

A composition density functional theory for mixtures based upon an infinitely polydisperse reference. I. Formalism and theory

David A. Kofke^{a)} and Eduardo D. Glandt

Department of Chemical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6393

(Received 19 September 1988; accepted 25 September 1989)

A general, statistical mechanical theory which relates the properties of mixtures of different compositions is presented. It is developed within a semigrand canonical framework, and thus the mixtures are formally described by species chemical potential differences, rather than directly by composition. The introduction of a set of n -particle composition distribution functions leads to a composition-space superposition approximation (CSSA), which forms the only approximate part of the treatment. A functional expansion of the canonical partition function in terms of the composition density is used to develop systematic corrections to the CSSA. Infinitely polydisperse mixtures [D. A. Kofke and E. D. Glandt, *J. Chem. Phys.* **90**, 439 (1989)] are shown to be the composition-space analogs of homogeneous pure fluids, and the scaling properties of these mixtures make them ideal as a reference in the theory. The required input is the density-invariant composition of the infinitely polydisperse reference. The validity of the method is demonstrated on hard-particle fluids using accurate equations of state from the literature. Although based on a polydisperse reference, the treatment is equally applicable to discrete, i.e., conventional mixtures. In its most stringent test—the prediction of *pure-fluid* properties—the theory based on an infinitely polydisperse reference displays quantitative agreement with known behavior.

I. INTRODUCTION

In recent years, a literature has developed based upon the application of the density functional theory of classical statistical mechanics¹ to the study of inhomogeneous phases, and in particular to the first order freezing transitions in single- and multicomponent systems.² An important component of these approaches is the application of a functional perturbation theory to express the structure of the *inhomogeneous* crystal in terms of the known structure of the *homogeneous* fluid. When viewed from the proper perspective, there exists an analogy between an inhomogeneous pure fluid and a homogeneous multicomponent mixture which suggests that the density functional theory may be applied to the study of the latter. Specifically, if the molecules of a mixture are (conceptually) permitted to explore identities while under the influence of an applied chemical potential “field,” then composition may be viewed as another dimension, with its own set of correlation functions. Thus, density-functional concepts may be used to relate the properties of mixtures of different compositions, having different “structures” on the composition axis. Of course, unlike the studies of freezing, it is not possible to construct a reference mixture which has an absolutely homogeneous composition; there must always be upper bound to any species-identity coordinate. Indeed, the most natural reference—the pure fluid—is extremely inhomogeneous in composition. However, it is possible to construct a mixture which has a homogeneous *chemical potential* distribution over the entire (infinite) range of species identities. To be fully homogeneous, such a mixture must also be polydisperse, containing a continuum of species.³ In

earlier work,^{4,5} we demonstrated that such “infinitely polydisperse” mixtures have very convenient scaling properties, a feature which may make them especially well suited to serve as a reference in a theory for mixtures.

In fact, there exists an entire family of infinitely polydisperse mixtures which are suitable for use as reference substances. These fluids are characterized by a chemical potential distributions which are logarithmic. For example, the distribution of chemical potentials $\mu(\sigma)$ in a mixture of infinitely polydisperse hard spheres is

$$\beta\mu(\sigma) = \beta\mu(\sigma_0) + c_0 \ln \frac{\sigma}{\sigma_0}, \quad (1)$$

where c_0 is an imposed dimensionless parameter which characterizes the distribution, σ is the hard sphere diameter and σ_0 is the diameter of an arbitrary reference component; $\beta = 1/k_B T$, with k_B Boltzmann's constant and T the temperature. This form introduces no characteristic length scales; as a consequence, a simple—and sometimes analytic—representation of many properties can be obtained. Dimensioned quantities such as the pressure and the composition can only be reduced by the density, which provides the single independent characteristic length scale. When expressed in a reduced form, these properties become independent of the density. In particular, we have shown^{4,5} that, for a polydisperse hard-sphere mixture characterized by the chemical potential distribution of Eq. (1), the equation of state can be determined exactly, and is given by

$$Z \equiv \frac{\beta P}{\rho} = \frac{4 + c_0}{3}, \quad (2)$$

where P is the pressure and ρ is the number density. In the homogeneous case $c_0 = 0$, the compressibility factor $\beta P/\rho$ is $4/3$ at all densities.

^{a)} Present address: Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, NY 14260.

In an infinitely polydisperse system (i.e., infinitely polydisperse in all characteristic molecular length scales), the density dependence is trivial. Instead, the significant quantity is c_0 , which has the same qualitative effect that the density has in a pure fluid. The limit $c_0 \rightarrow -1$, in which Z approaches unity, corresponds to the low-density limit of the pure fluid. As c_0 is increased, the system becomes more "dense" in the sense that more of the volume is occupied. The composition of an infinitely polydisperse mixture is not an independent quantity, nor is it as simple to evaluate as the pressure. However, like the pressure, it too can be scaled by the density to yield an invariant distribution. Because of its scaling properties, this distribution is easily determined at any arbitrary density given its form for one density. For hard spheres, some examples of these invariant distributions are shown in Fig. 1. It is this trivial dependence of most properties on the density that makes infinitely polydisperse mixtures such an appealing reference substance.

In this work, we shall borrow only a few of the concepts of density functional theory as it is now used. The grand-canonical ensemble is most convenient for the study of phase transitions, and thus modern density functional theory is formulated in this representation. We are instead concerned with developing a theory for the description of the general properties of mixtures, with no particular emphasis on phase equilibria. A hybrid of the canonical and grand-canonical ensembles provides the best framework for this development. This formalism is reviewed in Sec. II. A set of n -particle composition functions is defined in Sec. III, and a superposition approximation relating these functions is also introduced. The conditions for validity of this approximation are discussed and systematic corrections to it are provided. In Secs. IV and V the mixture theory is developed in a general form, suitable for any reference fluid. The infinitely polydisperse reference is then introduced in Sec. VI. In Sec. VII the validity of the theory is demonstrated with simple hard-core fluids, for which accurate equations of state are

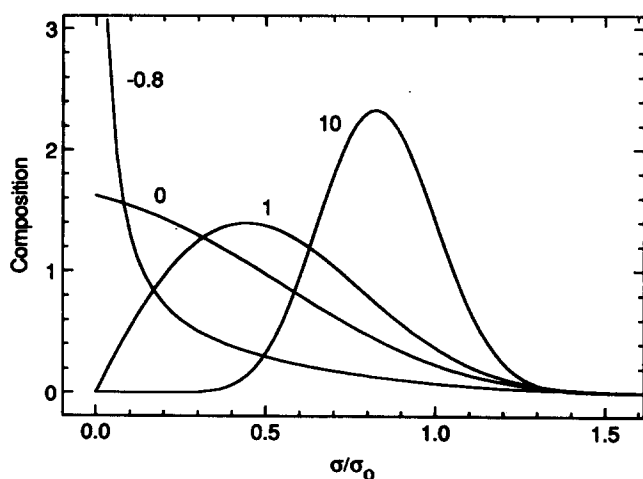


FIG. 1. Typical invariant composition distributions of infinitely polydisperse hard spheres. The chemical potential distributions for these mixtures are of the form $\beta\mu(\sigma) = \beta\mu(\sigma_0) + c_0 \ln(\sigma/\sigma_0)$, where c_0 is indicated for each curve.

known. Although the focus here is on mixtures with potentials characterized by a single length scale, the generalization follows directly from concepts presented here and in Ref. 4.

II. SEMIGRAND ENSEMBLE

The semigrand canonical free energy Y is defined^{5,6} as a Legendre transform of the canonical Helmholtz free energy A . In the polydisperse limit

$$\begin{aligned} \beta Y &\equiv \beta A - N \int_{\Omega} p(\mathbf{I}) [\beta\mu(\mathbf{I}) - \beta\mu(\mathbf{I}_0)] d\mathbf{I} \\ &= -\beta P V + N\beta\mu(\mathbf{I}_0), \end{aligned} \quad (3)$$

where V is the volume and N is the total number of molecules. The functions $p(\mathbf{I})$ and $\mu(\mathbf{I})$ are the composition and chemical potential distributions, respectively. The quantity \mathbf{I} represents a set of ω species-designating parameters, and is defined over the ω -dimensional domain Ω ; \mathbf{I}_0 is the label of an arbitrarily chosen reference species.

The fundamental differential equation in this ensemble is

$$\begin{aligned} d(\beta Y) &= U d\beta - \beta P dV + \beta\mu(\mathbf{I}_0) dN \\ &\quad - N \int_{\Omega} p(\mathbf{I}) \delta[(\beta\Delta\mu(\mathbf{I}))] d\mathbf{I}, \end{aligned} \quad (4)$$

where U is the internal energy and $\Delta\mu \equiv \mu(\mathbf{I}) - \mu(\mathbf{I}_0)$. Also, the partition function is^{5,6}

$$\Upsilon = \frac{1}{N!} \int_{(\mathbf{I}_0)} d\mathbf{I}^{(N)} \left\{ \prod_{i=1}^N q(\mathbf{I}_i) \exp[\beta\Delta\mu(\mathbf{I}_i)] \right\} Z_N, \quad (5)$$

where $q(\mathbf{I}) = q^{\text{int}}(\mathbf{I})/\Lambda^3(\mathbf{I})$; $q^{\text{int}}(\mathbf{I})$ is the internal partition function for a molecule of species \mathbf{I} , while $\Lambda(\mathbf{I}) = h/(2\pi m(\mathbf{I})k_B T)^{1/2}$ is the thermal de Broglie wavelength, with h Planck's constant and $m(\mathbf{I})$ the mass of \mathbf{I} . The notation (N) is used to represent an integral for each of the N molecules. Thus $\int_{(\mathbf{I}_0)} d\mathbf{I}^{(N)} \equiv \int d\mathbf{I}_1 \int d\mathbf{I}_2 \cdots \int d\mathbf{I}_N$. The configurational integral Z_N is

$$Z_N = \int_{(\mathbf{I}_0)}^V d\mathbf{r}^{(N)} \exp[-\beta U(\mathbf{r}^{(N)}, \mathbf{I}^{(N)})], \quad (6)$$

where \mathbf{r} is the vector of particle coordinates and orientations. For this ensemble, the bridge equation is

$$\beta Y = -\ln \Upsilon. \quad (7)$$

It is convenient to separate from the chemical potential those contributions due to translational and internal degrees of freedom. Accordingly, the *configurational* chemical potential μ_c is defined

$$\beta\mu_c(\mathbf{I}) \equiv \beta\mu(\mathbf{I}) + \ln q(\mathbf{I}). \quad (8)$$

The configurational chemical potential may be further separated into an ideal gas part and a residual μ_r ,

$$\beta\mu_c(\mathbf{I}) = \ln \rho p(\mathbf{I}) + \beta\mu_r(\mathbf{I}). \quad (9)$$

When the configurational distribution is used in place of $\mu(\mathbf{I})$, Eq. (5) becomes

$$\Upsilon = \frac{1}{N!} [q(\mathbf{I}_0)]^N \int_{(N)} d\mathbf{I}^{(N)} \left\{ \prod_{i=1}^N \exp[\beta \Delta \mu_c(\mathbf{I}_i)] \right\} Z_N, \quad (10)$$

where $\Delta \mu_c = \mu_c(\mathbf{I}) - \mu_c(\mathbf{I}_0)$.

III. COMPOSITION DISTRIBUTION FUNCTIONS

In analogy with the formalism developed to characterize spatial distributions,⁷ it is useful to define a set of correlation functions on the domain of composition space

$$p^{(n)}(\mathbf{I}_1, \mathbf{I}_2, \dots, \mathbf{I}_n) \equiv \frac{1}{\Upsilon} \frac{[q(\mathbf{I}_0)]^N}{N!} \int_{(N-n)} d\mathbf{I}^{(N-n)} \times Z_N \prod_{i=1}^N \exp[\beta \Delta \mu_c(\mathbf{I}_i)]. \quad (11)$$

The specific n -particle composition distribution function given here is equal to the probability density that molecule 1 has identity \mathbf{I}_1 , molecule 2 has identity \mathbf{I}_2 , etc. It is non-negative and normalized to unity. Generic distribution functions may be defined

$$P^{(n)}(\mathbf{I}_1, \mathbf{I}_2, \dots, \mathbf{I}_n) \equiv \frac{N!}{(N-n)! \prod n_i!} \times p^{(n)}(\mathbf{I}_1, \mathbf{I}_2, \dots, \mathbf{I}_n), \quad (12)$$

where n_i is the number of times species \mathbf{I} appears in the list $(\mathbf{I}_1, \dots, \mathbf{I}_n)$, with the product taken over all species in the list. The generic n -particle composition distribution function measures the probability density that *any* molecule has identity \mathbf{I}_1 , *any other* has identity \mathbf{I}_2 , etc. It is readily shown that these functions can be expressed as functional derivatives of the semigrand partition function

$$P^{(n)}(\mathbf{I}_1, \mathbf{I}_2, \dots, \mathbf{I}_n) = \frac{1}{\prod n_i!} \frac{1}{\Upsilon} \left(\frac{\delta^n \Upsilon}{\prod_{i=1}^n \delta[\exp(-\beta \Delta \mu_c(\mathbf{I}_i))]} \right)_{T, V, N} \times \prod_{i=1}^n [\exp(-\beta \Delta \mu_c(\mathbf{I}_i))]. \quad (13)$$

In particular

$$P^{(1)}(\mathbf{I}_1) \equiv N p^{(1)}(\mathbf{I}_1) = \left(\frac{\delta \ln \Upsilon}{\delta[\beta \Delta \mu_c(\mathbf{I}_1)]} \right)_{T, V, N}. \quad (14)$$

Comparison of Eq. (14) with Eqs. (4) and (7) reveals that the specific 1-particle composition distribution function $p^{(1)}(\mathbf{I})$ is indeed equivalent to the mixture composition $p(\mathbf{I})$.^{8,9}

Despite the obvious similarity between the composition and spatial distribution functions, there is an important distinction between them which must be emphasized. In configuration space, it is the *distance* between two molecules which determines their interaction energy. One manifestation of this fact is steric exclusion, which causes multiparticle spatial correlation functions [e.g., $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$] to vanish at small separations. As a result, superposition approximations [e.g., $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \approx \rho^{(1)}(\mathbf{r}_1) \rho^{(1)}(\mathbf{r}_2)$] must break down in the most important case in which the molecules are near one another. In contrast, the difference in *identities* of two molecules—their “separation” in composition space—has no di-

rect bearing on their intermolecular energy. Thus, there is no inherent reason why two molecules in a semigrand ensemble cannot have similar or even the same identities. It should therefore be quite reasonable to make the general composition-space superposition approximation (CSSA)

$$p^{(n)}(\mathbf{I}_1, \mathbf{I}_2, \dots, \mathbf{I}_n) \approx \prod_{i=1}^n p^{(1)}(\mathbf{I}_i). \quad (15)$$

This equation implies that the identities adopted by the n molecules are independent. There are two situations in which this is so. Obviously, it is true for an ideal gas, and thus the relation is generally valid at high temperature or at low density. The second, more interesting case occurs when the overall composition of the “constrained” system is not too different from the thermodynamic average $p^{(1)}(\mathbf{I})$. Indeed, the function $p^{(n)}$ constrains the identities of n particles, while the identities of the other $N-n$ are allowed to fluctuate. This constrained system has an overall composition which is determined by both the constrained and fluctuating particles. For $n \ll N$, the n “frozen” molecules will have a negligible effect on the overall composition, and the approximation will be valid. However, for $n = O(N)$, the identities $\mathbf{I}_1, \dots, \mathbf{I}_n$ are significant, and the approximation may not always hold.¹⁰ A formal development is provided in the Appendix which quantifies these statements and prescribes corrections to the CSSA. The principal result from the Appendix is, for $n = N$

$$p^{(N)}(\mathbf{I}_1, \dots, \mathbf{I}_N) = \left[\prod_{i=1}^N p^{(1)}(\mathbf{I}_i) \right] \mathcal{P}[p^{(1)}] \times \exp[N \mathcal{R}(\mathbf{I}^{(N)}; p^{(1)})]. \quad (16)$$

$\mathcal{P}[p(\mathbf{I})]$ is a probability density functional which measures the frequency of occurrence the composition $p(\mathbf{I})$ in a semigrand ensemble. Here it is merely a normalization constant, and is evaluated at the most probable (i.e., equilibrium) composition $p^{(1)}$. More important is the quantity \mathcal{R} , which is a functional expansion of the residual chemical potential distribution about the composition $p^{(1)}$. Although it depends on the identities of all $\mathbf{I}^{(N)}$, it may be broken up into a sum of two-body terms, three-body terms, etc.,

$$\mathcal{R}(\mathbf{I}^{(N)}; p^{(1)}) = \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N \mathcal{R}^{(2)}(\mathbf{I}_i, \mathbf{I}_j; p^{(1)}) + \frac{1}{N^3} \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N \mathcal{R}^{(3)}(\mathbf{I}_i, \mathbf{I}_j, \mathbf{I}_k; p^{(1)}) + \dots, \quad (17)$$

where, for example, the two-particle contribution can be written

$$\mathcal{R}^{(2)}(\mathbf{I}_i, \mathbf{I}_j; p^{(1)}) = -\frac{1}{2!} \int \int d\mathbf{I}' d\mathbf{I}'' \frac{\delta \beta \Delta \mu_c(\mathbf{I}')}{\delta p(\mathbf{I}'')} \Big|_{p=p^{(1)}} \times [\delta(\mathbf{I}_i - \mathbf{I}') - p^{(1)}(\mathbf{I}')] [\delta(\mathbf{I}_j - \mathbf{I}'') - p^{(1)}(\mathbf{I}'')], \quad (18)$$

where δ is the Dirac δ function. The functional derivative here is taken at constant temperature and density, and is

evaluated at the equilibrium composition $p^{(1)}$. As the distribution of the $\mathbf{I}^{(N)}$ (which is represented through the δ functions) deviates from $p^{(1)}$, the higher order terms in \mathcal{R} become more significant. In the case where the $\mathbf{I}^{(N)}$ are distributed precisely according to $p^{(1)}$, \mathcal{R} vanishes and Eq. (15) is recovered (note that \mathcal{R} also vanishes in the ideal gas limit, when the residual chemical potential is negligible).

Equations (16)–(18) can be combined to give a result similar to a well-known equation from density functional theory.² In one important step in the development of the theory, the logarithm of the (inhomogeneous) crystal density is evaluated via a functional expansion about the (homogeneous) fluid density. The coefficients of this expansion are the direct correlation functions $c^{(n)}$. Indeed, just as $p^{(n)}(\mathbf{I}^{(n)})$ is analogous to the n -particle correlation function $\rho^{(n)}(\mathbf{r}^{(n)})$, the functional derivative $\delta[\beta\Delta\mu_c(\mathbf{I}_1)]/\delta p(\mathbf{I}_2)$ in Eq. (18) is in fact the composition analog of the configurational direct correlation function $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$.

IV. THEORY

We are now prepared to develop a theory which relates the free energies of two mixtures of different compositions, i.e., systems having different “structures” in composition space. Using Eq. (10) and the bridge equation, the free energy Y for a mixture with configurational chemical potential distribution $\beta\Delta\mu_c(\mathbf{I})$ may be written in terms of that of an arbitrary reference mixture Y_o which is at the same temperature and density, but which differs in the distribution of configurational chemical potential differences (and composition)

$$\beta Y = \beta Y_o - \ln \left\langle \prod_{i=1}^N \exp[\beta\Delta\mu_c(\mathbf{I}_i) - \beta\Delta\mu_{co}(\mathbf{I}_i)] \right\rangle_o. \quad (19)$$

Here, the angle brackets represent a semigrand canonical ensemble average over species identities, weighted by the reference-state configurational chemical potential difference distribution, $\beta\Delta\mu_{co}(\mathbf{I})$. The subscript o is used to designate a property of the fluid in this reference state, and should not be confused with \mathbf{I}_o , the identity of an arbitrary reference component.

Equation (19) is exact. It may alternatively be expressed in terms of the N -particle composition function of the reference mixture, $p_o^{(N)}(\mathbf{I}^{(N)})$

$$\beta Y = \beta Y_o - \ln \left\{ \int_{(\mathbf{I}^{(N)})} d\mathbf{I}^{(N)} p_o^{(N)}(\mathbf{I}^{(N)}) \times \prod_{i=1}^N \exp[\beta\Delta\mu_c(\mathbf{I}_i) - \beta\Delta\mu_{co}(\mathbf{I}_i)] \right\}. \quad (20)$$

This form is suitable for the introduction of the corrected CSSA, Eq. (16)

$$\beta Y = \beta Y_o - \ln \left\{ \int_{(\mathbf{I}^{(N)})} d\mathbf{I}^{(N)} \left[\prod_{i=1}^N p_o(\mathbf{I}_i) \times \exp[\beta\Delta\mu_c(\mathbf{I}_i) - \beta\Delta\mu_{co}(\mathbf{I}_i)] \right] \times \mathcal{P}[p_o] \exp[N\mathcal{R}(\mathbf{I}^{(N)}, p_o)] \right\}, \quad (21)$$

where the reference composition is simply written p_o , rather than $p_o^{(1)}$. For small values of the difference $[\beta\Delta\mu_c(\mathbf{I}) - \beta\Delta\mu_{co}(\mathbf{I})]$, the identities sampled by each molecule are weighted by $p_o(\mathbf{I})$, and thus the only significant contributions to the integral come about when the collective distribution of the \mathbf{I}_i is itself very close to p_o . Then, to a first approximation, \mathcal{R} may be neglected together, yielding a very simple expression for the free energy

$$Y[\beta\Delta\mu] = Y[\beta\Delta\mu_o] - N \ln \int p_o(\mathbf{I}) \times \exp[\beta\Delta\mu_c(\mathbf{I}) - \beta\Delta\mu_{co}(\mathbf{I})] d\mathbf{I}. \quad (22)$$

This equation is the principal result of the theory. It concisely expresses the free energy of a system characterized by a distribution of chemical potentials $\Delta\mu_c(\mathbf{I})$ in terms of that of a reference of known chemical potential distribution $\Delta\mu_{co}(\mathbf{I})$ and known composition $p_o(\mathbf{I})$. The only approximation made in deriving this expression is the CSSA, Eq. (15).

The derivation of the CSSA (presented in the Appendix) is based upon a functional series expansion of $\Delta\mu_c$; this approximation renders the theory a mean-field treatment. If corrections to the CSSA—the terms represented by \mathcal{R} in Eq. (16)—are included in the theory, it is not possible to derive an equation of the simplicity of Eq. (22) without introducing further approximations. For example, introduction of $\mathcal{R}^{(2)}$ results in an N -dimensional integral which cannot be separated—the expression is isomorphic to a partition function for pair-wise interacting molecules; approximate methods for the treatment of such integrals are available.⁷ Despite these complications, the contributions from \mathcal{R} to some of the other thermodynamic properties may be included—without additional approximation—by exploiting the superposition properties of $p^{(n)}$. However, such corrections may often be unnecessary. We will show that Eq. (22) is itself capable of providing very precise estimates of the thermodynamic properties, if the reference is chosen well.

V. THERMODYNAMIC PROPERTIES

Here, we use the theory of the previous section to derive expressions for the pressure, the internal energy, and the chemical potential $\mu(\mathbf{I}_o)$ of an arbitrary mixture. First, functional differentiation of Eq. (22) with respect to the distribution of chemical potential differences yields the composition as⁸

$$p(\mathbf{I}) = -\frac{1}{N} \left(\frac{\delta(\beta Y)}{\delta[\beta\Delta\mu_c(\mathbf{I})]} \right)_{\beta, \rho} = \frac{p_o(\mathbf{I}) \exp[\beta\Delta\mu_c(\mathbf{I}) - \beta\Delta\mu_{co}(\mathbf{I})]}{\int d\mathbf{I}' p_o(\mathbf{I}') \exp[\beta\Delta\mu_c(\mathbf{I}') - \beta\Delta\mu_{co}(\mathbf{I}')]} \quad (23)$$

This expression may then be introduced into the equation of state, which follows from the density derivative, to produce a remarkably simple formulation for the compressibility factor $Z = \beta P/\rho$

$$Z = \frac{\rho}{N} \left(\frac{\partial(\beta Y)}{\partial \rho} \right)_{\beta, N, \beta \Delta \mu} \\ = Z_o - \rho \int d\mathbf{I} p(\mathbf{I}) \frac{\partial}{\partial \rho} [\ln p_o(\mathbf{I})] \quad (24)$$

(the compressibility factor Z should not be confused with the configurational integral Z_N). The perturbation is computed by averaging the density derivative of the reference composition $p_o(\mathbf{I})$, weighted by the composition $p(\mathbf{I})$ of the mixture of interest. This is certainly a convenient form, because the mixture of interest is usually described in terms of its composition, rather than by its chemical potential distribution. A similar expression can be derived for the internal energy

$$\beta U = \beta \left(\frac{\partial(\beta Y)}{\partial \beta} \right)_{V, N, \beta \Delta \mu} \\ = \beta U_o - N\beta \int d\mathbf{I} p(\mathbf{I}) \frac{\partial}{\partial \beta} [\ln p_o(\mathbf{I})]. \quad (25)$$

The correction terms in Eqs. (24) and (25) can actually be expressed in terms of the difference in compositions $\Delta p(\mathbf{I}) \equiv p(\mathbf{I}) - p_o(\mathbf{I})$, because normalization of $p_o(\mathbf{I})$ insures, e.g., that

$$\int p_o(\mathbf{I}) \frac{\partial}{\partial \rho} [\ln p_o(\mathbf{I})] d\mathbf{I} = \int \frac{\partial p_o(\mathbf{I})}{\partial \rho} d\mathbf{I} = 0. \quad (26)$$

The chemical potential of the reference component $\beta\mu(\mathbf{I}_o) = (\partial Y / \partial N)_{\beta, V, \beta \Delta \mu}$ can most easily be obtained from the semigrand free energy $\beta Y / N = \beta\mu(\mathbf{I}_o) - Z$. Thus

$$\beta\mu(\mathbf{I}_o) = \beta\mu_o(\mathbf{I}_o) + (Y - Y_o) / N + (Z - Z_o). \quad (27)$$

By combining Eqs. (22) and (23), the difference in free energies may be expressed in terms of the composition at \mathbf{I}_o , and a compact expression may be written in terms of the residual chemical potential differences $\Delta\mu_r(\mathbf{I})$

$$\beta\mu_r(\mathbf{I}_o) = \beta\mu_{r_o}(\mathbf{I}_o) + (Z - Z_o), \quad (28)$$

where $(Z - Z_o)$ may be obtained from Eq. (24).

If the residual \mathcal{R} is not entirely neglected, some of the expressions may still be formulated in a simple fashion. For example, if \mathcal{R} is truncated after $\mathcal{R}^{(2)}$, then the equation of state may be expressed

$$Z = Z_o - \rho \int p(\mathbf{I}) \frac{\partial}{\partial \rho} \ln p_o(\mathbf{I}) d\mathbf{I} - \frac{\rho}{2} \int \int p(\mathbf{I}') p(\mathbf{I}'') \\ \times \frac{\partial}{\partial \rho} \mathcal{R}_o^{(2)}(\mathbf{I}', \mathbf{I}'') d\mathbf{I}' d\mathbf{I}''. \quad (29)$$

If $p(\mathbf{I})$ is considered independent of density, this equation may be written

$$Z = Z_o - \rho \int p(\mathbf{I}') \frac{\partial}{\partial \rho} \ln p_o(\mathbf{I}') d\mathbf{I}' \\ - \frac{\rho}{2} \frac{\partial}{\partial \rho} \int \int \frac{\delta \beta \Delta \mu_r(\mathbf{I}')}{\delta p(\mathbf{I}'')} \Big|_{p=p_o} \\ \times \Delta p(\mathbf{I}') \Delta p(\mathbf{I}'') d\mathbf{I}' d\mathbf{I}'', \quad (30)$$

where again $\Delta p(\mathbf{I}) \equiv p(\mathbf{I}) - p_o(\mathbf{I})$ is the difference between the composition of the mixture of interest and the composition of the reference. The first-order [in $\Delta p(\mathbf{I})$] correction to Z is not altered when the $\mathcal{R}^{(2)}$ correction is introduced.

Beginning with Eq. (21) for the free energy, it may be shown that this term is in fact unchanged regardless of the order of $\mathcal{R}^{(n)}$ included in the expansion. In other words, the first-order expansion for Z in terms of $\Delta p(\mathbf{I})$ given by Eq. (24) is correct to all orders in $\Delta\mu_c(\mathbf{I}) - \Delta\mu_{c_o}(\mathbf{I})$. It is fortuitous that the lowest-order expansion succeeds in producing this result.

VI. INFINITELY POLYDISPERSE REFERENCE

The formalism and theory presented above are general, and make no use of the infinitely polydisperse mixtures reviewed in Sec. I; the choice of the reference is still open. There are two criteria to satisfy in choosing a reference for a theory. First, the reference must in some sense be "simpler" than the fluid of interest; its properties must already be known, or must at least be significantly easier to evaluate. At the same time, the reference must be sufficiently similar to the fluid of interest so as to render a valid approximation. Such a delicate balance is often difficult to achieve, but if attained it can result in a theory of great power. An excellent example is given by the success of perturbation expansions based upon hard-core potentials. As will be shown, the infinitely polydisperse mixtures introduced in Ref. 4 and reviewed in Sec. I provide a well-balanced reference for the theory outlined above. These mixtures are also appealing because, as described in Sec. I, they contribute to an analogy with density functional theory which is useful to consider in developing the proposed theory.

For simplicity of presentation, we will implement the theory for a fluid with a single identifying parameter σ which has units of length. The most general case, when the intermolecular potential contains more than one parameter, can be derived from the discussion here and from the Appendix of Ref. 4.

For the logarithmic distribution of configurational chemical potential differences given in Eq. (1), the equation of state in D dimensions must satisfy^{4,5}

$$D(Z_o - 1) = c_o + 1 \quad (31)$$

(the o subscript reminds us that these are the properties of what will be the reference mixture in the theory above). The configurational chemical potential distribution is

$$\beta\mu_{c_o}(\sigma) = \ln[\rho K_o(c_o)] + (c_o + 1) \ln \sigma^* \quad (32)$$

where $\sigma^* = \sigma \rho^{1/D}$ and where $K_o(c_o)$ is independent of density. Further, because all lengths scale with the density, the composition must be of the form

$$p_o(\sigma; \rho, \beta) \equiv \rho^{1/D} p_o^*(\sigma^*; \beta), \quad (33)$$

where p_o^* is invariant with density. The density derivative required by the theory can be expressed in terms of a derivative of this invariant composition with respect to its distributed parameter σ^*

$$\frac{\partial}{\partial \rho} \ln p_o(\sigma; \rho) = \frac{1}{D\rho} \left[1 + \sigma^* \frac{d}{d\sigma^*} \ln p_o^*(\sigma^*) \right]. \quad (34)$$

The reduced composition distribution of the infinitely polydisperse reference, $p_o^*(\sigma^*)$, is the central input to the calculations. It is assumed that it, along with $K_o(c_o)$ in Eq. (32),

is known for at least one value of c_0 . These quantities may be evaluated, e.g., by computer simulation.

Because of their scaling properties, infinitely polydisperse mixtures meet the simplicity criterion required of a reference. At the same time, the selection of c_0 can be exploited to satisfy the second criterion, to make the reference similar to the fluid of interest. Thus c_0 is chosen to make first-order corrections to the thermodynamic properties vanish. The most suitable choice would eliminate the correction to the free energy Y in Eq. (22). However, the free energy here is expressed in terms of $\beta\Delta\mu_c(\mathbf{I})$, which is not most convenient. Instead, c_0 can be chosen to eliminate the leading correction to the compressibility factor—which is expressed in terms of $p(\mathbf{I})$ —and thus satisfy

$$\int d\sigma p(\sigma) \left\{ 1 + \sigma \frac{d}{d\sigma} \ln \left[\rho^{-1/D} p_o(\rho^{1/D} \sigma; c_0) \right] \right\} = 0. \quad (35)$$

Then, the compressibility factor and the residual chemical potential of *all* species have the same values in the reference fluid as they do in the fluid of interest. Since the expansion was formed for a reference of the same density, equivalence of compressibility factors implies that the pressures must also be the same. Thus, a reference fluid can indeed be chosen that is very much like the fluid of interest. Within the CSSA, they differ only in a constant in their $\Delta\mu$ distributions (or, equivalently, their free energies) and, of course, in their compositions.

VII. APPLICATION TO HARD-PARTICLE FLUIDS

A. Hard rods in one dimension

Mixtures of hard particles in one dimension are convenient systems to study because their thermodynamic properties can be expressed analytically. The equation of state of a hard rod mixture is^{9,11}

$$\frac{\beta P}{\rho} = \frac{1}{1 - \rho s_1}, \quad (36)$$

where s_1 is the first moment, about the origin, of the distribution of rod lengths. The n th such moment is

$$s_n = \int_0^\infty \sigma^n p(\sigma) d\sigma. \quad (37)$$

The chemical potential of a rod of length σ is^{9,11}

$$\beta\mu(\sigma) = -\ln \left[\frac{q^{\text{int}}(\sigma)}{\Lambda(\sigma)} \right] + \ln \rho p(\sigma) - \ln(1 - \rho s_1) + \frac{\rho\sigma}{(1 - \rho s_1)}. \quad (38)$$

If the distribution of configurational chemical potentials obeys Eq. (1), $\beta\mu_c(\sigma) - \beta\mu_c(\sigma_0) = c_0 \ln(\sigma/\sigma_0)$, then the reduced composition is given by a Schultz distribution^{4,5}

$$p_o^*(\sigma^*) = \frac{(c_0 + 2)^{c_0 + 1}}{\Gamma(c_0 + 1)} \sigma^{*c_0} \exp[-(2 + c_0)\sigma^*], \quad (39)$$

where Γ is the gamma function; p^* is defined in Eq. (33), and $\sigma^* \equiv \rho\sigma$. It can also be shown that

$$\rho s_{1o} = \frac{1 + c_0}{2 + c_0}, \quad (40)$$

$$Z_o = 2 + c_0, \quad (41)$$

and

$$\beta\mu_{ro}(\sigma^*) = \ln(c_0 + 2) + (c_0 + 2)\sigma^*. \quad (42)$$

Using these relations to describe the reference fluid, the lowest-order theory predicts

$$Z = 1 + (2 + c_0)\rho s_1 \quad (43)$$

$$\beta\mu_r(\sigma) = \ln(c_0 + 2) - (c_0 + 1) + (c_0 + 2)\rho(\sigma + s_1). \quad (44)$$

As seen in Fig. 2, Eq. (43) provides a poor approximation to the equation of state. However, if c_0 is optimized by making the lowest-order correction vanish [Eq. (35)]

$$c_0 = -\frac{2 - \rho s_1}{1 - \rho s_1} \quad (45)$$

then the formulation becomes exact.

It is of interest to investigate the effect of the higher order corrections. To apply the second-order correction, the functional derivative of the residual chemical potential is needed. For the hard rod system

$$\left(\frac{\delta[\beta\Delta\mu_r(\sigma_1)]}{\delta p(\sigma_2)} \right)_{\beta, \rho} = \frac{\rho^2}{(1 - \rho s_1)^2} (\sigma_1 - \sigma_0)(\sigma_2 - s_1). \quad (46)$$

The two-body residual is symmetric in σ_1 and σ_2

$$\mathcal{R}_o^{(2)}(\sigma_1, \sigma_2) = \frac{1}{2} \frac{\rho^2}{(1 - \rho s_{1o})^2} (\sigma_1 - s_{1o})(\sigma_2 - s_{1o}). \quad (47)$$

With an infinitely polydisperse reference, the second-order theory then predicts for the compressibility factor

$$Z = 1 + (c_0 + 2)\rho s_1 + (c_0 + 2)^2 \rho s_1 (\rho s_1 - \rho s_{1o}), \quad (48)$$

where ρs_{1o} is given in terms of c_0 by Eq. (40). Equation (48) is displayed in Fig. 2 for several values of c_0 . For a given reference, the extended treatment does not result in a uniform improvement of the prediction. For densities in which

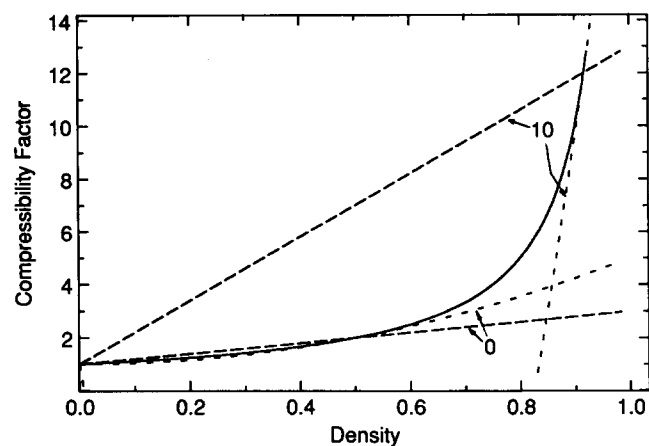


FIG. 2. Equation of state of single component hard rods. The solid line is the exact result. The long- and short-dashed lines are the results of the first- and second-order theories, respectively, with infinitely polydisperse reference fluids of $c_0 = 0$ and 10, as indicated.

the first-order theory is poor, the estimate is made worse. However, in the vicinity of the density where the first order treatment is exact (again for a given c_0), the prediction is improved considerably.

Interestingly, the *slope* of the equation of state as well as its value are both exact in the second-order theory at the optimal c_0 . This treatment has much in common with a virial expansion, with the important exception that the reference in this expansion is a dense rather than an extremely rarefied fluid. The virial nature of the treatment is apparent in the separation of the residual \mathcal{R} into terms containing two particles, three particles, etc., [Eq. (17)]. In this sense, the infinitely polydisperse mixture may be thought of as a generalized ideal gas which is suitable for use as a reference for dense phases.

B. Hard spheres in three dimensions

The Carnahan and Starling¹² equation of state for pure hard spheres ($D = 3$) was extended to mixtures by Mansoori *et al.*¹³

$$Z = \frac{1}{1 - \xi_3} + \frac{3\xi_1\xi_2}{\xi_0(1 - \xi_3)^2} + \frac{3\xi_2^3}{\xi_0(1 - \xi_3)^3} - \frac{\xi_3\xi_2^3}{\xi_0(1 - \xi_3)^3}, \quad (49)$$

where $\xi_0 \equiv (\pi/6)\rho$ and $\xi_n \equiv \xi_0 s_n$. We have verified by Monte Carlo simulation⁴ that Eq. (49) can be applied to accurately predict the infinitely polydisperse composition and chemical potential of the reference species $\mu(\sigma_0)$ in mixtures for which c_0 is at least as large as 30. The reduced composition is of the form

$$p^*(\sigma^*) = \sigma^{*c_0} \exp[a_0 + a_1\sigma^* + a_2\sigma^{*2} + a_3\sigma^{*3}], \quad (50)$$

where the a_i 's are functions only of c_0 , and must be determined numerically.⁴ Insertion of Eq. (50) into Eq. (24) produces an approximation to the equation of state

$$Z = 1 + \frac{1}{3} a_1 \rho^{1/3} s_1 + \frac{2}{3} a_2 \rho^{2/3} s_2 + a_3 \rho s_3, \quad (51)$$

where s_n is the n th moment of the composition of the mixture of interest [Eq. (37)]. This (still unoptimized) equation produces the correct ideal gas limit. According to Eq. (35), c_0 should be chosen to satisfy

$$1 + c_0 + a_1(c_0) \rho^{1/3} s_1 + 2a_2(c_0) \rho^{2/3} s_2 + 3a_3(c_0) \rho s_3 = 0, \quad (52)$$

where the dependence of the a_i 's on c_0 has been emphasized. The density and the moments in Eq. (52) are those of the fluid of interest.

We have applied this formulation to mixtures of hard spheres with a Gaussian distribution of diameters, i.e.,

$$p(\sigma) = \frac{1}{\sqrt{2\pi(s_2 - \sigma_0^2)}} \exp\left[-\frac{(\sigma - \sigma_0)^2}{2(s_2 - \sigma_0^2)}\right] \quad (53)$$

for various values of the reduced second moment s_2/σ_0^2 and reduced density $\rho\sigma_0^3$. The predicted equation of state is compared to Eq. (49) in Fig. 3. The agreement—although inexact—is remarkable; quantitative agreement is seen at all densities. The calculation for $s_2 = 0$ represents the most stringent test of the theory: the invariant composition distributions for infinitely polydisperse mixtures predicts the

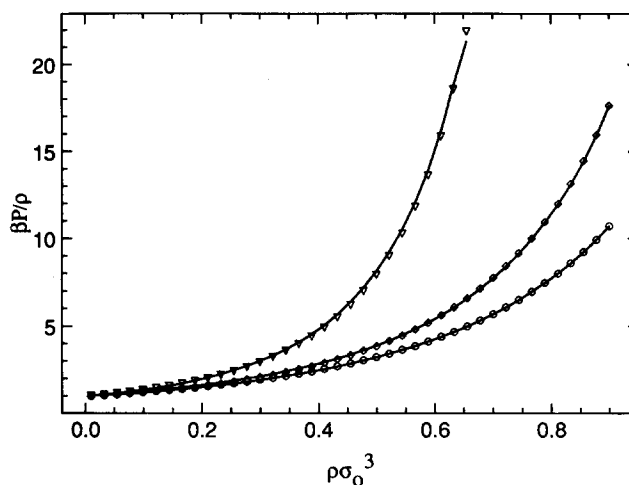


FIG. 3. Equation of state of mixtures of hard spheres with Gaussian distributions of diameters of mean σ_0 and variances $0.5\sigma_0^2$ (triangles), $0.25\sigma_0^2$ (diamonds), and 0.0 (circles). The lines represent predictions from the proposed theory, and the points are "exact" values given by Eq. (49).

equation of state of *pure* hard spheres with great accuracy. As shown by Fig. 4, excellent performance is also seen in the prediction of the chemical potential for this limiting case.

The theory developed here is based upon a reference which is at the same *density* as the mixture to be described. An alternative formulation may be developed which is based upon a reference at the same *pressure*.⁵ For an arbitrary choice of c_0 , it turns out that the isobaric reference provides a much better prediction than does the isochoric.⁵ Indeed, for hard rods, the isobaric treatment provides an exact description of the equation of state, regardless of the choice of the reference c_0 . Of course, in the first-order treatment (i.e., without \mathcal{R}) with c_0 chosen according to Eq. (35), the theories are equivalent.

VII. SUMMARY

In this work we have presented a general theory which relates the properties of mixtures of one composition to the

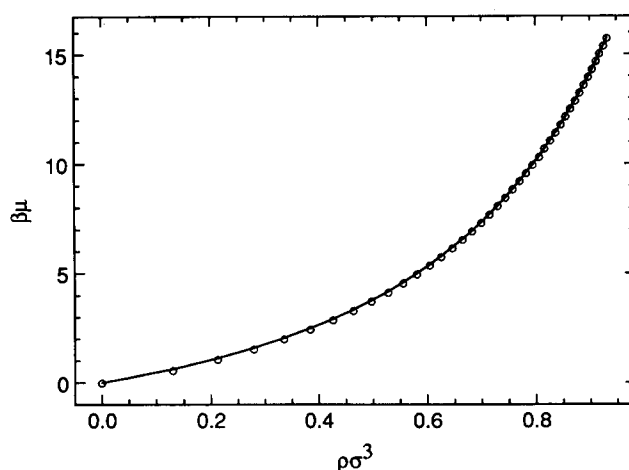


FIG. 4. Chemical potential of a pure fluid of hard spheres. The line represents the prediction of the proposed theory, and the points were computed from the equation of state of Carnahan and Starling (Ref. 12).

properties of mixtures of a different composition. The theory may be used to accurately predict the properties of all types of mixtures, be they polydisperse or discrete, and even pure fluids. A semigrand canonical framework is employed, and thus the principal quantity which characterizes the mixtures is the distribution of chemical potential differences. The main assumption in the treatment is a composition-space superposition approximation (CSSA), for which systematic corrections can be developed.

The treatment gains great power from the introduction of an "infinitely polydisperse" reference, which is very easily characterized. The principal inputs to the theory are the infinitely polydisperse compositions, which should be known for several values of c_0 . For hard particles, the scaling properties of the infinitely polydisperse reference allow density derivatives of the composition to be expressed as derivatives with respect to the diameter, a feature which greatly simplifies the implementation of the theory. These compositions are easily tabulated in Monte Carlo simulations, and thus the treatment may be used to evaluate the properties of many types of mixtures from a very few simulations. This application will be demonstrated in a subsequent paper¹⁴ which describes a study of freezing in hard sphere mixtures.

The concept of an infinitely polydisperse reference may be applied to virtually any type of molecular interaction model, and goes well beyond the example of infinitely polydisperse diameters. To each parameter in an intermolecular potential there corresponds a chemical potential parameter c_0 . To apply the full theory, the composition of the mixture must be known for each set of values that the c_0 's may adopt. In the case of intermolecular potentials with three or even more parameters, the full characterization of this multidimensional space would be quite formidable. However, it still represents a great reduction in complexity when compared to the characterization of the full equations of state of mixtures of every conceivable composition. Thus, this theory presents a suitable starting point from which further studies may be based.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences. D. A. K. would also like to thank the DuPont corporation for the award of a predoctoral fellowship.

APPENDIX A: JUSTIFICATION OF CSSA FOR $n \ll N$

A recursion relation follows directly from Eq. (13)

$$\frac{\delta P^{(n)}(\mathbf{I}_1, \dots, \mathbf{I}_n)}{\delta[\beta\Delta\mu_c(\mathbf{I}_{n+1})]} = P^{(n+1)}(\mathbf{I}_1, \dots, \mathbf{I}_{n+1}) - P^{(n)}(\mathbf{I}_1, \dots, \mathbf{I}_n)P^{(1)}(\mathbf{I}_{n+1}) + n_{\mathbf{I}_{n+1}}P^{(n+1)}(\mathbf{I}_1, \dots, \mathbf{I}_{n+1}) + P^{(n)}(\mathbf{I}_1, \dots, \mathbf{I}_n) \sum_{i=1}^n \delta(\mathbf{I}_i - \mathbf{I}_{n+1}) \quad (\text{A1})$$

(note that the last two terms on the right-hand side are zero when none of the \mathbf{I}_i are the same). This exact relation may

instead be written in terms of the specific distribution functions

$$\frac{\delta p^{(n)}(\mathbf{I}_1, \dots, \mathbf{I}_n)}{\delta[\beta\Delta\mu_c(\mathbf{I}_{n+1})]} = \frac{(N-n)}{1+n_{\mathbf{I}_{n+1}}} p^{(n+1)}(\mathbf{I}_1, \dots, \mathbf{I}_{n+1}) - Np^{(n+1)}(\mathbf{I}_1, \dots, \mathbf{I}_n) p^{(1)}(\mathbf{I}_{n+1}) + \frac{n_{\mathbf{I}_{n+1}}}{1+n_{\mathbf{I}_{n+1}}} p^{(n+1)}(\mathbf{I}_1, \dots, \mathbf{I}_n) + p^{(n)}(\mathbf{I}_1, \dots, \mathbf{I}_n) \sum_{i=1}^n \delta(\mathbf{I}_i - \mathbf{I}_{n+1}). \quad (\text{A2})$$

For $n \ll N$, the first two terms on the right-hand side of Eq. (A2) are at least a factor of N greater than all other terms (on either side), and thus in this case the equation may be simplified

$$p^{(n+1)}(\mathbf{I}_1, \dots, \mathbf{I}_{n+1}) = p^{(n)}(\mathbf{I}_1, \dots, \mathbf{I}_n) p^{(1)}(\mathbf{I}_{n+1}) + O(N^{-1}) \quad [n = O(1)]. \quad (\text{A3})$$

Repeated application of Eq. (A3) yields

$$p^{(n)}(\mathbf{I}_1, \dots, \mathbf{I}_n) = \prod_{i=1}^n p^{(1)}(\mathbf{I}_i) + O\left(\frac{n}{N}\right) \quad [n = O(1)] \quad (\text{A4})$$

which verifies Eq. (15) for small n .

APPENDIX B: DERIVATION OF CORRECTIONS TO CSSA

To examine the opposite extreme, for which $n = O(N)$, it is necessary to introduce a different type of composition distribution function. Let $\mathcal{P}[p(I)]$ be the probability density that a particular realization of a semigrand mixture is of composition $p(\mathbf{I})$. With the proper identification the argument $p(\mathbf{I})$, this probability functional can be directly related to the N -particle distribution functions introduced in Sec. III. Accordingly, let

$$\tilde{p}(\mathbf{I}; \mathbf{I}_1, \mathbf{I}_2, \dots, \mathbf{I}_N) \equiv \frac{1}{N} \sum_{i=1}^N \delta(\mathbf{I} - \mathbf{I}_i) \quad (\text{B1})$$

then it can be reasoned that

$$\mathcal{P}[\tilde{p}(\mathbf{I}; \mathbf{I}_1, \dots, \mathbf{I}_N)] = P^{(N)}(\mathbf{I}_1, \dots, \mathbf{I}_N). \quad (\text{B2})$$

Then Eq. (12) can be used to show

$$\mathcal{P}[\tilde{p}(\mathbf{I}; \mathbf{I}_1, \dots, \mathbf{I}_N)] = \exp\left[-N \int \tilde{p}(\mathbf{I}) \ln \tilde{p}(\mathbf{I}) d\mathbf{I}\right] \times p^{(N)}(\mathbf{I}_1, \dots, \mathbf{I}_N), \quad (\text{B3})$$

where Stirling's approximation has been used to evaluate the factorials. The functional \mathcal{P} is introduced because, in contrast to $p^{(N)}$, its dependence on the overall distribution of the $\mathbf{I}^{(N)}$ is explicit.

For macroscopic systems away from a critical point, semigrand fluctuations in composition, like fluctuations in density, are very small. Thus it is appropriate to expand $\mathcal{P}[p(\mathbf{I})]$ about its most probable value, $\mathcal{P}[\hat{p}(\mathbf{I})]$

$$\begin{aligned} \ln \mathcal{P}[p] = & \ln \mathcal{P}[\hat{p}] + \int \frac{\delta \ln \mathcal{P}}{\delta p(\mathbf{I}')} \Big|_{p=\hat{p}} \Delta \hat{p}(\mathbf{I}') d\mathbf{I}' \\ & + \frac{1}{2} \int \int \frac{\delta^2 \ln \mathcal{P}}{\delta p(\mathbf{I}') \delta p(\mathbf{I}'')} \Big|_{p=\hat{p}} \Delta \hat{p}(\mathbf{I}') \Delta \hat{p}(\mathbf{I}'') \\ & \times d\mathbf{I}' d\mathbf{I}'' + \dots, \end{aligned} \quad (\text{B4})$$

where $\Delta \hat{p}(\mathbf{I}) = p(\mathbf{I}) - \hat{p}(\mathbf{I})$ is the deviation of p from its most probable value. The functional derivatives, which are taken at constant temperature and density, are evaluated at \hat{p} . Accordingly, the first derivative must be zero, and, using Eqs. (11) and (B3)

$$\begin{aligned} \frac{\delta \ln \mathcal{P}}{\delta p(\mathbf{I})} \Big|_{p=\hat{p}} = & \frac{\delta}{\delta p(\mathbf{I})} \left[-N \int p(\mathbf{I}) \ln p(\mathbf{I}) d\mathbf{I} \right. \\ & \left. + \ln Z_N[p(\mathbf{I})] \right] + N\beta \Delta \mu_c(\mathbf{I}) = 0. \end{aligned} \quad (\text{B5})$$

With this relation, higher order derivatives may be written in terms of $\beta \Delta \mu_c(\mathbf{I})$, and the expansion for \mathcal{P} becomes

$$\begin{aligned} \ln \mathcal{P}[p(\mathbf{I})] = & \ln \mathcal{P}[\hat{p}(\mathbf{I})] - \frac{1}{2} N \int \int \frac{\delta \beta \Delta \mu_c(\mathbf{I}')}{\delta p(\mathbf{I}'')} \Big|_{p=\hat{p}} \\ & \times \Delta \hat{p}(\mathbf{I}') \Delta \hat{p}(\mathbf{I}'') d\mathbf{I}' d\mathbf{I}'' + \dots \end{aligned} \quad (\text{B6})$$

Upon separating the configurational chemical potential into an ideal gas part and a residual part according to Eq. (9), the ideal gas contributions to $\Delta \mu_c$ ($\Delta \mu_c^{\text{id}}(\mathbf{I}) = \ln[p(\mathbf{I})/p(\mathbf{I}_0)]$) may be summed to all orders in $\Delta \hat{p}$, with the result

$$\ln \mathcal{P}[p] = \ln \mathcal{P}[\hat{p}] + N \int p(\mathbf{I}) \ln \frac{\hat{p}(\mathbf{I})}{p(\mathbf{I})} d\mathbf{I} + N\mathcal{R}[p, \hat{p}], \quad (\text{B7})$$

where \mathcal{R} is the residual expansion

$$\begin{aligned} \mathcal{R}[p, \hat{p}] = & -\frac{1}{2!} \int \int \frac{\delta \beta \Delta \mu_r(\mathbf{I}')}{\delta p(\mathbf{I}'')} \Big|_{p=\hat{p}} \\ & \times \Delta \hat{p}(\mathbf{I}') \Delta \hat{p}(\mathbf{I}'') d\mathbf{I}' d\mathbf{I}'' \\ & - \frac{1}{3!} \int \int \int \frac{\delta^2 \beta \Delta \mu_r(\mathbf{I}')}{\delta p(\mathbf{I}'') \delta p(\mathbf{I}''')} \Big|_{p=\hat{p}} \\ & \times \Delta \hat{p}(\mathbf{I}') \Delta \hat{p}(\mathbf{I}'') \Delta \hat{p}(\mathbf{I}''') d\mathbf{I}' d\mathbf{I}'' d\mathbf{I}''' + \dots \end{aligned} \quad (\text{B8})$$

If Eq. (B4) is used to approximate $\mathcal{P}[\tilde{p}]$ [with \tilde{p} given by Eq. (B1)] and the result is introduced into Eq. (B3), Eq. (16) results (where it has been recognized that \hat{p} , the location of the maximum in the functional \mathcal{P} , is the average 1-particle distribution function $p^{(1)}$).

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