

# Infinitely polydisperse fluids

David A. Kofke and Eduardo D. Glandt

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

(Received 1 August 1988; accepted 21 September 1988)

A generalized semigrand formalism for polydisperse fluids is presented and is used to derive a thermodynamic consistency equation. In the infinitely polydisperse limit—corresponding to a flat distribution of chemical potential differences—a characteristic parameter is eliminated, and the description of the mixture is greatly simplified. In the case of infinitely polydisperse hard spheres, the absence of a characteristic diameter implies that all quantities must scale to the density, which provides the only length. This leads to an exact equation of state which, remarkably, is  $PV/Nk_B T = 4/3$  at all densities. The treatment is generalized, to show that there exists a whole family of stationary composition distributions which have invariant compressibility factors. Monte Carlo simulation is used to verify these results, and applications to other potentials are discussed. Infinitely polydisperse fluids provide a convenient starting point for new mixture theories.

## I. INTRODUCTION

Polydisperse mixtures are described by a continuous probability density of one or more particle attributes, such as particle size, as opposed to a discrete set of mole fractions. Thus, they may be viewed as containing an infinite number of components. Colloids and polymers are almost invariably polydisperse. It has been several decades since the introduction of polydispersity as a model of multicomponent molecular mixtures,<sup>1,2</sup> but only recently has it received widespread attention.<sup>3-9</sup> In particular, the limit of nearly monodisperse mixtures (“narrow cuts”) has been used to construct perturbation theories with a pure, monodisperse component as the reference fluid.<sup>7,9,10</sup> In this work we examine the opposite limit, in which the activity of all species, up to infinite size, is nonzero and possibly unbounded.

In what follows, we will describe a new and interesting class of fluid mixtures—termed “infinitely polydisperse”—which are distinguished not by their intermolecular potential, but by a specific form of the distribution of their chemical potentials. The necessary framework to describe these mixtures is provided by a semigrand ensemble, which was introduced in previous work<sup>7,8</sup> and is reviewed in Sec. II. Infinitely polydisperse mixtures are interesting because their properties, when properly expressed in a dimensionless form, are invariant with density, and in some cases can be determined analytically. The key concepts can be demonstrated most simply for the particular case of hard particles in arbitrary dimension. This is done in Secs. III and IV, and it is shown, e.g., that the equation of state of infinitely polydisperse hard spheres can be expressed analytically, and for a uniform activity distribution it is  $PV/Nk_B T = 4/3$  at all densities. This surprising result is verified by Monte Carlo computer simulations in the semigrand canonical ensemble. In Sec. V fluids with attractive interactions are considered. In the Appendix, the formalism is generalized to include model systems with an arbitrary number of length and energy parameters. In each section, an important step is the development of a new rigorous consistency equation which applies to polydisperse fluid mixtures. This equation is in itself a significant result.

## II. SEMIGRAND ENSEMBLE

The semigrand canonical ensemble<sup>7,8</sup> provides a convenient statistical mechanical formalism for dealing with polydisperse systems. The semigrand free energy  $Y$  is a Legendre transform of the Helmholtz free energy  $A$ , and in the polydisperse limit is<sup>7,8</sup>

$$\beta Y \equiv \beta A - N \int_{\Omega} p(\mathbf{I}) [\beta \mu(\mathbf{I}) - \beta \mu(\mathbf{I}_0)] d\mathbf{I}, \quad (1)$$

where  $\beta = 1/k_B T$ , with  $k_B$  Boltzmann's constant and  $T$  the temperature. The functions  $p(\mathbf{I})$  and  $\mu(\mathbf{I})$  represent the composition and chemical potential distributions, respectively. The quantity  $\mathbf{I}$  represents a set of  $\nu$  species-designating parameters, and is defined over the  $\nu$ -dimensional domain  $\Omega$ ;  $\mathbf{I}_0$  is the label of an arbitrarily chosen reference species. Usually,  $\nu$  is about 2 or 3. For example, the species identity of a molecule in a mixture of Lennard-Jones particles may be specified by both its  $\sigma$  and  $\epsilon$  parameters, thus  $\mathbf{I} = [\sigma, \epsilon]$ .

The fundamental differential equation in this ensemble is

$$d(\beta Y) = U d\beta - \beta P dV + \beta \mu(\mathbf{I}_0) dN - N \int_{\Omega} p(\mathbf{I}) \delta[\beta \mu(\mathbf{I}) - \beta \mu(\mathbf{I}_0)] d\mathbf{I}, \quad (2)$$

where  $U$ ,  $P$ ,  $V$ ,  $N$  are the internal energy, pressure, (hyper) volume, and total number of particles, respectively. With suitable definitions of  $P$  and  $V$ , Eq. (2) is applicable to systems of arbitrary dimensionality. The free energy  $Y$  is a function of  $T$ ,  $V$ , and  $N$ , and a functional of the distribution of chemical potential differences,  $\beta \mu(\mathbf{I}) - \beta \mu(\mathbf{I}_0)$ . It is convenient to separate the contributions to the chemical potential due to translational and internal degrees of freedom. Accordingly, the configurational chemical potential is defined:

$$\beta \mu_c(\mathbf{I}) \equiv \beta \mu(\mathbf{I}) - \ln \left[ \frac{\Lambda^D(\mathbf{I})}{q^{\text{int}}(\mathbf{I})} \right], \quad (3)$$

where  $q^{\text{int}}(\mathbf{I})$  is the internal partition function for a molecule of species  $\mathbf{I}$  while  $\Lambda(\mathbf{I}) = h[\beta/2\pi m(\mathbf{I})]^{1/2}$  is its corresponding thermal de Broglie wavelength, with  $m(\mathbf{I})$  the mass and

$h$  Planck's constant;  $D$  is the dimensionality. Substitution of Eq. (3) into Eq. (2) yields

$$d(\beta Y) = U_\mu d\beta - \beta P dV + \beta \mu_c(\mathbf{I}_0) dN - N \int_{\Omega} p(\mathbf{I}) \delta[\beta \mu_c(\mathbf{I}) - \beta \mu_c(\mathbf{I}_0)] d\mathbf{I}, \quad (4)$$

where  $U_\mu$  includes the temperature dependence of the internal partition function

$$U_\mu \equiv U - N \int_{\Omega} p(\mathbf{I}) \frac{d}{d\beta} \left[ \ln \frac{q^{\text{int}}(\mathbf{I})}{q^{\text{int}}(\mathbf{I}_0)} \right] d\mathbf{I}. \quad (5)$$

Note that the dependence of  $\Lambda(\mathbf{I})$  and  $\Lambda(\mathbf{I}_0)$  cancel.

The semigrand partition function is expressed by summing the canonical partition function over all compositions, weighted by the distribution of activities. In terms of the configurational chemical potentials, this may be written

$$\Upsilon = \frac{1}{N!} \left[ \frac{q^{\text{int}}(\mathbf{I}_0)}{\Lambda^D(\mathbf{I}_0)} \right]^N \int_{(N)} d\mathbf{I}^{(N)} \int_{(N)} d\mathbf{r}^{(N)} \times \exp[-\beta U(\mathbf{r}^{(N)}, \mathbf{I}^{(N)})] \times \exp \left\{ \sum_{i=1}^N [\beta \mu_c(\mathbf{I}_i) - \beta \mu_c(\mathbf{I}_0)] \right\}, \quad (6)$$

where  $d\mathbf{I}^{(N)}$  is used to represent  $N$  integrals, one for each molecule, over  $\Omega$ ;  $\mathbf{I}_i$  is the identity vector for molecule  $i$ . An analogous interpretation applies to  $d\mathbf{r}^{(N)}$ ; the domain of each  $\mathbf{r}$  corresponds to all positions (over  $V$ ) and orientations (normalized to unity) of a molecule. When written with explicit arguments, as in Eq. (6), the internal energy  $U[\mathbf{r}^{(N)}, \mathbf{I}^{(N)}]$  represents that for particular configuration and choice of species parameters. The semigrand free energy is related to the partition function through the bridge equation

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

### III. INFINITELY POLYDISPERSE HARD PARTICLES

In this section, we consider the case when the identity vector is comprised of just one parameter, which has units of length and which will represent a hard-particle diameter. As a reminder that this is a special case, the parameter will be designated  $\sigma$  rather than  $I$ .

The distribution of configurational chemical potential differences may be written in general form as a power series in  $(\sigma - \sigma_0)$ , plus a logarithmic term

$$\beta \mu_c(\sigma) - \beta \mu_c(\sigma_0) = c_0 \ln \left( \frac{\sigma}{\sigma_0} \right) + \sum_{n=1}^{\infty} c_n (\sigma - \sigma_0)^n. \quad (8)$$

With this parametrization, the independent variables are now the set of coefficients  $c_n$  and the reference-species diameter  $\sigma_0$ , which are chosen in lieu of the chemical potential distribution. Other functional series can be used in place of Eq. (8). For example, if it is desired to allow for components which are present in discrete quantities, then terms of the form  $[c_i \ln \delta(\sigma - \sigma_i)]$ , where  $\delta$  is the Dirac- $\delta$  function, can be included. Introduction of Eq. (8) into Eq. (4) yields a

new form for the fundamental equation

$$d(\beta Y) = -\beta P dV + \beta \mu_c(\sigma_0) dN - N \sum_{n=0}^{\infty} m_n dc_n + N \left[ c_0 + \sigma_0 \sum_{n=1}^{\infty} n c_n m_{n-1} \right] d \ln \sigma_0, \quad (9)$$

where  $m_n$  is the  $n$ th moment of the composition about the  $\sigma_0$  species

$$m_n = \int_0^{\infty} d\sigma p(\sigma) (\sigma - \sigma_0)^n \quad (10a)$$

and

$$m_0 = \int_0^{\infty} d\sigma p(\sigma) \ln \left( \frac{\sigma}{\sigma_0} \right) d\sigma. \quad (10b)$$

Reduced variables may not be defined by

$$V^* = V/\sigma_0^D, \quad c_n^* = c_n \sigma_0^n, \quad m_n^* = m_n/\sigma_0^n.$$

When written in terms of these quantities, the fundamental equation becomes

$$d(\beta Y) = -\beta P \sigma_0^D dV^* + \beta \mu_c(\sigma_0) dN - N \sum_{n=0}^{\infty} m_n^* dc_n^* + N \left[ -DZ + c_0 + \sum_{n=1}^{\infty} n c_n^* (m_{n-1}^* + m_n^*) \right] d \ln \sigma_0, \quad (11)$$

where  $Z$  is the compressibility factor  $\beta P/\rho$  with  $\rho = N/V$ . This equation is useful because it isolates the dependence on  $\sigma_0$ , which defines all length scales.

With the choice for the distribution of configurational chemical potential differences given by Eq. (8), and using the reduced parameters defined above, the partition function may also be written in dimensionless form

$$\Upsilon = \frac{1}{N!} \left[ \frac{q^{\text{int}}(\sigma_0)}{\Lambda^D(\sigma_0)} \right]^N \sigma_0^{N(D+1)} \times \int_{(N)} d\sigma^{*(N)} \int_{(N)} \exp\{-\beta U([\sigma_0 \mathbf{r}^*]^{(N)}, [\sigma_0 \sigma^*]^{(N)})\} \times \left( \prod_{i=1}^N \sigma_i^{*c_0} \right) \exp \left[ \sum_{i=1}^N \sum_{n=1}^{\infty} c_n^* (\sigma_i^* - 1)^n \right], \quad (12)$$

where  $\sigma^* = \sigma/\sigma_0$  and  $\mathbf{r}^* = \mathbf{r}/\sigma_0$ . The expression for the internal energy may be simplified if it is noted that the hard-particle pair potential is of the form  $f(r/\sigma)$ , i.e., it is a homogeneous function of degree 0 of its length parameters  $r$  and  $\sigma$ . Therefore

$$\beta U([\sigma_0 \mathbf{r}^*]^{(N)}, [\sigma_0 \sigma^*]^{(N)}) = \beta U(\mathbf{r}^{*(N)}, \sigma^{*(N)}). \quad (13)$$

The dependence of the partition function upon  $\sigma_0$  is thus entirely contained in the term  $\sigma_0^{N(D+1)}$  which premultiplies the integral [the term  $q^{\text{int}}(\sigma_0)/\Lambda^D(\sigma_0)$  is a constant representing the value of  $q^{\text{int}}(\sigma)/\Lambda^D(\sigma)$  when evaluated at  $\sigma_0$ ; it does not depend upon  $\sigma_0$  itself]. Upon taking the derivative of Eq. (12) with respect to  $\sigma_0$  and comparing it to Eq. (11) via the bridge equation, it is found that

$$D(Z-1) = 1 + c_0 + \sum_{n=1}^{\infty} n c_n^* (m_{n-1}^* + m_n^*). \quad (14)$$

This is a consistency equation applicable to hard-particle

systems, and it has some very interesting consequences. In particular, if all of the coefficients but  $c_0$  are set to zero, i.e., if the distribution of configurational chemical potentials is logarithmic,

$$\beta\mu_c(\sigma) - \beta\mu_c(\sigma_0) = c_0 \ln\left(\frac{\sigma}{\sigma_0}\right), \quad (15)$$

then the dependence of  $Z$  on all of the moments vanishes and the equation of state can be easily determined analytically

$$Z = \frac{1}{D}(D + 1 + c_0). \quad (16)$$

Remarkably, for this particular distribution, the compressibility factor is independent of density. This is because the choice of the chemical potential distribution results in the elimination of any characteristic molecular length scale. There remains only one independent length scale, i.e.,  $\rho^{-1/D}$ , and thus all dimensioned quantities, such as  $\beta p$ , must have constant values when reduced by it. Systems characterized by such a distribution of configurational chemical potential differences are what we term "infinitely polydisperse" fluids. Some examples of this type of distribution are shown in Fig. 1. The scaling that give rise to the simple, analytic form for the equation of state also allows a simplified description of *all* properties of the fluid. This includes quantities related to the composition, such as its moments, and to the structure.

One of the reasons why hard-particle fluids play a singular role in liquid theory is that, lacking a characteristic energy, their properties show no temperature dependence. In the same manner, infinitely polydisperse fluids lack a characteristic length, and their properties show no density dependence. Infinitely polydisperse hard particles combine these two features, and their thermodynamic space reduces to a single point.

#### IV. SOME RESULTS FOR HARD-PARTICLE FLUIDS

In this section we demonstrate the validity of the concepts presented above with simple hard-particle systems.

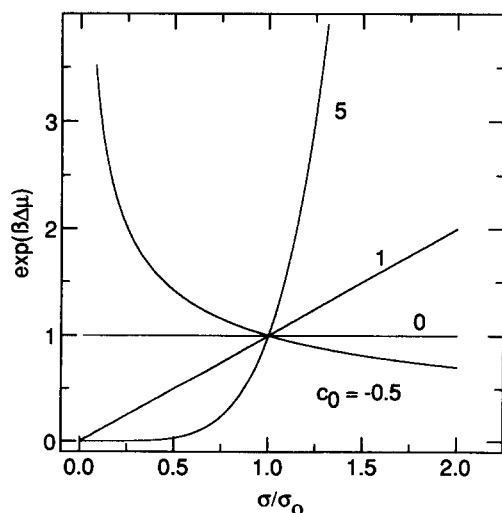


FIG. 1. Typical fugacity-ratio distributions  $\exp[\beta\mu_c(\sigma) - \beta\mu_c(\sigma_0)]$  which characterize infinitely polydisperse mixtures.

The one-dimensional, hard-rod fluid is most convenient because all of its properties have been determined analytically. We show that infinitely polydisperse hard rods must have a composition which is of the form of a Schultz or gamma distribution. We study in more detail the three-dimensional analog—infinitely polydisperse hard spheres. Results are presented from Monte Carlo simulations which verify that the generalized Carnahan–Starling equation of state can be used to accurately predict the compositions of infinitely polydisperse hard spheres; composition-averaged radial distribution functions are also presented.

#### A. Hard rods

The equation of state of a hard rod mixture is<sup>3</sup>

$$\beta P = \frac{\rho}{1 - \rho s_1}, \quad (17)$$

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

$$s_n = \int_0^\infty \sigma^n p(\sigma) d\sigma. \quad (18)$$

The chemical potential of a rod of length  $\sigma$  is given by<sup>3</sup>

$$\begin{aligned} \beta\mu(\sigma) = & -\ln\left[\frac{q^{\text{int}}(\sigma)}{\Lambda(\sigma)}\right] \\ & + \ln \rho p(\sigma) - \ln(1 - \rho s_1) + \frac{\rho\sigma}{(1 - \rho s_1)}. \end{aligned} \quad (19)$$

If the distribution of configurational chemical potentials is logarithmic, i.e., is given by Eq. (15), then Eq. (19) yields for the composition

$$p(\sigma) = p(\sigma_0) \left(\frac{\sigma}{\sigma_0}\right)^{c_0} \exp\left[-\frac{\rho}{1 - \rho s_1}(\sigma - \sigma_0)\right], \quad (20)$$

where  $p(\sigma_0)$  is determined by normalization. This is an implicit equation, because it expresses the composition in terms of its first moment,  $s_1$ . Insertion of Eq. (20) into Eq. (18) results in an algebraic equation for  $s_1$ , which when solved yields

$$\rho s_1 = \frac{1 + c_0}{2 + c_0}. \quad (21)$$

This corresponds to the equation of state  $Z = 2 + c_0$ , in accordance with the consistency equation, Eq. (16). Also, the composition is given explicitly by

$$p(\sigma) = \rho \frac{(c_0 + 2)^{c_0 + 1}}{\Gamma(c_0 + 1)} (\rho\sigma)^{c_0} \exp[-(2 + c_0)\rho\sigma], \quad (22)$$

where  $\Gamma$  is the gamma function. This is the gamma or Schultz distribution.

We note several points: (1) The quantities expressed in Eqs. (21) and (22) do not depend upon  $\sigma_0$ . All lengths ( $\sigma$  and  $1/\rho$ ) are scaled by the density. The composition at any density can be trivially related to the composition at any other density. (2)  $c_0$  has no upper bound. As it becomes infinite, the fluid approaches close packing, which is also space filling. (3)  $c_0$  has a lower bound of  $-1$ . Values smaller

than this yield unphysical results. In fact, it can be ascertained from Eq. (16) that this lower limit applies to all systems which have purely repulsive intermolecular potentials, regardless of the dimensionality  $D$ .

### B. Hard spheres

One of the most successful theories for hard-particle fluids is that of Percus and Yevick,<sup>11</sup> later extended to the multicomponent and polydisperse cases.<sup>12</sup> Because of its approximate nature, this theory yields two different equations of state for the hard sphere fluid, depending on whether the virial or the compressibility equation is used. Carnahan and Starling<sup>13</sup> proposed the highly accurate semiempirical combination  $Z = (Z_v + 2Z_c)/3$ , where  $Z_v$  and  $Z_c$  are the virial and compressibility solutions, respectively. This was later extended to mixtures by Mansoori *et al.*<sup>14</sup> All three formulations for the equation of state may be written in the general form

$$Z = \frac{1}{1 - \xi_3} + \frac{3\xi_1\xi_2}{\xi_0(1 - \xi_3)^2} + \frac{3\xi_2^3}{\xi_0(1 - \xi_3)^3} - k \frac{\xi_3\xi_2^3}{\xi_0(1 - \xi_3)^3}, \quad (23)$$

where  $\xi_n = (\pi/6)\rho s_n$ , and  $s_n$  is the  $n$ th moment of the composition about the origin [Eq. (18)];  $k = 0$  corresponds to the compressibility solution,  $k = 3$  to the virial, and  $k = 1$  to the Carnahan–Starling combination. We have applied these equations to systems of infinitely polydisperse hard spheres ( $D = 3$ ), with the logarithmic configurational chemical potential distribution of Eq. (15). From Eq. (16), the equation of state must satisfy

$$Z = \frac{4 + c_0}{3}. \quad (24)$$

Using standard thermodynamic manipulations, the distribution of configurational chemical potentials can be deduced from Eq. (23),

$$\beta\mu_c(\sigma) = \ln \rho p(\sigma) - \ln(1 - \xi_3) + \Psi_1\sigma + \Psi_2\sigma^2 + \Psi_3\sigma^3, \quad (25)$$

where

$$\Psi_1 \equiv \frac{3\xi_2}{(1 - \xi_3)}, \quad (26a)$$

$$\Psi_2 \equiv \frac{3\xi_1}{(1 - \xi_3)} + \left[ k + \frac{3}{2}\xi_3(1 - k) \right] \frac{3\xi_2^2}{\xi_3(1 - \xi_3)^2} + \frac{3k\xi_2^2}{\xi_3^2} \ln(1 - \xi_3), \quad (26b)$$

$$\Psi_3 \equiv \frac{3\xi_1\xi_2}{(1 - \xi_3)^2} + \left[ k + \frac{3}{2}\xi_3(1 - k) \right] \frac{\xi_2^3(3\xi_3 - 1)}{\xi_3^2(1 - \xi_3)^3} + \frac{3}{2}(1 - k) \frac{\xi_2^3}{\xi_3(1 - \xi_3)^2} - 2k \frac{\xi_2^3}{\xi_3^3} \ln(1 - \xi_3) - \left( 1 - k \frac{\xi_2^3}{\xi_0\xi_3^2} \right) \frac{\xi_0}{1 - \xi_3}. \quad (26c)$$

It is simple to show from Eq. (25) that to satisfy Eq. (15) the

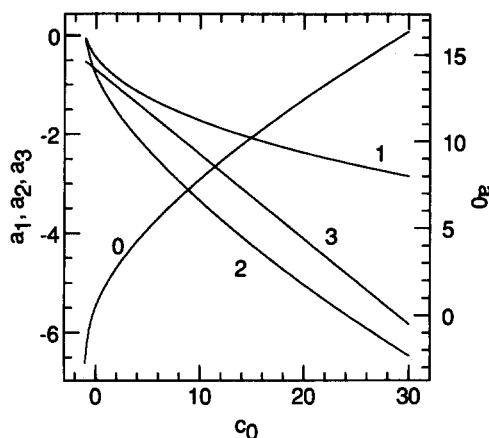


FIG. 2. Coefficients of the composition for mixtures of infinitely polydisperse hard spheres, as determined from the equation of state of Mansoori *et al.* (Ref. 14). The composition is given by  $p(\sigma) = \rho^{1/3}(\rho^{1/3}\sigma)^{c_0} \exp[a_0 + a_1\sigma + a_2\sigma^2 + a_3\sigma^3]$ .

composition distribution must have the form

$$\rho^{-1/3}p(\sigma) = (\rho^{1/3}\sigma)^{c_0} \exp(a_0 + a_1\sigma + a_2\sigma^2 + a_3\sigma^3). \quad (27)$$

As with the hard-rod composition, this expression is implicit; it must be solved numerically in conjunction with Eq. (18) for  $n = 1, 2$ , and 3. It is then found that the  $a_i$ 's, when reduced by the density, are functions only of  $c_0$ . These are shown in Fig. 2 for the equation of Mansoori *et al.* Compositions for several values of  $c_0$  are displayed in Fig. 3. Also, the compressibility factors from all three equations of state are indeed independent of the density, and do obey Eq. (24).

Although the equations of state based on the Percus–Yevick theory are known to be accurate for fluids with hard-core potentials, they have not been tested in the limit of the widely different particle sizes (aside from the consistency check described above). For this reason, we have performed Monte Carlo simulations of infinitely polydisperse mixtures

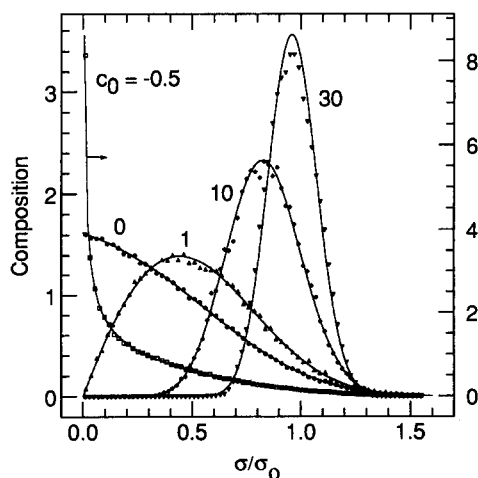


FIG. 3. Compositions of infinitely polydisperse hard spheres for several values of  $c_0$ . The points represent values from Monte Carlo simulation, while the lines were computed from the equation of state of Mansoori *et al.* (Ref. 14).

TABLE I. First three moments about the origin of the composition of infinitely polydisperse hard spheres. Values were computed from Monte Carlo simulation (MC), and from three equations of state based upon the Percus-Yevick approximation: compressibility (C), virial (V), and the Mansoori *et al.* combination (CS).

$c_0$	MC	CS	C	V
		$s_1$		
-0.5	0.2814(5) <sup>a</sup>	0.2808	0.2806	0.2808
0.0	0.4043(2)	0.4037	0.4035	0.4041
1.0	0.5371(8)	0.5374	0.5367	0.5386
10.0	0.8350(1)	0.8336	0.8298	0.8424
30.0	0.9609(0)	0.9610	0.9544	0.9778
		$s_2$		
-0.5	0.1685(6)	0.1684	0.1683	0.1685
0.0	0.2533(4)	0.2528	0.2526	0.2534
1.0	0.3650(5)	0.3646	0.3638	0.3663
10.0	0.7260(2)	0.7236	0.7269	0.7391
30.0	0.9361(1)	0.9359	0.9231	0.9691
		$s_3$		
-0.5	0.1346(7)	0.1348	0.1347	0.1349
0.0	0.1985(5)	0.1983	0.1979	0.1989
1.0	0.2893(8)	0.2884	0.2875	0.2905
10.0	0.6548(6)	0.6516	0.6425	0.6728
30.0	0.9242(1)	0.9233	0.9046	0.9729

<sup>a</sup>The number of parentheses indicates the estimated error (95% confidence interval) in the last digit of the value, e.g., 0.2814(5) means  $0.2814 \pm 0.0005$ .

of additive hard spheres, with  $c_0$  equal to -0.5, 0, 1, 10, and 30. These simulations were carried out for  $N = 32, 108, 256$ , and 500 hard spheres. The results of the 256- and 500-particle runs are identical within statistical error, and thus the 500-particle system can be considered representative of a macroscopic system. Typical runs sampled  $2 \times 10^6$  configurations, including  $0.5 \times 10^6$  used for equilibration and thus not included in the averages. Errors were computed by the

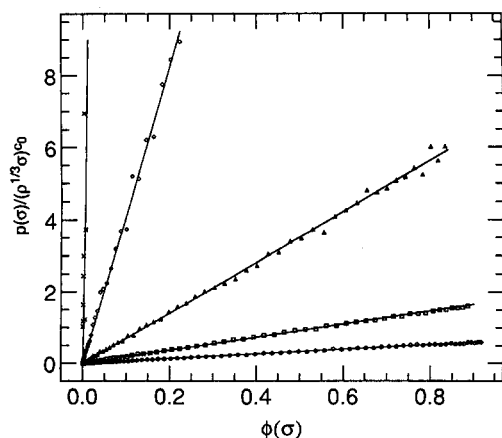


FIG. 4. Reduced composition  $p(\sigma)/[\rho^{1/3}(\rho^{1/3}\sigma)^{c_0}]$  plotted against the insertion average of a sphere of diameter  $\sigma$ ,  $\phi(\sigma)$ , as computed by Monte Carlo simulation for several values of  $c_0$ : -0.5 (circles); 0.0 (squares); 1.0 (triangles); 10.0 (diamonds); 30.0 (crosses). The slopes of the lines, which represent the best fit to the data, are equal to the constant  $K$  defined in Eq. (30). The values of the ordinates for  $c_0 = 10.0$  and  $c_0 = 30.0$  have been divided by  $10^2$  and  $10^4$ , respectively.

TABLE II. The parameter  $K$  which determines the absolute value of the configurational chemical potential of infinitely polydisperse hard spheres:  $\beta\mu_c(\sigma) = \ln \rho^{4/3}K + c_0 \ln(\rho^{1/3}\sigma)$ . Values were determined both by Monte Carlo simulation and by the equation of state of Mansoori *et al.*

$c_0$	$\ln K$	
	Equation of state	Monte Carlo
-0.5	-0.424	$-0.473 \pm 0.007$
0.0	0.593	$0.608 \pm 0.003$
1.0	1.92	$1.96 \pm 0.01$
10.0	8.24	$8.32 \pm 0.01$
30.0	17.01	$17.15 \pm 0.01$

method of Kolafa.<sup>15</sup> In accordance with the Monte Carlo algorithm for this ensemble,<sup>8</sup> new configurations were generated by moving or changing the size of randomly selected particles. If there resulted in no overlap with other particles, the new configurations were accepted with probability  $(\sigma_{\text{new}}/\sigma_{\text{old}})c_0$ .

In Table I the first three moments as computed from the simulations are compared with those predicted by the three forms of the equation of state. As expected, the equation of Mansoori *et al.* produces the best agreement. Its accuracy is evident when compared with the simulated composition, presented in Fig. 3, although the agreement diminishes somewhat as  $c_0$  increases. This is perhaps due to the fact that at larger values of  $c_0$ , the volume fraction increases and the convergence of the simulations is poorer. It is also seen that as  $c_0$  increases, the composition becomes more peaked. Interestingly, as  $c_0$  approaches infinity the infinitely polydisperse mixture approaches a pure fluid at close packing. The residual chemical potentials, defined as

$$\beta\mu_r(\sigma) = \beta\mu_c(\sigma) - \ln \rho p(\sigma), \quad (28)$$

were calculated by insertion averaging. Two hundred insertions were attempted after every  $2N$  Monte Carlo moves. For hard spheres, the insertion average of a particle of diameter  $\sigma$ ,  $\phi(\sigma)$ , is the fraction of random insertions which result in no overlap with another sphere. The insertion average is of course a monotonically decreasing function of diameter. The intercept at  $\sigma = 0$  is simply the fraction of the volume which is unoccupied, and thus can be expressed in terms of the third moment of the composition distribution:  $\phi(0) = 1 - (\pi/6)\rho s_3$ . The insertion average is related to the residual chemical potential by<sup>16,17</sup>

$$\beta\mu_r(\sigma) = -\ln \phi(\sigma), \quad (29)$$

and thus to the configurational chemical potential by

$$\begin{aligned} \beta\mu_c(\sigma) &= \ln \rho p(\sigma) - \ln \phi(\sigma) \\ &= \ln[\rho^{4/3}K(c_0)] + c_0 \ln(\rho^{1/3}\sigma), \end{aligned} \quad (30)$$

where the last equality results from the fact that the distribution of chemical potential differences is logarithmic; the constant  $K$  defined by this equation is dimensionless. In Fig. 4 is plotted  $p(\sigma)/(\rho^{1/3}\sigma)^{c_0}$  vs  $\phi(\sigma)$ , as determined from the simulations. In accordance with Eq. (30), the dependence is linear with zero intercept. The slopes, equal to  $K$ , are presented in Table II and are compared with the predictions of

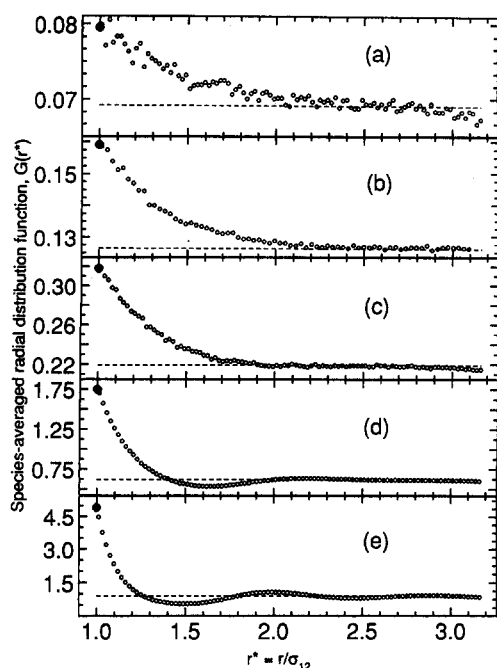


FIG. 5. Species-averaged radial distribution functions, as defined in Eq. (31), plotted against separation reduced by the collision diameter, for several values of  $c_0$ ; (a)  $-0.5$ ; (b)  $0.0$ ; (c)  $1.0$ ; (d)  $10.0$ ; (e)  $30.0$ . The open circles are results of Monte Carlo simulation, and the filled circles represent the value at the contact required to satisfy the consistency equation, Eq. (24). The dashed lines represent the asymptotic values for large separations,  $(s_3 + 3s_1s_2)/4$ .

the equation of state of Mansoori *et al.* The agreement is excellent.

We have also defined a species-averaged radial distribution function,  $G(r^*)$ , which can be used for calculation of the pressure. For a fluid polydisperse in diameters, the pressure equation can be written

$$Z = 1 - \frac{2\pi}{3} \int_0^\infty dr^* r^{*3} \frac{d(\beta u)}{dr^*} \times \left\{ \int_0^\infty d\sigma_1 \int_0^\infty d\sigma_2 \rho \sigma_{12}^3 g(r^*; \sigma_1, \sigma_2) p(\sigma_1) p(\sigma_2) \right\}, \quad (31)$$

where  $g(r; \sigma_1, \sigma_2)$  is the standard radial distribution function, and  $r$  is now reduced by the collision diameter  $r^* = r/\sigma_{12}$ . The quantity in braces defines  $G(r^*)$  which, for infinitely polydisperse mixtures, is invariant with density. For hard particles, the derivative of  $\beta u$  is simply a Dirac  $\delta$  function,  $-\delta(r^* - 1)$ , and thus the compressibility factor is given by

$$Z = 1 + \frac{2\pi}{3} G(1). \quad (32)$$

The simulation averages of the invariant pair correlation function  $G(r^*)$  are presented in Fig. 5. The intercepts at  $r^* = 1$  result in compressibility factors of  $(4 + c_0)/3$ , which provide another verification of the formalism and the simulation algorithm. As with the standard radial distribution function,  $G(r^*)$  approaches a constant value for large  $r^*$ , which in the present case is equal to the third moment of the distribution of collision diameters. This limit can be expressed in terms of the composition moments:  $\langle \sigma_{12}^3 \rangle = (s_3 + 3s_1s_2)/4$ , and is also shown in the figure. The deviations at large values of the separation are due to finite-sample effects.

## V. FLUIDS WITH ATTRACTIVE INTERACTIONS

Energetic parameters cannot be treated as easily as the size parameters were above. In the simplest case,  $\mathbf{I}$  is composed of two species-identifying parameters,  $\sigma$  and  $\epsilon$ , which have dimensions of length and energy, respectively. The notation  $\mathbf{I}$  will be used to represent the set  $\{\sigma, \epsilon\}$  when convenient. In analogy to Eq. (8), the distribution of configurational chemical potential differences can be expressed in the form of a bivariate power series

$$\beta \mu_c(\mathbf{I}) - \beta \mu_c(\mathbf{I}_0) = c_{0(\sigma)} \ln\left(\frac{\sigma}{\sigma_0}\right) + c_{0(\epsilon)} \ln\left(\frac{\epsilon}{\epsilon_0}\right) + \sum_{i,j=0}^{\infty} c_{ij} (\sigma - \sigma_0)^i (\epsilon - \epsilon_0)^j. \quad (33)$$

The coefficient  $c_{00}$  must necessarily be zero. Introduction of Eq. (33) into the fundamental equation yields

$$d(\beta Y) = U d\beta - \beta P dV + \beta \mu(\mathbf{I}_0) dN - N m_{0(\sigma)} dc_{0(\sigma)} - N m_{0(\epsilon)} dc_{0(\epsilon)} - N \sum_{i,j=0}^{\infty} m_{ij} dc_{ij} + N \left[ c_{0(\sigma)} + \sigma_0 \sum_{i,j=0}^{\infty} i c_{ij} m_{(i-1)j} \right] d \ln \sigma_0 + N \left[ c_{0(\epsilon)} + \epsilon_0 \sum_{i,j=0}^{\infty} j c_{ij} m_{i(j-1)} \right] d \ln \epsilon_0, \quad (34)$$

where  $m_{ij}$  is the joint moment of the composition about the  $\mathbf{I}_0$  species

$$m_{ij} \equiv \int_0^\infty d\sigma \int_0^\infty d\epsilon p(\sigma, \epsilon) (\sigma - \sigma_0)^i (\epsilon - \epsilon_0)^j \quad (35a)$$

and

$$m_{0(I)} \equiv \int_0^\infty \ln\left(\frac{I}{I_0}\right) p(I) dI, \quad (35b)$$

where  $I = \sigma$  or  $\epsilon$ ; the composition  $p(I)$ , expressed as a function of one argument, is a marginal distribution in which the other argument has been integrated out. It is evident from Eq. (34) that the coefficients  $c_{ij}$  in the expansion of the configurational chemical potential are thermodynamic conjugates of the moments  $m_{ij}$  of the composition.

As an aside, we note that this formalism has general utility as a basis for the Monte Carlo simulation of polydisperse fluids. In addition to those outlined in Sec. IV, simulations of this type have been performed for particles interacting with the Lennard-Jones potential, with polydispersity exhibited in the size and energy parameters, both individually and together.<sup>8</sup> The study used a Gaussian distribution of activities, in which  $c_2$  was varied over a wide range while all other coefficients were set to zero. Other ensembles can be created by further Legendre transforming some of the  $m_{ij}dc_{ij}$  terms, thereby allowing selected moments of the composition to be imposed, while the overall composition still fluctuates. If  $I$  represents the particle diameter, for example, the third moment may be fixed and simulations performed at constant packing fraction.

In addition to those defined in Sec. III, reduced variables may be defined by

$$\beta^* = \beta\epsilon_0, \quad U^* = U/N\epsilon_0, \quad P^* = P\sigma_0^D/\epsilon_0, \quad \mu^* = \mu/\epsilon_0, \quad c_{ij}^* = c_{ij}\sigma_0^i\epsilon_0^j, \quad m_{ij}^* = m_{ij}/\sigma_0^i\epsilon_0^j.$$

When written in terms of these quantities, the fundamental equation becomes

$$\begin{aligned} d(\beta Y) = & U^* d\beta^* - \beta^* P^* dV^* + \beta^* \mu^* (\mathbf{I}_0) dN - N \left[ m_{0(\sigma)} dc_{0(\sigma)} + m_{0(\epsilon)} dc_{0(\epsilon)} + \sum_{i,j=0}^{\infty} m_{ij} dc_{ij}^* \right] \\ & + N \left[ -DZ + c_{0(\sigma)} + \sum_{i,j=0}^{\infty} ic_{ij}^* (m_{i-1j}^* + m_{ij}^*) \right] d \ln \sigma_0 \\ & + N \left[ -\beta^* U^* + c_{0(\epsilon)} + \sum_{i,j=0}^{\infty} jc_{ij}^* (m_{i(j-1)}^* + m_{ij}^*) \right] d \ln \epsilon_0. \end{aligned} \quad (36)$$

As before, the partition function can be rewritten in a dimensionless form, in which all lengths and energies are reduced by the reference-component length and energy scales,  $\sigma_0$  and  $\epsilon_0$ . It can similarly be shown that its dependence on  $\sigma_0$  and  $\epsilon_0$  is solely through multiplicative terms of the form  $\sigma_0^{N(D+1)}\epsilon_0^N$ . Consistency equations may again be derived, and are given by

$$D(Z-1) = 1 + c_{0(\sigma)} + \sum_{i,j=0}^{\infty} ic_{ij} (m_{i-1j}^* + m_{ij}^*) \quad (37a)$$

and

$$\beta^* U^* = 1 + c_{0(\epsilon)} + \sum_{i,j=0}^{\infty} jc_{ij}^* (m_{i(j-1)}^* + m_{ij}^*). \quad (37b)$$

It is not possible to obtain the infinitely polydisperse limit of Eqs. (37a) and (37b) by simply setting all the non- $c_0$  terms to zero. Arbitrarily large values of the energy parameters would then be allowed, resulting in the divergence of some of the moments  $m_{ij}$ , even with  $c_{0(\epsilon)}$  chosen to be less than zero. Thus, some of the products  $c_{ij}m_{ij}$  would not necessarily vanish, and it is likely that they too would diverge. As shown above for hard rods and spheres, this is not the case for length parameters, which are limited by packing constraints. This is not a practical difficulty because the energy parameter of a particular species is invariably correlated with its size, a fact that we can also apply here. To avoid the introduction of any new characteristic lengths or energies, this dependence must be of the form

$$\epsilon = \epsilon_0 \left( \frac{\sigma}{\sigma_0} \right)^\alpha. \quad (38)$$

The consistency equation becomes

$$\begin{aligned} D(Z-1) + \alpha\beta^* U^* = & 1 + c_{0(\sigma)} \\ & + \sum_{n=1}^{\infty} nc_n^* (m_n^* + m_{n-1}^*), \end{aligned} \quad (39)$$

where the chemical potential distribution is in terms of  $\sigma$

alone. The infinitely polydisperse case follows from this, and any reduced parameters will have the same value for all states of equal  $\beta\rho^{-\alpha/D}$ .

It would be highly desirable to be able to allow the energy parameters to fluctuate independently of the size parameters, because then, given values for the set of  $c_0$ 's, the entire thermodynamic space of temperature and density would be described by a single point in that space. Unfortunately, it does not seem possible to do this. However, the concept of an infinitely polydisperse mixture is still of great value, because with it the thermodynamic space necessary to describe the fluid is reduced from the  $\beta$ - $\rho$  plane to the axis  $\beta\rho^{-\alpha/D}$ .

A general form for the consistency equation, applicable in the case of more than two simultaneously distributed parameters, is presented in the Appendix.

## VII. DISCUSSION

Since there is no restriction on the form of the intermolecular potential required to derive consistency equations and to define infinitely polydisperse mixtures, there is large and diverse set of systems to which these ideas can be applied. A simple example is provided by a fluid of "soft" spheres, which interact according to the purely repulsive potential:

$$u(r) = \epsilon \left( \frac{\sigma}{r} \right)^n. \quad (40)$$

The internal energy and the compressibility factor of the soft-sphere fluid are trivially related:

$$Z = 1 + \frac{n}{3}\beta U. \quad (41)$$

The model has only one parameter— $\epsilon\sigma^n$ —and thus  $\epsilon$  and  $\sigma$  cannot vary independently. Imposing the dependence given by Eqs. (38), (39), and (41) can be combined, yielding exact expressions for the energy and the pressure:

$$\beta U = \frac{1}{n + \alpha}, \quad (42a)$$

$$Z = 1 + \frac{n}{3(n + \alpha)}. \quad (42b)$$

The hard sphere result,  $Z = 4/3$ , is recovered in the limit  $n \rightarrow \infty$ .

The formalism is not restricted to pairwise additive or to centrally symmetric potentials.<sup>10</sup> Equations are presented in the Appendix for application of these ideas to systems with an arbitrary number of length and energy parameters, and hence an arbitrary degree of complexity. Rigorous consistency equations may always be derived, and, within the bounds discussed in Sec. V, the infinitely polydisperse case may be used to produce an analytic equation of state. These results also hold, with minor modifications, when the limit of infinite polydispersity is taken at constant pressure instead of constant number density. The only characteristic length in the isobaric case is  $(\beta P)^{-1/D}$ . Alternatively, if only the volume of the system and the value of the logarithmic chemical potential distribution at one  $\mathbf{I}$  are fixed, in the grand-canonical representation, then  $\rho$  is determined through Eq. (30).

In summary, we have described a novel class of mixtures, which we term infinitely polydisperse, that have convenient scaling properties. The formalism upon which these fluids are based is a semigrand ensemble, in which the distribution of chemical potential differences is an independent quantity. By imposing a distribution which depends logarithmically upon the species-identifying parameters, length and energy scales characteristic of individual molecules are removed. Infinitely polydisperse fluids represent a subset of the class of generalized conformal fluids, and indeed this is the origin of their scaling properties. Their unique feature is that there remains only *one* independent length scale, even though there are many components in the mixture. This allows their properties to be easily cataloged, and even permits some to be determined analytically. Consequently, this type of model system can play the role for mixtures that the hard sphere system holds for pure fluids. In future work,<sup>10</sup> we will present a perturbation theory based upon an infinitely polydisperse reference, that is successful in the description of a wide variety of mixtures, polydisperse, discrete, and even pure fluids.

## ACKNOWLEDGMENT

This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences.

## Appendix: Potentials with more than two parameters

In the preceding derivations, all lengths and energies were scaled by the parameters  $\sigma_0$  and  $\epsilon_0$ , which were factored

from the partition function to derive the consistency equations, and which were eliminated from the equations in the limit of infinite polydispersity. If the intermolecular potential depends upon additional dimensional parameters, either lengths or energies, these must also be scaled. This can be accomplished in two ways. For example, consider a system in which the molecules are characterized by two length parameters,  $\sigma$  and  $\sigma'$ . The parameter  $\sigma'$  may be treated as  $\sigma$ , and the partition function integrated over all  $\sigma$  and  $\sigma'$ , weighted by an imposed distribution  $\mu_c(\sigma, \sigma') - \mu_c(\sigma_0, \sigma'_0)$ . Alternatively, the value of  $\sigma'$  for each molecule may be reduced by the value of  $\sigma$  for that molecule, so that  $\sigma'$  is essentially replaced by the new variable  $\sigma'/\sigma$ , a dimensionless aspect ratio. This ratio may be fixed at a particular value or may be made to fluctuate independently of  $\sigma$ . Depending upon which approach is used to reduce  $\sigma'$ , the consistency equation will be different.

We shall now consider the general case of an arbitrary number of size and energy parameters. As in Sec. II, let  $\nu$  represent the number of species-identifying parameters in  $\mathbf{I}$ , and let the  $i$ th parameters in  $\mathbf{I}$  have units of (length) <sup>$D a_i$</sup> (energy) <sup>$b_i$</sup> , which defines the set of parameters  $\{a_i\}$  and  $\{b_i\}$ , some of which may be zero. The distribution of configurational chemical potential differences may be expressed in the form of a generalized power series, again including logarithmic terms:

$$\begin{aligned} \beta\mu_c(\mathbf{I}) - \beta\mu_c(\mathbf{I}_0) &= \sum_{j=1}^{\nu} c_{0(j)} \ln\left(\frac{I_j}{I_{j0}}\right) + \sum_{n_1=0}^{\infty} \cdots \sum_{n_{\nu}=0}^{\infty} c_{n_1 n_2 \cdots n_{\nu}} \prod_{j=1}^{\nu} (I_j - I_{j0})^{n_j}. \end{aligned} \quad (\text{A1})$$

The independent variables are represented by the components of  $\mathbf{I}_0$  and the set of coefficients  $c_{0(j)}$  and  $c_{ij \cdots n}$ , with  $c_{00 \cdots 0} \equiv 0$ .

Characteristic molecular length and energy parameters  $\sigma_0$  and  $\epsilon_0$  can be constructed from two arbitrary species-identifying parameters, labeled  $\mathbf{I}_1$  and  $\mathbf{I}_2$ . Then  $\sigma$  and  $\epsilon$  are defined

$$\begin{aligned} \sigma &\equiv \left[ \frac{I_1}{I_2^{b_1/b_2}} \right]^{b_2/D(a_1 b_2 - a_2 b_1)}, \\ \epsilon &\equiv \left[ \frac{I_1^{a_2/a_1}}{I_2} \right]^{a_1/(a_2 b_1 - a_1 b_2)}. \end{aligned} \quad (\text{A2})$$

With  $\sigma_0$  and  $\epsilon_0$  used to reduce all quantities, the fundamental equation is written in dimensionless form

$$\begin{aligned} d(\beta Y) &= U^* d\beta^* - \beta^* P^* dV^* + \beta^* \mu^*(\mathbf{I}_0) dN - N \sum_{j=1}^{\nu} m_{0(j)} dc_{0(j)} - N \sum_{n_1=0}^{\infty} \cdots \sum_{n_{\nu}=0}^{\infty} m_{n_1 n_2 \cdots n_{\nu}}^* dc_{n_1 n_2 \cdots n_{\nu}} \\ &+ N \sum_{j=3}^{\nu} \left[ c_{0(j)} + \sum_{n_1=0}^{\infty} \cdots \sum_{n_{\nu}=0}^{\infty} n_j c_{n_1 n_2 \cdots n_{\nu}}^* m_{n_1 \cdots (n_j-1) \cdots n_{\nu}} \right] d \ln I_j^* \\ &+ N \left[ -DZ + \sum_{j=1}^{\nu} a_j T_j \right] d \ln \sigma_0 + N \left[ -\beta U + \sum_{j=1}^{\nu} b_j T_j \right] d \ln \epsilon_0, \end{aligned} \quad (\text{A3})$$



where  $T_j$  is defined

$$T_j \equiv c_{0(j)} + \sum_{n_1=0}^{\infty} \cdots \sum_{n_v=0}^{\infty} n_j c_{n_1 \cdots n_v} (m_{n_1 \cdots n_v}^* + I_{j0}^* m_{n_1 \cdots (n_j-1) \cdots n_v}^*) \quad (\text{A4})$$

Also,  $m_{ij \cdots k}$  is the joint moment

$$m_{n_1 n_2 \cdots n_v} \equiv \int_{\Omega} p(\mathbf{I}) \prod_{j=1}^v (I_j - I_{j0})^{n_j} d\mathbf{I} \quad (\text{A5a})$$

and

$$m_{0(j)} \equiv \int_{\Omega} \ln\left(\frac{I_j}{I_{j0}}\right) p(I_j) dI_j \quad (\text{A5b})$$

As outlined in Sec. III, the partition function may also be manipulated to isolate a single length and a single energy scale. As done in Secs. III and V, it can then be shown that the dependence of the partition function upon  $\sigma_0$  and  $\epsilon_0$  is again through multiplicative terms:  $\sigma_0^{ND(1+a)} \epsilon_0^{Nb}$ , where  $a = \sum_j a_j$  and  $b = \sum_j b_j$ . Thus, with Eq. (A3), a generalized set of consistency equations may be written

$$(Z - 1) = \sum_{j=1}^v a_j (1 + T_j), \quad (\text{A6a})$$

$$\beta^* U^* = \sum_{j=1}^v b_j (1 + T_j). \quad (\text{A6b})$$

For the infinitely polydisperse case,  $T_j = c_{0(j)}$ , and these become analytic equations of state. As discussed in the previous section, care must be exercised with infinitely polydisperse energy parameters. If the energy scale is coupled to the length scale through a dependence of the form Eq. (38),

then there is a single consistency equation

$$(Z - 1) + \alpha \beta^* U^* = \sum_{j=1}^v (a_j + ab_j) (1 + T_j). \quad (\text{A7})$$

<sup>1</sup>Th. De Donder, *L'Affinite* (deuxieme partie) (Gauthier-Villars, Paris, 1931).

<sup>2</sup>R. Aris and G. R. Gavalas, *Philos. Trans. R. Soc. London Ser. A* **260**, 351 (1966).

<sup>3</sup>J. J. Salacuse and G. Stell, *J. Chem. Phys.* **77**, 3715 (1982); J. J. Salacuse, *ibid.* **81**, 2468 (1984); G. Stell and P. A. Rikvold, *Chem. Eng. Commun.* **51**, 233 (1987).

<sup>4</sup>J. A. Gualtieri, J. M. Kincaid, and G. Morrison, *J. Chem. Phys.* **77**, 521 (1982); K. A. Johnson, D. A. Jonah, J. M. Kincaid, and G. Morrison, *ibid.* **82**, 5178 (1985).

<sup>5</sup>R. McRae and A. D. J. Haymet, *J. Chem. Phys.* **88**, 1114 (1988).

<sup>6</sup>For an application of conformal solution theory to polydisperse systems, see E. Dickinson, *J. Chem. Soc. Faraday Trans 2* **76**, 1458 (1980).

<sup>7</sup>J. G. Briano and E. D. Glandt, *J. Chem. Phys.* **80**, 3336 (1984).

<sup>8</sup>D. A. Kofke and E. D. Glandt, *J. Chem. Phys.* **87**, 4881 (1987).

<sup>9</sup>J. M. Kincaid, G. Morrison, and E. Lindeberg, *Phys. Lett. A* **96**, 471 (1983); J. M. Kincaid, R. A. MacDonald, and G. Morrison, *J. Chem. Phys.* **87**, 5425 (1987).

<sup>10</sup>D. A. Kofke and E. D. Glandt (to be published).

<sup>11</sup>J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**, 1 (1958); E. Thiele, *J. Chem. Phys.* **39**, 474 (1963); M. S. Wertheim, *Phys. Rev. Lett.* **10**, 321 (1963).

<sup>12</sup>J. I. Lebowitz, *Phys. Rev. A* **133**, 895 (1964); L. Blum and G. Stell, *J. Chem. Phys.* **71**, 42 (1979); **72**, 2212(E) (1980); A. Vrij, *ibid.* **71**, 3267 (1979).

<sup>13</sup>N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).

<sup>14</sup>G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, Jr., *J. Chem. Phys.* **54**, 1523 (1971).

<sup>15</sup>J. Kolafa, *Mol. Phys.* **59**, 1035, (1986).

<sup>16</sup>B. Widom, *J. Chem. Phys.* **39**, 2805 (1963).

<sup>17</sup>This relation is strictly correct only for canonical-ensemble simulations. As discussed in Ref. 8, with semigrand-ensemble simulations it is necessary to first compute  $\mu(I_0)$  by integrating the insertion averages over all diameters. The full distribution  $\mu(I)$  then follows from the imposed distribution of chemical potential differences. However, in practice it is usually permissible to apply Eq. (12) regardless of the ensemble; the fact that  $\phi(\sigma)$  is linearly related to  $p(\sigma)/\sigma^{z_i}$  indicates that this is the case here.