Elements of  $\hat{\chi}(0)$  diverge as  $T \rightarrow T_s$  from above, and below that temperature,  $\hat{\chi}(k)$  ceases to be positive definite. For all  $T > T_s$ ,  $\hat{\chi}(k)$  remains finite and positive definite. For large  $N$ , Schweizer and Curro show that  $T_s \sim N^{1/2}$ . We will show shortly that such temperatures are well below the temperatures at which the homogeneous blend is thermodynamically stable. As such, the Gaussian model remains robust throughout the physically accessible homogeneous fluid states. However, if one were to apply the often used assumption, as Schweizer and Curro did, that the breakdown in stability is associated with a demixing transition, then one would predict a critical temperature for the transition,  $T_c$ , which would scale as  $T_c \sim N^{1/2}$ . This prediction is at odds with Flory's  $T_c \sim N$  [12]. Recent experiments [17] and simulations [18] indicate that Flory's scaling prediction is correct. (The precise value of  $T_c$  in Flory's estimate is, however, somewhat high [18] for reasons that will soon be discussed.)

On the basis of perturbation theory [14], one may argue that indeed,  $T_c \sim N$ . For simplicity, we confine the argument here to the idealized case of a perfectly symmetric athermal blend of  $A$  and  $B$  chains made asymmetric through a perturbation  $u_{AB}(r) = -\beta v_{AB}(r)$ . The Helmholtz free energy per unit volume (in units of  $k_B T$ ) is [19]

$$f = f_0 + \rho x(1-x)\beta\bar{v}, \quad (3.25)$$

where

$$\beta\bar{v} = \beta\rho \int d\mathbf{r} g^{(0)}(r) v_{AB}(r) + \beta\rho \int_0^1 d\lambda \int d\mathbf{r} \Delta g_{AB}^{(\lambda)}(r) v_{AB}(r). \quad (3.26)$$

Here,  $x$  is the mole fraction of, say,  $A$  chains, and  $\rho$  is the total monomer density. For the perfectly symmetric reference system,  $f$  is  $f_0$ , and the radial distribution functions,  $g_{ij}(r)$ , are all the same,  $g^{(0)}(r)$ . The changes in the radial distribution functions due to  $v_{AB}(r)$  are  $\Delta g_{ij}^{(\lambda)}(r) = g_{ij}[r; \lambda v_{AB}(r)] - g^{(0)}(r)$  at  $\lambda = 1$ .

From stoichiometric considerations, one may show that [19]

$$f_0 = \frac{1}{N} \rho [x \ln x + (1-x) \ln(1-x)] + \Delta f_0, \quad (3.27)$$

where  $\Delta f_0$  is a function of  $N$  and  $\rho$ , but for the perfectly symmetric athermal reference, it is independent of  $\beta$  and  $x$ . Similarly,  $g^{(0)}(r)$  is a function of  $\rho$  and independent of  $\beta$  and  $x$ . In that case,  $\beta\bar{v}$  is a generalization of Flory's  $\chi$  parameter that accounts for short-ranged pair correlations. The first term in (3.26) is the mean-field estimate of  $\beta\bar{v}$ , with the mean computed with the reference-system metric. The second integral accounts for fluctuations about that mean.

For large  $N$ , it is straightforward to use Eqs. (3.25)–(3.27) to analyze the phase equilibria at fixed  $\rho$ . There is a demixing critical point at  $x = \frac{1}{2}$ . In the evaluation of its temperature, one finds that the mean-field or high-temperature approximation to  $\beta\bar{v}$  dominates, giving

$$k_B T_c = 2N\rho \int d\mathbf{r} g^{(0)}(r) v_{AB}(r). \quad (3.28)$$

This formula ignores contributions to  $T_c$  of the order of  $N^0$ . It seems to be the exact result for this system resting only on the assumption that  $\Delta g_{AB}^{(\lambda)}(r)$  vanishes as  $\beta \rightarrow \infty$ , and near the critical point, it is therefore proportional to a nonzero negative power of  $N$ . The RISM-MSA theory obeys this reasonable assumption. Hence its implied free energy is in accord with Eq. (3.28).

A fully consistent theory of the polymer-blend structure would yield a concentration pair-correlation function with a divergent correlation length at the critical point given by (3.28). This consistency is not satisfied by the Gaussian field model whose pair correlations we estimate with the RISM-MSA equations. It predicts finite  $\hat{\chi}(0)$  under all homogeneous fluid conditions. The same is true for any form of mean-field theory.

The RPA [2(b)] is frequently employed to interpret experiments [20]. It corresponds to Eqs. (2.3) and (3.24) with  $c_{ij} = c_0$ , and it might not seem to suffer from the above mentioned inconsistency. That theory, however, is far less tenable. Through the compressibility theorem, the RPA yields a spinodal, and a mean-field prediction of phase coexistence in agreement with Flory. In this sense, the RPA predicts an infinite correlation length at a critical point. But it contains no aspects of repulsive-force screening. As such, its estimate of the  $\chi$  parameter and  $T_c$  is too large, as if  $g^{(0)}(r)$  were replaced by unity in Eq. (3.28). [Due to the correlation hole [2,10],  $g^{(0)}(r) \leq 1$ , approaching 1 only at large  $r$ .] Worse, however, is that with an integrable  $v_{AB}(r)$  where  $\hat{v}_{AB}(0) > 0$ , one may show that the RPA predicts  $\Delta g_{AB}^{(\lambda)}(r) \rightarrow -\infty$  as  $r \rightarrow 0+$ . The thermodynamic consequences of this violation of the excluded volume conditions are severe. They were detailed long ago in the context of a related model [21]. The free energy obtained from (3.25) and (3.26) with RPA formula for  $\Delta g_{AB}^{(\lambda)}(r)$  possesses catastrophic pathologies along the entire supposed spinodal which cannot be bridged by a Maxwell construction.

The RPA evidently predicts overly large fluctuation ef-

fects from potentials that perturb packing forces. The errors of this theory could be examined experimentally with measurements of polymer blend structures performed at high pressures so as to control densities and thereby separate the different roles of packing and temperature. At fixed densities, the RPA predicts large temperature dependence due to its prediction that  $u(r)$  strongly influences fluid structure. In contrast, the Gaussian field model with excluded volume predicts small effects due to perturbation potentials. The prediction is physically reasonable since small forces cannot generally compete with packing at high fluid densities [22]. In the context of the model, packing effects are the only source of nonlinearities. Structural features found in nature that must be attributable to potential tails fall outside the realm of the Gaussian field model. For example, even at high temperatures well above  $T_c$ , one expects clustering of chains consistent with the effective  $\chi$  parameter,  $\beta\bar{v}$ . Schweizer and Yethiraj [11(b)] have noted that even in this case of weak clustering, the RISM-MSA theory underestimates its consequences on  $\hat{\chi}(0)$  by a factor of  $N^{1/2}$ . It may be possible to treat these structural effects perturbatively with the Gaussian field model serving as a reference. This strategy has proved fruitful in the study of simple liquids [13]. Schweizer and Yethiraj's closures [11] of the RISM equation could be viewed as forms of such perturbation theories.

#### IV. DISCUSSION

The two classes of systems treated in Secs. II and III provide physically relevant examples where predictions of the Gaussian field model can be worked through analytically. More generally, asymptotic regimes for complicated systems can be so analyzed perturbatively [4]. Otherwise, some degree of numerical work is required in the form of basis-function expansions to evaluate integrals involving  $\chi_{\text{in}}^{-1}$ . Even so, one may write down a compact expression for the response function of the model fluid as influenced by an arbitrary excluding manifold. It can be computed by twice differentiating Eq. (2.7). In the general case, the interior region, "in," need not be spherical nor a thread. The result is

$$\begin{aligned} \delta\langle\rho(\mathbf{r})\rangle/\delta\phi(\mathbf{r}') &= \chi(|\mathbf{r}-\mathbf{r}'|) \\ &- \int_{\text{in}} d\mathbf{r}'' \int_{\text{in}} d\mathbf{r}''' \chi(|\mathbf{r}-\mathbf{r}''|) \\ &\quad \times \chi_{\text{in}}^{-1}(\mathbf{r}'', \mathbf{r}''') \chi(|\mathbf{r}'''-\mathbf{r}'|). \end{aligned} \quad (4.1)$$

Note that  $u(r)$  plays no role in this expression. This formula holds for the Gaussian model irrespective of whether  $\chi(|\mathbf{r}-\mathbf{r}'|)$  is determined self-consistently. The excluding manifold could define the boundaries of a confined fluid. It would be of interest to see what structural aspects of confined fluids could be understood with this formula [23].

It would also be of interest to extend our development to  $D = 2$  manifolds — models of lamellar phases [24]. Here, and in the  $D = 1$  case too, the self-consistent analysis of the manifold structure should be carried out. This, for example, would include the computation of the intrachain distribution function,  $\omega(|\mathbf{r}-\mathbf{r}'|; t-t')$ , with the same model that provides a theory for the interchain pair-correlation function,  $g(r)$ . The starting point for such a computation is clear enough. In particular, the partition function as a functional of  $\mathbf{r}(t)$  provides the solvation contribution to the potential of mean force governing the intrachain statistics. In the Gaussian model with  $u = 0$ , this partition function, or influence functional [25], is proportional to

$$(\det \chi_{\text{in}})^{-1} \exp\left(-\frac{1}{2}\rho^2 \sum_{t,t'} \chi_{\text{in}}^{-1}(t,t')\right). \quad (4.2)$$

(This expression generalizes slightly Li and Kardar's [4].) It might be profitable to examine the relationship between this influence functional and that introduced by Chandler and co-workers [7] in the RISM theory of polymers.

In addition to noting its difficulty in treating divergent correlation lengths self-consistently, one should bear in mind the limitations of the Gaussian model at small length scales. It does not describe well the particulate nature of matter. This deficiency is manifested, for example, in the unphysical divergence of (4.2) in the low-density limit. Pressed to small enough length scales, the Gaussian model will also permit negative densities, and it will not sustain interfaces. It is thus not too surprising that under extreme conditions, the PY and MSA  $g(r)$ 's can be negative. Evidently, this field-theoretic model must be used with care, not unlike that required when applying the analogous Langevin equation to dynamics of the liquid state. Specifically, these linear models seem best used to mimic the effects of a bath while the objects of primary consideration are considered explicitly. It is remarkable that generally sensible results are obtained even at very small length scales when the bath so modeled is treated self-consistently.

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