

# Free Energy of Multicomponent Systems Employing Partial NNPf's

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A new scheme analogous to that employed for the determination of the free energy of classical single-component systems, with arbitrary many-body interaction potentials at arbitrary densities and temperatures, is extended to classical multicomponent systems. Self-consistency of the scheme has been shown for some limiting conditions, including the noninteraction limit. Thermodynamic expressions are obtained which are natural extensions of those for the single-component case and readily reduce to their correct forms in the single-component limit. Application to the simple case of low-density mixtures of hard particle gases in 3-D is outlined. It is expected (as in the single-component case) that progressive application to more complex systems (such as quantum mixed systems) will be done under a single mathematical framework, as provided in this paper.

## I. Introduction

By following procedures identical to those of a previous paper,<sup>1</sup> we have developed a new scheme analogous to that for single-component systems for the determination of the free energy of classical multicomponent systems with arbitrary many-body interaction potentials and at arbitrary densities and temperatures. The concepts of generalized order and the reduced one-particle phase space, employed for single-component systems, are found to appear in an identical manner in the counterpart scheme for multicomponent systems. Statistical arguments, which led to the notion of NNPf's (nearest-neighbor probability density functions) for single-component systems, are seen to lead to analogous probability distributions, which are now termed PNNPf's (partial NNPf's), for multicomponent systems. PNNPf's have, however, not been fully developed in the present paper for interacting systems. Their full development is deferred to a subsequent paper. The formalism developed is therefore applied, at this time, only to low-density systems in an approximate fashion. It is also argued that the new scheme (for determining the free energy) remains valid for long-range interparticle interaction potentials provided overall charge neutrality among particles of different species remains (thus giving credence to the suitability of the scheme for a variety of realistic material systems).

In another recent work,<sup>2</sup> the above "exact" scheme is shown to converge and to provide the well-known exact result for the free energy of single-component hard rod fluids in 1-D. The use of NNPf's (or PNNPf's) in the investigation of fluids and material systems has had some attention but with little written in the literature. As far back as 1956, Reiss<sup>3</sup> used the first nearest-neighbor distribution functions (ordinarily used for single-component systems) to analyze a two-component system after suitable modifications. The distribution functions allowed for the formulation of the degree of "pairing" between oppositely charged ions in a material medium. Other works involving the

use of NNPf's (mainly for single components) have also been carried out by a number of authors and some reviews are provided by Bhattacharjee,<sup>4</sup> Edgal and Huber,<sup>2</sup> and Torquato.<sup>4</sup> (See also ref 5 where the above exact scheme has been applied in approximate fashions for some simple but realistic single-component systems).

Other methods<sup>6</sup> for investigating multicomponent systems are also available in the literature and are known to usually provide varying degrees of success. These methods, which include such schemes as perturbational and variational techniques, density functional and integral equation methods, graphical expansion schemes, conformal solution theories, etc., occasionally bear some similarity (though not directly the same method) with the new scheme of this paper (employing NNPf's). See, in particular, ref 7.

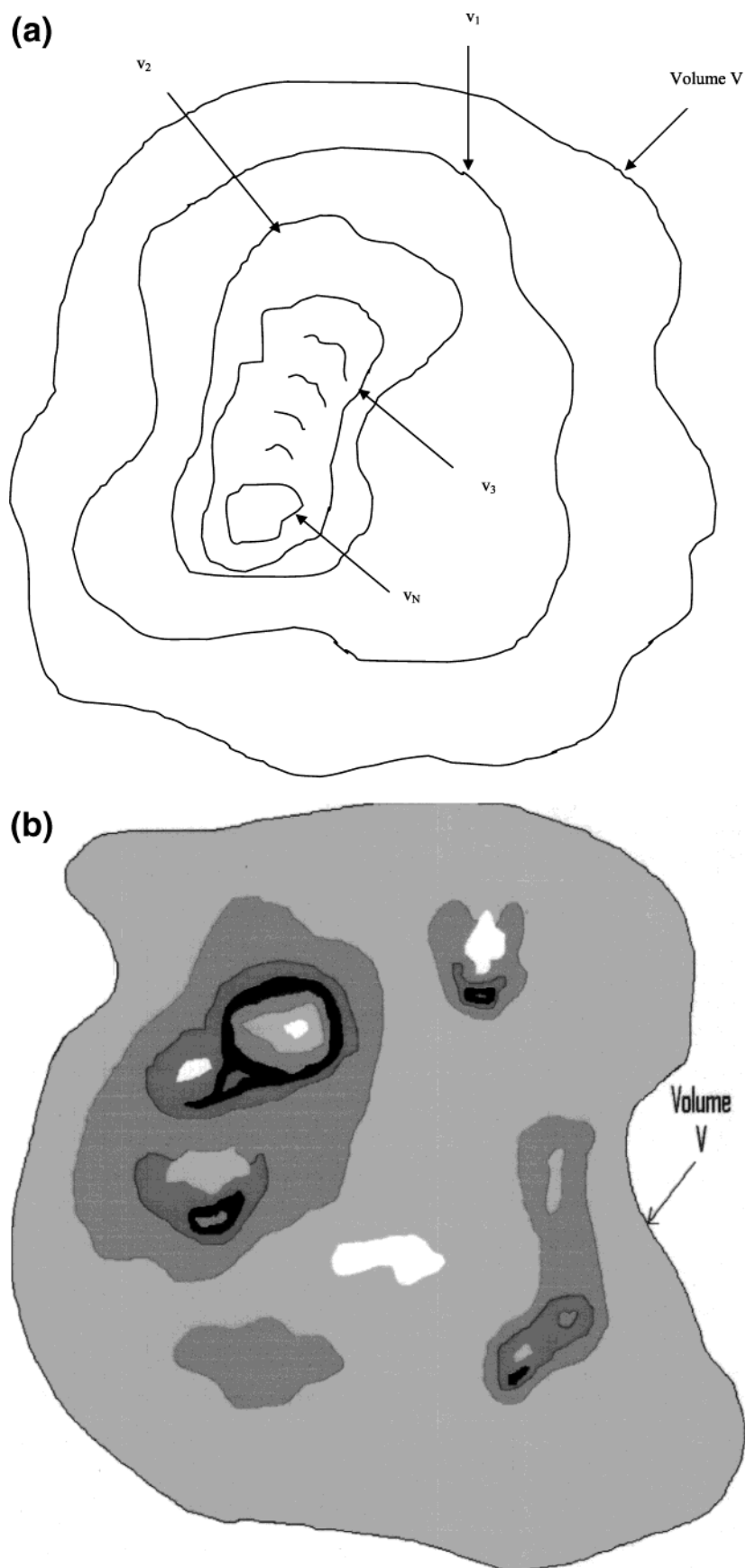
In section II, the notion of generalized order (used for evaluating the multidimensional integral for the partition function) is encountered, whereby the following may be recalled from Edgal.<sup>1</sup> If  $v_n$  may be regarded as the set of points which have "currently" been "visited" (or traced out) by the  $n^{\text{th}}$  labeled particle (in the multidimensional integral), then the generalized ordering scheme ensures that the  $(n + 1)^{\text{th}}$  labeled particle may trace out the set of points satisfying the relation  $\varnothing \subseteq v_{n+1} \subseteq v_n$ . It is assumed that  $N$  particles (some of which may be of different species for multicomponent systems), reside in volume  $V$ , and are labeled 1,2,..., $N$ . (The notation  $A \subseteq B$  implies that  $A$  contains points which are a subset or are equivalent to the set of points contained in  $B$ ).  $\varnothing$  is the null set. The  $v_i$ 's are not limited to being simply connected sets but may be multiply connected in general. In a second form of the generalized ordering scheme,  $v_n$  is taken as the set of points that may *not* currently be visited (or traced out) by the  $n^{\text{th}}$  labeled particle. Hence, generalized order ensures in this case that the points containing the  $(n + 1)^{\text{th}}$  particle may *not* currently trace out, satisfy the relation  $v_n \subseteq v_{n+1} \subseteq V$ . (Clearly, the above relations are seen as extensions of the simple ordering scheme that employs the notations  $>$  or  $<$  for magnitudes).

See Figure 1 for an illustration of the generalized ordering scheme. Figure 1a is the simple case where the volumes  $V$ ,  $v_1$ ,  $v_2$ , ... constitute simply connected regions. In the first form of

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**Figure 1.** (a) Illustration of the generalized ordering scheme for the simple case where at any stage of the ordering process, the volumes  $V$ ,  $v_1$ ,  $v_2$ , ... constitute *simply* connected sets. (See text for further description). (b) Illustration of the generalized ordering scheme for the *more general* case where at any stage of the ordering process, the volumes  $V$ ,  $v_1$ ,  $v_2$ , ... may constitute *multiply* connected sets. (See text for further description).

the generalized ordering scheme, the volumes  $v_1, v_2, \dots$  (at any stage of the generalized ordering scheme) are *enclosed within* the correspondingly labeled boundaries. In the second form of the generalized ordering scheme, the volumes  $v_1, v_2, \dots$  (at any stage of the generalized ordering scheme) are all regions within volume  $V$ , except regions enclosed within the correspondingly labeled boundaries.

Figure 1b, on the other hand, is the more general case where volumes  $V, v_1, v_2, \dots$  may constitute multiply connected regions. For simplicity, only volumes  $V, v_1, v_2$ , and  $v_3$  are shown using different shades of gray. Five shades of gray are shown. The lightest shade of gray (clear or white), called gray-0, depicts *voids* in volume  $V$  where particle centers may never visit. The next deeper shade of gray, called gray-1, depicts the region of volume  $V$ . The next deeper shade of gray, called gray-2 (said to be contained within gray-1 region) is used to determine region  $v_1$ . The next deeper shade of gray, called gray-3 (said to be contained within gray-2 region) is used to determine region  $v_2$ . Finally, the deepest shade of gray (dark or black), called gray-4 (said to be contained within gray-3 region) is used to determine region  $v_3$ . Observe that all regions covered by gray- $n$  are also covered by gray- $(n-1)$ , gray- $(n-2)$ , ..., gray-1 (where  $n = 2, 3$ , and 4 for our special case). In the *first form* of the generalized ordering scheme, for a given stage of the ordering scheme, regions colored gray-2 represent volume  $v_1$ , regions colored gray-3 represent volume  $v_2$ , and regions colored gray-4 represent volume  $v_3$ . In the *second form* of the generalized ordering scheme (and for a given stage of the ordering scheme), regions outside gray-2 but within volume  $V$  (or gray-1) represent volume  $v_1$ , regions outside gray-3 but within volume  $V$  represent volume  $v_2$ , and regions outside gray-4 but within volume  $V$  represent volume  $v_3$ . (The reader may mentally conceive of more shades of gray to represent  $v_4, v_5, \dots, v_N$ ).

Statistical arguments which lead to the notion of PNNPDF's are also provided in section II. The concept of the "reduced" one-particle phase space, along with developments in section II, are used to provide in section III an iterative scheme (involving use of local neighborhood MCMD calculations) for calculating partition functions for multicomponent systems. Also in section III, other matters are treated, such as the issue of the allowed range for interparticle interaction potentials, reformulation for the law of mass action for equilibrium mixtures in the presence of interactions, etc. Application of the above formalism to low-density interacting gas mixtures in 3-D is subsequently given in section IV. PNNPDF's for the poisson gas mixture are given in this section and these are used in providing the equation of state for *binary mixtures of hard spheres* at low densities. The second virial coefficient obtained from this result is in exact agreement with that of the literature. In the Appendix, some consistency arguments are given, showing that known exact results are reproduced by the scheme in certain limiting conditions. A brief summary of the scheme of this paper is also presented in the Appendix for the single (pure) component case to help the reader.

## II. Some Statistical Notions for Multicomponent Systems

The developments in a previous paper<sup>1</sup> are closely followed (with some necessary extensions) to determine partition functions for multicomponent systems. Consider a multicomponent system with  $n$  constituents in a volume  $V$  with the  $i^{\text{th}}$  constituent having  $N_i$  particles. The total number of particles is  $N_1 + N_2 + \dots + N_n = N$ . Partial densities involve  $\rho_i = N_i/V$ . The classical partition function for this system is  $\tilde{Z}(N_1, N_2, \dots, N_n, V)$ . We may write  $h^N \tilde{Z}(N_1, \dots, N_n, V) = Z(N_1, \dots, N_n, V)$  where:

$$Z(N_1, N_2, \dots, N_n, V) = \frac{1}{N_1! N_2! \dots N_n!} \int \dots \int e^{-\beta E(\bar{X}_{k_1}, \bar{X}_{k_2}, \dots, \bar{X}_{k_N})} d\bar{X}_{k_1} d\bar{X}_{k_2} \dots d\bar{X}_{k_N} \quad (1)$$

$h$  is Planck's constant,  $f_N$  may be written as  $c_1 N_1 + c_2 N_2 + \dots + c_n N_n$ , where  $c_i$  is an appropriately chosen integer so that  $\tilde{Z}(N_i) = Z(N_i)/h^{c_i N_i}$  is dimensionless. It follows also that  $\tilde{Z}(N_1, \dots, N_n, V) = Z(N_1, \dots, N_n, V)/h^N$  is dimensionless.  $E(\bar{X}_{k_1}, \bar{X}_{k_2}, \dots, \bar{X}_{k_N})$  is energy for a given microstate.  $\bar{X}_{k_i}$  ( $i = 1, 2, \dots, N$ ) are the canonical coordinates of particles and are *not ordered in the generalized sense*. The first subscript  $k_i$  indicates the species of particle associated with a coordinate variable and, hence, may assume any of the values  $1, 2, \dots, n$ . When all coordinates are displayed in a group (such as in the argument for the energy  $E$ ), there must be exactly  $N_j$  of the coordinates for which the first subscript of the coordinates assumes the value  $j$ . (This is because there are  $N_j$  particles of the  $j^{\text{th}}$  species).  $\beta = 1/k_B T$  where  $k_B$  is Boltzmann constant and  $T$  is temperature. A coordinate  $\bar{X}_{k_i}$  may be represented as  $(\bar{r}_{k_i}, \bar{l}_{k_i})$  where  $\bar{r}_{k_i}$  and  $\bar{l}_{k_i}$  stand for the translational and internal coordinates, respectively. (Internal coordinates are said to include all canonically conjugate coordinates). The coordinates may next be partially ordered (as in the previous subsection, see also Edgall<sup>1</sup>) and, hence, written as  $X'_{k_i} = (r'_{k_i}, l_{k_i})$  with  $i = 1$  for the first labeled particle,  $i = 2$  for the second labeled particle, ...,  $i = N$  for the  $N^{\text{th}}$  labeled particle. As indicated above, there may be  $N_j$  of the coordinates  $X'_{k_i}$  ( $i = 1, 2, \dots, N$ ) with  $k_i = j$  (for the  $j^{\text{th}}$  species). The volume traced out by the translational portion of the coordinate of the  $i^{\text{th}}$  labeled particle (ie.,  $r'_{k_i}$ ) which may be of any species may be written as  $v_i$ . The volume  $v_i$  may be said to have the following property (according to the first version of the generalized ordering scheme for instance)  $0 \leq v_i \leq v_{i-1}$  for  $i = 1, 2, \dots, N$  (where  $v_0 = V$ ). Eq 1 may therefore be written in terms of the new coordinates as

$$Z(N_1, N_2, \dots, N_n, V) = \sum_{k_1, \dots, k_N} \int \dots \int e^{-\beta E} \prod_{i=1}^N dX'_{k_i} \quad (2)$$

where the sum is over different distinct combinations of allowed  $k_1, \dots, k_N$  values. (Remember that exactly  $N_j$  of the  $k_i$ 's must assume the value  $j$ ). This implies a total of  $(N!)/(N_1! \dots N_n!)$  terms for the sum. (This is actually the number of distinct ways the particles may be relabeled or assigned to the volumes  $v_1, \dots, v_N$ ).

These terms can be grouped as follows: the  $i^{\text{th}}$  group ( $i = 1, \dots, n$ ) has terms for which the first labeled particle associated with the volume  $v_1$  is a particle of the  $i^{\text{th}}$  species (ie.,  $k_1 = i$ ). The  $i^{\text{th}}$  group involves  $[(N-1)!]/[N_1! \dots (N_i-1)! \dots N_n!]$  terms. Eq 2 may therefore be written as

$$Z(N_1, N_2, \dots, N_n, V) = \sum_{m=1}^n \int [ \sum_{k_2, \dots, k_N} \int \dots \int e^{-\beta E} \prod_{i=2}^N dX'_{k_i} ] dX'_{m1} \quad (3)$$

The first group discussed above involves the  $m = 1$  summand of the outer sum of eq 3, the second group involves the  $m = 2$  summand of the outer sum, etc.

Clearly, the square brackets of the  $j^{\text{th}}$  summand involves integrating the Boltzmann factor over the possible distinct configurations of all particles (excluding the particle of the  $j^{\text{th}}$  species, which is the first labeled particle) in volume  $v_1$  traced out by the translational coordinates  $r'_{j1}$  of the excluded particle. This is the partition function (including the factor  $h^{N-c_j}$ ) for

the  $N - 1$  particles (ie., the 2nd labeled, 3rd labeled, ...,  $N^{\text{th}}$  labeled particles) in volume  $v_1$ , with the first labeled particle providing an external field (or influence).

The energy,  $E$ , in the square brackets of the  $j^{\text{th}}$  summand may be split up as  $E = E_{j1} + E_{j2}$ , where  $E_{j1}$  is energy of the system for a given microstate when interaction with the first labeled particle (of the  $j^{\text{th}}$  species) is turned off and  $E_{j2}$  is the contribution when interaction with the first labeled particle (of the  $j^{\text{th}}$  species) is turned on for a given micro-state. Hence, the  $j^{\text{th}}$  term involving the  $j^{\text{th}}$  summand of eq 3 may be rewritten as

$$\int \left[ \sum_{k_2, \dots, k_N} \int \dots \int e^{-\beta(E_{j1} + E_{j2})} \prod_{i=2}^N dX'_{ki} \right] dX'_{j1} = \int Z(N_1, \dots, N_{j-1}, N_j - 1, N_{j+1}, \dots, N_n, v_1) \times \left[ \sum_{k_2, \dots, k_N} \int \dots \int g'_{X'_{j1}}(X'_{k_2}, X'_{k_3}, \dots, X'_{k_N}) e^{-\beta E_{j2}} \prod_{i=2}^N dX'_{ki} \right] dX'_{j1} \quad (4)$$

$Z(N_1, \dots, N_{j-1}, N_j - 1, N_{j+1}, \dots, N_n, v_1)$  is the partition function (including the factor  $h^{f_{N-j}}$ ) for the  $N - 1$  particles (ie., the 2nd labeled, 3rd labeled, ...,  $N^{\text{th}}$  labeled particles) in volume  $v_1$  (remember interactions with the first labeled particle is excluded).  $g'_{X'_{j1}}(X'_{k_2}, \dots, X'_{k_N})$  is the probability density of a given configuration of the  $N - 1$  particles (in volume  $v_1$ ) for given value of  $X'_{j1}$ , and this may be expressed as

$$g'_{X'_{j1}}(X'_{k_2}, \dots, X'_{k_N}) = \frac{\exp(-\beta E_{j1})}{\sum_{k_2, \dots, k_N} \int \dots \int \exp(-\beta E_{j1}) \prod_{i=2}^N dX'_{ki}}$$

(The volume over which the translational parts of the variables  $X'_{ki}$  are restricted in the denominator integral is  $v_1$ ). The derivation of the above probability density function assumes no interaction between the first labeled particle and other particles.

As in the previous paper,<sup>1</sup> the term in square brackets on the right-hand side (rhs) of eq 4 is the average of  $e^{-\beta E_{j2}}$  (written as  $p_j(X'_{j1}, v_1)$ ) over the phase space  $Z(N_1, \dots, N_{j-1}, N_j - 1, N_{j+1}, \dots, N_n, v_1)$ . This quantity depends on  $v_1$  and the coordinate  $X'_{j1}$  in general, and the functional form the quantity is said to have depends on the species (which, in this case, is  $j$ ) whose particle is said to be the first labeled particle (hence the subscript  $j$ ). Also, as in the previous paper,<sup>1</sup>  $E_{j2}$  is expected to depend mainly on the coordinates of the first few nearest neighbors of the origin (said to be situated at  $X'_{j1}$ ). Hence  $p_j(X'_{j1}, v_1)$  may be written in terms of NNPDF's as

$$p_j(X'_{j1}, v_1) = \sum_{(l)} \int \dots \int g_{X'_{j1}}^{(l)}(X_{k_1}, X_{k_2}, \dots, X_{k_m}) e^{-\beta E_{j2}} \prod_{i=1}^m dX_{ki} \quad (5)$$

where  $X_{ki} = (r_{ki}, I_{ki})$ . Note that the energy  $E_{j2}$  may now be rewritten in terms of the  $X_{ki}$  coordinates.  $g_{X'_{j1}}^{(l)}(X_{k_1}, X_{k_2}, \dots, X_{k_m})$  is referred to as a "partial NNPDF", and it is the probability density for the occurrence of the  $i^{\text{th}}$  nearest neighbor of species  $k_i$  (with internal coordinates  $I_{ki}$ ) at  $r_{ki}$  (relative to the origin at  $r'_{j1}$ ), for  $i = 1, \dots, m$ . Clearly, the PNNPDF describes a "general multicomponent point process" (the analogue of the general point process for pure systems)<sup>1</sup> since interaction between the particle at the origin  $X'_{j1}$  and its nearest neighbors are excluded.

Observe also that the  $X_{ki}$  coordinates are automatically partially ordered since they describe nearest-neighbor configurations requiring  $|r_{ki}| \leq |r_{kj}|$  for  $j > i$ . The superscript  $(l)$  in the PNNPDF indicates a specific choice of values for  $k_1, k_2, \dots, k_m$  (This indicates a specific choice as to which species may be said to constitute the first nearest neighbor, second nearest neighbor, etc.). The number of such choices (which is the number of terms in the sum of eq 5) that may be made is clearly seen to be  $n^m$  (This assumes  $m \leq N_i$  for  $i = 1, 2, \dots, n$ , and hence, the choice of species for the first, second, etc. nearest neighbor may each be made in  $n$  ways). If  $e^{-\beta E_{j2}}$  is set equal to unity in eq 5, the normalization condition on the PNNPDF's requires the sum of eq 5 to add up to unity.  $p_j(X'_{j1}, v_1)$  may be evaluated employing methods which are ready extensions of those (including the numerical scheme) suggested for evaluating  $p(X'_{j1}, v_1)$  of the previous paper<sup>1</sup> on single-component systems. Following steps similar to those of the previous paper, the average of  $p_j(X'_{j1}, v_1)$  over the phase space  $\Omega_j dv_1$  (where  $\Omega_j$  is the size of space of the internal coordinates of  $X'_{j1}$  of the  $j^{\text{th}}$  species) may be determined and written as  $\langle p_j \rangle$ ; this may be seen to be a function of  $v_1$  with a functional form depending on the species  $j$  (whose particle is said to be the first labeled particle). Equation 3 may therefore be rewritten as

$$Z(N_1, N_2, \dots, N_n, V) = \sum_{i=1}^n \int_0^V Z(N_1, \dots, N_{i-1}, N_i - 1, N_{i+1}, \dots, N_n, v_1) \langle p_i \rangle \Omega_i dv_1 \quad (6)$$

In simple cases (as for single-component systems),  $\langle p_i \rangle$  may be replaced by  $p_i(X'_{i1}, v_1)$ , which is expected to depend on  $v_1$  only. A detailed discussion for PNNPDF's in interacting systems is not provided in this paper but is deferred to a subsequent paper. Suffice it to say that similar to single-component systems, an accurate knowledge of  $Z(N_1, \dots, N_n, V)$  is expected to lead to an accurate formulation of PNNPDF's (for the ordinary and general multicomponent point processes).

### III. Free Energy Determination and Other Developments for Equilibrium Mixtures

An iterative scheme is next provided for accurately obtaining  $Z(N_1, \dots, N_n, V)$ . Because of its similarity with that of the more simple case for single-component systems, a brief summary of the iterative scheme for pure systems<sup>1,8</sup> is given in the Appendix to help the reader. First, it is clear, as in the case for single-component systems, that  $Z(N_1, \dots, N_n, V)$  has a dimension of  $\prod_{i=1}^n (\Omega_i V)^{N_i}$ . In the noninteraction limit, eq 3 may be written (displaying appropriate factors and the domain of integration which conform with the generalized ordering scheme) as

$$Z(N_1, \dots, N_n, V) = \sum_{m=1}^n \frac{(N-1)! \prod_{i=1}^n (\Omega_i)^{N_i}}{N_1! \dots (N_m - 1)! \dots N_n!} \times \left[ \int_0^V \int_0^{v_1} \dots \int_0^{v_{N-2}} \int_0^{v_{N-1}} dv_N dv_{N-1} \dots dv_1 \right] = \frac{(N-1)! (N_1 + \dots + N_n)}{N_1! \dots N_n!} \left[ \prod_{i=1}^n (\Omega_i)^{N_i} \right] \left[ \frac{V^N}{N!} \right] = \frac{1}{N_1! \dots N_n!} \prod_{i=1}^n (\Omega_i V)^{N_i}$$

Note that it is actually assumed that for  $N_i = 1$  and  $N_{j(j \neq i)} = 0$ ,



$Z$  yields  $\Omega_i V$ , and is the size (actually the “Boltzmann’s weighted size”) of the one-particle phase space of the  $i^{\text{th}}$  species. For instance, for point particles with no internal structure,  $\Omega_i = (2\pi m_i k_B T)^{3/2}$ , where  $m_i$  is the  $i^{\text{th}}$  species particle mass. In the presence of interaction with other particles, we may envisage employing the reduced one-particle phase space, and hence, write the following dimensionally consistent expression:

$$Z(N_1, \dots, N_n, V) = \frac{1}{N_1! \dots N_n!} \prod_{i=1}^n (\epsilon \Omega_i V)^{N_i} \quad (7)$$

where  $\epsilon$  is dimensionless and is some function of  $N_1, \dots, N_n, V$ . Note that the temperature dependence of  $\epsilon$  and  $Z$  is to be understood and will usually not be explicitly indicated. Employing eq 7 in eq 6, and differentiating eq 6 with respect to  $V$  yields

$$N \epsilon^{N-1} (N_1, \dots, N_n, V) \left[ \epsilon(N_1, \dots, N_n, V) + V \frac{\partial \epsilon(N_1, \dots, N_n, V)}{\partial V} \right] = \sum_{i=1}^n \langle p_i \rangle N_i \epsilon^{N-1} (N_1, \dots, N_{i-1}, N_i - 1, N_{i+1}, \dots, N_n, V) \quad (8)$$

Considering that 1 is microscopic compared to  $N_i$  ( $i = 1, 2, \dots, n$ ), we may then write

$$\epsilon(N_1, \dots, N_{i-1}, N_i - 1, N_{i+1}, \dots, N_n, V) = \epsilon(N_1, \dots, N_n, V) - \frac{\partial \epsilon(N_1, \dots, N_n, V)}{\partial N_i}$$

By assuming  $\epsilon$  may be written as a function only of the partial densities ( $\rho_1, \dots, \rho_n$ ), and of course the temperature  $T$  as well, the governing equation for  $\epsilon$  then may be written as

$$\left( \epsilon - \rho_1 \frac{\partial \epsilon}{\partial \rho_1} - \rho_2 \frac{\partial \epsilon}{\partial \rho_2} - \dots - \rho_n \frac{\partial \epsilon}{\partial \rho_n} \right) = \sum_{i=1}^n \alpha_i \langle p_i \rangle \left( 1 - \frac{1}{\epsilon V} \frac{\partial \epsilon}{\partial \rho_i} \right)^{N-1}$$

where  $\alpha_i = (N_i/N)$  is the “mole fraction” of the  $i^{\text{th}}$  constituent. In the thermodynamic limit, we then obtain

$$\left( 1 - \frac{\rho_1}{\epsilon} \frac{\partial \epsilon}{\partial \rho_1} - \frac{\rho_2}{\epsilon} \frac{\partial \epsilon}{\partial \rho_2} - \dots - \frac{\rho_n}{\epsilon} \frac{\partial \epsilon}{\partial \rho_n} \right) = \sum_{i=1}^n \alpha_i \langle p_i \rangle \exp \left( - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right) \quad (9)$$

By making an initial guess for  $Z$  for all allowed partial densities ( $\rho_1, \dots, \rho_n$ ) (such as the noninteraction expression in many cases), initial PNNPDF’s may be deduced from where  $\langle p_i \rangle$  may be determined (numerically for instance) for various allowed partial densities for use in eq 9. Observe, as earlier indicated in section II, that because only a few particles (a few tens or so) may usually be within the direct interaction influence of a given particle (even in the presence of long-range interaction at the highest solid state densities), only at most a few tens of (nearest neighbor) particles will therefore be usually needed in accurately computing  $E_{j2}$  and, thus, the statistical parameters  $\langle p_i \rangle$ . By using any of the standard methods<sup>1</sup>, eq 9 may then be solved numerically with  $\epsilon$  obtained as a function of  $\rho_1, \dots, \rho_n$ . This yields a new expression for  $Z(N_1, \dots, N_n, V)$ ; by iterating through

the above process a few times, a stable and accurate expression for  $Z(N_1, \dots, N_n, V)$  is expected.

In the noninteraction case,  $E_{j2} = 0$ , and thus  $\langle p_j \rangle = 1$ . Hence, eq 9 simplifies to

$$\epsilon \left( 1 - \frac{\rho_1}{\epsilon} \frac{\partial \epsilon}{\partial \rho_1} - \frac{\rho_2}{\epsilon} \frac{\partial \epsilon}{\partial \rho_2} - \dots - \frac{\rho_n}{\epsilon} \frac{\partial \epsilon}{\partial \rho_n} \right) = \sum_{i=1}^n \alpha_i \exp \left( - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right)$$

A trivial solution to this equation is clearly  $\epsilon = \text{const.} = \sum_{i=1}^n \alpha_i = 1$ , thus providing the correct result for the partition function.

We remark that an ad hoc implementation of the above scheme may provide approximate solutions which for some purposes may be economical for certain systems. The case for the single-component hard particle system for instance (where the “excluded volume” effect of each particle is used to approximately formulate  $\langle p \rangle$ ) is discussed in ref 1. Extension of this approach to the multicomponent hard sphere system should be readily done owing to the analogy between the above formalism and that for single-component systems.

Determining partition functions in the presence of *external fields* also requires a modification of the above formalism which closely patterns that followed for single-component systems<sup>1</sup>. The dependency on  $v_1$  of the external field distribution in the neighborhood of the boundary of  $v_1$  (as  $v_1$  varies from a desirable chosen minimum to a maximum of  $V$ ) may be expressed as a dependency on  $\rho_i$  or  $\rho$  (as well as possibly other parameters which describe the shape of  $v_1$  as it varies).  $\rho_i = N_i/v_1$  and  $\rho = N/v_1$ . The many-body potential expected to be featured in the PNNPDF’s will be influenced by the external fields at the boundary of  $v_1$ , and hence, may then be seen to necessarily be formulated with a dependency on  $\rho_i$  or  $\rho$ . The partial PNNPDF’s may then be written as  $g_{X'_{j1}}^{(l),\varphi}(X_{k1}, \dots, X_{k_m})$  with  $\varphi$  indicating external field parameters which generally depend on  $\rho_i$  or  $\rho$ . Also,  $E_{j2}$  may be rewritten as  $E_{j2,\varphi}$ . (Note that the formulation of the above energies may sometimes be quite complex as the external fields may have substantially different effects on different particle species, and may also have a many-body effect).  $\langle p_i \rangle$  must also be written as  $\langle p_i \rangle_\varphi$ . Assuming the same expression as in eq 7 for  $Z$  (now rewritten as  $Z_\varphi$ ), we find we obtain a similar result as eq 9 but with  $\langle p_i \rangle$  replaced by  $\langle p_i \rangle_\varphi$ .

In all of the above developments, the issue of the range of interparticle interaction should be brought into question. Limitations on interaction range may be determined by a thorough investigation of eq 5. It is assumed that contribution to the energy  $E_{j2}$  comes from neighboring particles. Consider a spherical shell of thickness  $d|r|$  and radius  $|r|$  with the point  $X'_{j1}$  as center. ( $X'_{j1}$  is the location of the first labeled particle). For large enough  $|r|$ , the volume of the shell is large and, hence, may be said to contain, often enough, a number of particles (of species  $i$ ) equal to  $\sim |r|^2 \rho_i d|r|$ . The total number of particles in the shell then is often enough  $\sim |r|^2 \rho d|r|$  (where  $\rho = \sum \rho_i$ ). Violations of the above property are assumed to occur with insignificant measure in phase space. If “often enough”, the fraction of particles whose effect is neutralized (such as in charge neutralization between different species) is  $1 - y$ , then the number of particles within the said shell that contribute to  $E_{j2}$  is often enough  $\sim y |r|^2 \rho d|r|$ . Without loss of generality, the average contribution to  $E_{j2}$  by each non neutralized particle in the shell may be said to follow a power law as  $\sim \pm (1/|r|^\gamma)$ ; hence, total contribution to  $E_{j2}$  by all nonneutralized particles beyond some large enough distance  $|r| = R$  is often enough

$$\approx \lim_{R' \rightarrow \infty} \pm y \rho \int_R^{R'} |r|^{2-t} d|r| = \begin{cases} \lim_{R' \rightarrow \infty} \pm \frac{y \rho}{3-t} (R'^{3-t} - R^{3-t}) & t \neq 3 \\ \lim_{R' \rightarrow \infty} \pm y \rho \ln \left( \frac{R'}{R} \right) & t = 3 \end{cases} \quad (10)$$

Hence  $E_{j2}$  may be said to be finite ranged as required, if interparticle interaction potentials fall off at long distances faster than  $1/|r|^3$ . Potentials that do not fall as fast as  $1/|r|^3$  are therefore considered “long-ranged”.

Also, eq 10 shows that, provided  $y \rightarrow 0$  (faster than  $R^{-3}$  for  $R$  large enough) or  $\rho \rightarrow 0$  for  $R$  finite,  $E_{j2}$  may similarly be considered finite ranged irrespective of the interparticle interaction range. (The first of the two conditions is actually what may be said to hold in most material systems where two charge types are usually involved. The Coulombic interaction potential is long-ranged, but the overall charge neutrality condition allows that, often enough,  $y \rightarrow 0$  very rapidly well before  $R$  gets as large as  $\sim V^{1/3}$ ). Note that fluctuations expected in  $y$  may be assumed to result in violation of the above stated behavior only over a portion of phase space with insignificant measure. This is evident as experience indicates that only charges within a Debye screening length from the surface of an uncharged body may usually have influence on an external point charge which is in microscopically close proximity to the body. Hence, the above conclusion on the short-range nature of  $E_{j2}$  (as well as that for the analogous energy  $E_2$  for single-component systems) is in order.

In single-component systems, NNPDP's were constructed in a previous paper assuming surface or boundary effects were negligible (see Edgal<sup>8</sup> for a detailed discussion of terminologies). The boundary energy,  $U_{\text{bdy}}$ , was required to be much smaller than the energy of interaction,  $U_{n+1}$ , between the particle at the origin and its  $n$  nearest neighbors (for  $n$  large enough). In light of the present arguments on  $E_{j2}$ , it is evident that  $U_{\text{bdy}} \ll U_{n+1}$  (for  $n$  large enough) if the interparticle interaction potential is not long-ranged (or if  $y \rightarrow 0$  fast enough at large enough distances, or  $\rho \rightarrow 0$ ). In fact,  $n$  does not need to be too large (say a few tens or so) in the construction of NNPDP's since boundary effects present themselves in a “reduced form”.<sup>8</sup> For partial NNPDP's (used in eq 5) for multicomponent systems, we may also expect to encounter similar concepts as surface or boundary effects and thus conclude that PNNPDP's may be readily constructed in situations where interparticle interactions are not long-ranged, or where  $y \rightarrow 0$  rapidly (at large enough distances), or  $\rho \rightarrow 0$ . Hence, we conclude that the methods of this paper are applicable in systems where interparticle interactions are not long-ranged, or where  $y \rightarrow 0$  rapidly enough (as expected in cases of overall charge neutrality), or  $\rho \rightarrow 0$ .

A brief investigation of a few thermodynamic functions of particular interest in treatments of multicomponent systems now follows. The chemical potential of component  $i$  is written as

$$\mu_i = \left( \frac{\partial F}{\partial N_i} \right)_{T, V, N_j (j \neq i)} = F(T, V, N_1, \dots, N_{i-1}, N_i + 1, N_{i+1}, \dots, N_n) - F(T, V, N_1, \dots, N_n)$$

where  $F = -k_B T \ln \tilde{Z}$  is the Helmholtz free energy. Hence, using eq 7, we have

$$\mu_i = -k_B T [(f_{N_i} - f_{N_i+1}) \ln h + \ln V + \ln \Omega_i - \ln(N_i + 1) + \ln(\tilde{\epsilon}^{N_i+1}) - \ln(\tilde{\epsilon}^N)]$$

where

$$f_{N_i} = c_i N_i$$

$$\tilde{\epsilon} = \epsilon(N_1, \dots, N_{i-1}, N_i + 1, N_{i+1}, \dots, N_n, V) = \epsilon(N_1, \dots, N_n, V) + \frac{\partial \epsilon(N_1, \dots, N_n, V)}{\partial N_i}$$

If  $\epsilon$  may be written as a function of  $\rho_1, \dots, \rho_n$  (and of course  $T$ ) only, then we get  $\partial \epsilon / \partial N_i = (1/V)(\partial \epsilon / \partial \rho_i)$ . Hence, we obtain

$$\mu_i = -k_B T \left[ (f_{N_i} - f_{N_i+1}) \ln h + \ln V + \ln \Omega_i - \ln(N_i + 1) + \ln \epsilon + \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right] = -k_B T \left[ \ln \left( \frac{\epsilon}{\rho_i} \right) + \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} + \ln \left( \frac{\Omega_i}{h^{f_{N_i+1} - f_{N_i}}} \right) \right] \quad (11)$$

The equation of state of the multicomponent system may be given as

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T, N_i} = \frac{k_B T}{(\epsilon V)^N} \frac{\partial (\epsilon V)^N}{\partial V} = \frac{\rho k_B T}{\epsilon} \left( \epsilon + V \frac{\partial \epsilon}{\partial V} \right)$$

$P$  is pressure. We may write

$$\frac{\partial \epsilon}{\partial V} = \frac{\partial \epsilon}{\partial \rho_1} \frac{\partial \rho_1}{\partial V} + \frac{\partial \epsilon}{\partial \rho_2} \frac{\partial \rho_2}{\partial V} + \dots + \frac{\partial \epsilon}{\partial \rho_n} \frac{\partial \rho_n}{\partial V}$$

Hence, we easily arrive at the expression

$$\phi = 1 - \frac{1}{\epsilon} \left( \rho_1 \frac{\partial \epsilon}{\partial \rho_1} + \rho_2 \frac{\partial \epsilon}{\partial \rho_2} + \dots + \rho_n \frac{\partial \epsilon}{\partial \rho_n} \right) \quad (12)$$

where  $\phi$  is the compressibility factor  $P/\rho k_B T$ .

Finally, we observe from eq 12 that we may rewrite

$$P = \rho k_B T - k_B T \sum_{i=1}^n \rho_i \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} = k_B T \sum_{i=1}^n \rho_i - k_B T \sum_{i=1}^n \rho_i \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} = \sum_{i=1}^n k_B T \rho_i \left( 1 - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right) = \sum_{i=1}^n P_i$$

where  $P_i$  may be regarded as the partial pressure of the  $i^{\text{th}}$  species. Clearly, the partial pressure depends on interaction and density of other particle species (via the variables  $\rho$  and  $\epsilon$ ). We may then rewrite the chemical potential for the  $i^{\text{th}}$  component, for instance, as

$$\mu_i = -k_B T \left( -\phi_i + 1 + \ln \left( \frac{\epsilon}{\rho_i} \right) \right) - k_B T \ln \left( \frac{\Omega_i}{h^{c_i}} \right) \quad (13)$$

where  $\phi_i = P_i/\rho_i k_B T$ . Also, considering the equation of reaction equilibrium  $\sum_i \nu_i \mu_i = 0$ , we may write

$$\sum_i \nu_i \left( -\phi_i + 1 + \ln \left( \frac{\epsilon}{\rho_i} \right) \right) + \sum_i \nu_i \ln \left( \frac{\Omega_i}{h^{c_i}} \right) = 0 \quad (14)$$

The  $\nu_i$ 's are stoichiometric coefficients in the balanced chemical equation for any one of several possible reactions independently occurring simultaneously in the system.  $\nu_i$  is assumed to be

positive for reactants and negative for products. Equation 14 easily leads to

$$\prod_{i=1}^n \rho_i^{v_i} = \prod_{i=1}^n (\epsilon e^{-\phi_i + 1})^{v_i} \prod_{i=1}^n \left( \frac{\Omega_i}{h^{c_i}} \right)^{v_i} \quad (15)$$

In the limit of a mixture of ideal gases,  $\phi_i \rightarrow 1$ ,  $\epsilon \rightarrow 1$  and eq 15 reduces to the well-known law of mass action.<sup>6</sup> Equation 15 shows how the law of mass action is modified if interaction (chemical, physical, etc. forces) between particles must be accounted for (at arbitrary densities and temperatures). From the detailed knowledge of the chemical potential, other functions, such as the fugacity, activity, excess thermodynamic functions, etc., all of which are usually defined on the basis of various physical motivations, may be obtained.<sup>6</sup> These functions are, however, not investigated in this paper.

#### IV. Simple Applications to Low-Density Interacting Gas Mixtures in 3-D

In the noninteraction limit, results of the previous section show that  $\epsilon \rightarrow 1$  and thus  $\phi \rightarrow 1$ . The noninteraction multicomponent system is a poisson point process for which the following poisson distribution holds

$$Prob(n_i, v) = \frac{1}{n_i!} (\rho_i v)^{n_i} e^{-\rho_i v} \quad (16)$$

( $Prob(n_i, v)$  is the probability that exactly  $n_i$  out of the total of  $N_i$  particles of species  $i$  occur in volume  $v$  within the larger volume  $V$ ). The same expression is true for the probability of finding exactly  $n$  particles, regardless of species type, in volume  $v$ , provided in eq 16,  $n_i$  is replaced by  $n$ , and  $\rho_i$  is replaced by  $\rho = N/V$ . A general multicomponent point process (GMPP) is defined with the origin arbitrarily situated within volume  $V$ . We may assume the  $i^{\text{th}}$  nearest neighbor of the origin is of species  $k_i$  (where  $k_1, \dots, k_m$  are numbers from the set  $1, 2, 3, \dots, n$ ).

The probability that a particle of species  $k_i$  (where  $i = 1, \dots, m$ ) is located in volume  $dr_{k_i} = |r_{k_i}|^2 \sin \theta_{k_i} d|r_{k_i}| d\theta_{k_i} d\phi_{k_i}$  (assuming that a particle already occupies each of the volumes  $dr_{k_1}, dr_{k_2}, \dots, dr_{k_{i-1}}$ ) while the remaining  $(N - i)$  particles in the system are in volume  $(V - dr_{k_1} - \dots - dr_{k_i})$  is the product of the probability that a particle (irrespective of the species) is located in  $dr_{k_i}$  (volumes  $dr_{k_1}, dr_{k_2}, \dots, dr_{k_{i-1}}$  being each already occupied by a particle), and the probability that the particle in question is of species  $k_i$ . The first probability in the product considers  $(N - i + 1)$  particles situated within volume  $V - dr_{k_1} - \dots - dr_{k_{i-1}}$  and involves the above noninteraction poisson distribution property. The product, therefore, yields (employing eq 16)  $\approx [\rho dr_{k_i}] [N_i/N] = \rho_{k_i} |r_{k_i}|^2 \sin \theta_{k_i} d|r_{k_i}| d\theta_{k_i} d\phi_{k_i}$ . (This probability may actually be stated as a conditional probability for the occupation of  $dr_{k_i}$  by a particle of species  $k_i$ , where the given event for the conditional probability involves a particle occupying each of the volumes  $dr_{k_1}, dr_{k_2}, \dots, dr_{k_{i-1}}$ ).

Next, we consider the volume portion within the sphere of radius  $|r_{k_m}|$  with the center at the origin, while the volume portion is, however, outside the volume elements  $dr_{k_1}, dr_{k_2}, \dots, dr_{k_m}$  (which are each occupied by a particle). This volume portion is of size  $(4/3) \pi |r_{k_m}|^3 - dr_{k_1} - dr_{k_2} - \dots - dr_{k_m}$  (and is part of the volume  $V - dr_{k_1} - dr_{k_2} - \dots - dr_{k_m}$  within which the remaining  $(N - m)$  particles reside). The probability that the remaining  $(N - m)$  particles may not reside in this volume

portion (but may reside within the remaining volume  $(V - (4/3) \pi |r_{k_m}|^3)$ ) is  $\approx e^{-(4/3) \pi \rho |r_{k_m}|^3}$ . (Note in all the above, it is assumed  $m \ll N_i$  for all  $i$ , and  $(4/3) \pi |r_{k_m}|^3 \ll V$  often enough).

Hence, considering that  $|r_{k_1}| \leq |r_{k_2}| \leq \dots \leq |r_{k_m}|$  the probability that the nearest neighbor (species  $k_1$ ) is in  $dr_{k_1}$ , the second nearest neighbor (species  $k_2$ ) is in  $dr_{k_2}$ , ..., the  $m^{\text{th}}$  nearest neighbor (species  $k_m$ ) is in  $dr_{k_m}$  becomes the product of all the above stated probabilities and is written as

$$g(r_{k_1}, r_{k_2}, \dots, r_{k_m}) dr_{k_1} \dots dr_{k_m} = [e^{-(4/3) \pi \rho |r_{k_m}|^3}] \prod_{j=1}^m [\rho_{k_j} |r_{k_j}|^2 \sin \theta_{k_j} d|r_{k_j}| d\theta_{k_j} d\phi_{k_j}] = (\rho_{k_1} \dots \rho_{k_m}) (|r_{k_1}|^2 \sin \theta_{k_1} \dots |r_{k_m}|^2 \sin \theta_{k_m}) \times [e^{-(4/3) \pi \rho |r_{k_m}|^3}] d|r_{k_1}| d\theta_{k_1} d\phi_{k_1} \dots d|r_{k_m}| d\theta_{k_m} d\phi_{k_m} \quad (17)$$

(In a previous work<sup>9</sup> on the single-component poisson fluid, conditional probabilities for "slightly" different events was also one method used to formulate probability distributions for nearest neighbors).  $g(r_{k_1}, \dots, r_{k_m})$  is a joint NNPf which will soon be referred to as a PNNPf for the multicomponent poisson (noninteracting) fluid. Figure 2 shows  $m$  nearest neighbors of an arbitrarily situated origin in an  $n$ -component system.

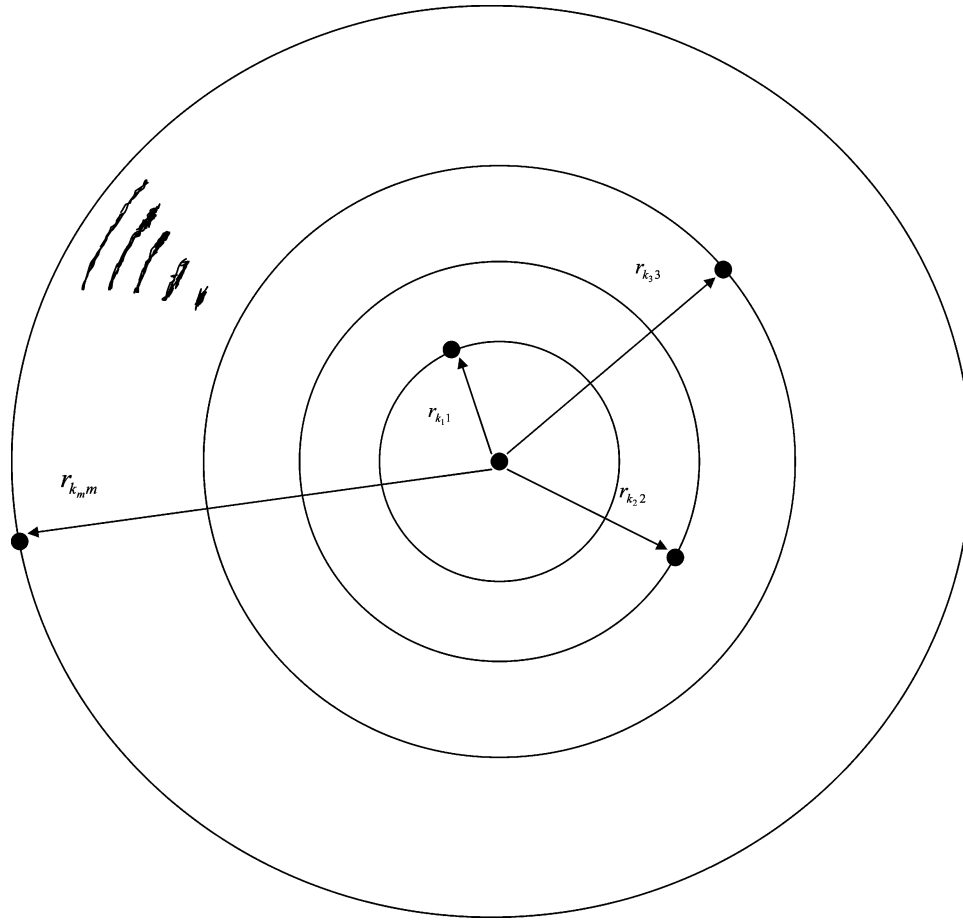
The probability for near equality of any two or more of the  $|r_{k_i}|$ 's may be expected to be vanishingly small, except possibly in the neighborhood of the solid phase for interacting systems. Probability distributions for internal coordinates of particles are assumed to be uniform (over their relevant spaces) in the poisson fluid (single or multicomponent), while all canonically conjugate coordinates may usually be assumed to already be integrated out (in the evaluation of the partition function) and are thus irrelevant in considerations of NNPf's for the poisson fluid. In the presence of interaction, very large magnitudes for canonically conjugate coordinates do not need to be considered as they may usually be expected to lead to negligibly small values for NNPf's (hence, reasonable cutoff values for canonically conjugate coordinates can be specified ab initio). Also, some of the internal coordinates (as well as some of all the canonically conjugate coordinates) may usually already be integrated out (as in the poisson case) for interacting systems. In eq 17, we may assume  $n_i$  out of the  $m$  nearest neighbors are of species  $i$ . Thus

$$n_1 + n_2 + n_3 + \dots + n_n = m \quad (18)$$

The nonnegative integers  $n_1, n_2, \dots, n_n$  satisfying eq 18 may be chosen in  $n^m$  distinct ways (since the species for the first, second, etc. nearest neighbors may each be chosen in  $n$  ways). The many possible choices for the species type of nearest neighbors implies  $g(r_{k_1}, \dots, r_{k_m})$  is a probability density function (pdf) which cannot normalize to unity on integration, and hence, is a pdf more properly referred to as a PNNPf. The PNNPf normalizes, as indicated in section II, as

$$\sum_{(I)} \int \dots \int g^{(I)}(r_{k_1}, \dots, r_{k_m}) \prod_{i=1}^m dr_{k_i} = 1 \quad (19)$$

The index  $(I)$  indicates a specific choice of values for  $k_1, \dots, k_m$  (of which there are  $n^m$  of such choices). Carrying out the integration of a typical term in the sum on the left-hand



**Figure 2.** The arbitrarily situated origin (center of concentric circles) and its  $m$  nearest neighbors in the  $n$  component system.  $\vec{r}_{k_i}$  is the location of the origin's  $i^{\text{th}}$  nearest neighbor (species  $k_i$ ) where  $k_i$  may be 1, 2, ...,  $n$ .

side (lhs) of eq 19 yields

$$\begin{aligned} & [(4\pi)^m \rho_1^{n_1} \rho_2^{n_2} \dots \rho_n^{n_n}] \int_0^\infty \int_0^{r_{k_m}} \dots \int_0^{r_{k_3}} \int_0^{r_{k_2}} \\ & (|r_{k_1}|^2 \dots |r_{k_m}|^2) e^{-(4/3)\pi\rho|r_{k_m}|^3} d|r_{k_1}| \dots d|r_{k_m}| = \\ & \frac{(4\pi)(\rho_1^{n_1} \rho_2^{n_2} \dots \rho_n^{n_n})}{3^{m-1}(m-1)!} \int_0^\infty |r_{k_m}|^{3m-1} e^{-(4/3)\pi\rho|r_{k_m}|^3} d|r_{k_m}| = \\ & \frac{(\rho_1^{n_1} \rho_2^{n_2} \dots \rho_n^{n_n})}{\rho^m} = \alpha_1^{n_1} \alpha_2^{n_2} \dots \alpha_n^{n_n} \quad (20) \end{aligned}$$

(where  $\alpha_1 + \alpha_2 + \dots + \alpha_n = 1$ ;  $n_1 + n_2 + \dots + n_n = m$ ). Hence, the different PNNPDF's for  $m$  nearest neighbors normalize to different values. The sum of eq 19 can therefore be rewritten as

$$\begin{aligned} \sum_{(l)} \alpha_1^{n_1} \alpha_2^{n_2} \dots \alpha_n^{n_n} &= \sum_{i_1=1}^n \dots \sum_{i_m=1}^n \alpha_{i_1} \alpha_{i_2} \dots \alpha_{i_m} = \\ & \sum_{i_1=1}^n \alpha_{i_1} \left( \sum_{i_2=1}^n \alpha_{i_2} \left( \dots \left( \sum_{i_{m-1}=1}^n \alpha_{i_{m-1}} \left( \sum_{i_m=1}^n \alpha_{i_m} \right) \right) \right) \right) = 1 \end{aligned}$$

(which is in conformity with eq 19). Clearly, eq 17 is valid as a PNNPDF for both GMPP and OMPP processes. (The OMPP process is the ordinary multicomponent point process where the arbitrarily situated origin coincides with a particle location). For OMPP, therefore, the PNNPDF is independent of the particle species at the origin. Hence, we may write

$$g_{X'_{j1}}(r_{k_1}, \dots, r_{k_m}) = g(r_{k_1}, \dots, r_{k_m})$$

$X'_{j1}$  is the origin. If  $X'_{j1}$  is located at the boundary of volume  $V$ , then we have (for a locally flat boundary) in a multicomponent poisson fluid

$$\begin{aligned} g_{X'_{j1}}(r_{k_1}, \dots, r_{k_m}) &= \\ & (\rho_{k_1} \dots \rho_{k_m}) (|r_{k_1}|^2 \dots |r_{k_m}|^2) (\sin \theta_{k_1} \dots \sin \theta_{k_m}) e^{-(2/3)\pi\rho|r_{k_m}|^3} \end{aligned} \quad (21)$$

Normalizing eq 21 employs the sum of eq 19; however, integration is over the infinite half space.

The results of eqs 17 and 21 are readily reproduced by integrating the expression given in section II for  $g'_{X'_{j1}}(X'_{k_2}, \dots, X'_{k_N})$  (setting  $E_{j1} = 0$ ). The integration is carried out over all variables, except the  $m$  variables, considered the coordinates of the  $m$  nearest neighbors of the origin. In the presence of interparticle interaction, the integration will also lead to appropriate expressions for PNNPDF's. In a subsequent paper (under preparation), PNNPDF's are rigorously derived in the presence of interaction (for the GMPP and OMPP). Comparison with partial  $n$ -tuple distribution functions (functions more commonly used in the literature<sup>6</sup> especially for binary systems), as well as the notion of the insignificance of surface and shape effects,<sup>8</sup> etc., will be more fully discussed in the subsequent paper. In a binary mixture, eq 21 may be written for the  $m = 1$  case for all the relevant PNNPDF's as

$$g_{X'_{j1}}(r_{j1}) dr_{j1} = \rho_j |r_{j1}|^2 \sin \theta_{j1} e^{-(2/3)\pi\rho|r_{j1}|^3} d|r_{j1}| d\theta_{j1} d\phi_{j1} \quad (22)$$



where for each  $i$ , we have that  $j$  may be 1 or 2 (and  $i = 1, 2$ ). These PNNPDF's will now be employed in the low-density ( $\rho$ ) limit for a binary mixture of hard particles involving spheres of radius  $b_1$  (density  $\rho_1$ ) and radius  $b_2$  (density  $\rho_2$ ). Equation 5 may then be evaluated for all the possible cases as

$$p_1(X'_{11}, V) = \sum_{(l)} \int g_{X'_{11}}^{(l)}(X_{k_1}) e^{-\beta E_{j2}} dX_{k_1} = \int g_{X'_{11}}(X_{11}) e^{-\beta E_{j2}} dX_{11} + \int g_{X'_{11}}(X_{21}) e^{-\beta E_{j2}} dX_{21} \quad (23a)$$

$$p_2(X'_{21}, V) = \sum_{(l)} \int g_{X'_{21}}^{(l)}(X_{k_1}) e^{-\beta E_{j2}} dX_{k_1} = \int g_{X'_{21}}(X_{11}) e^{-\beta E_{j2}} dX_{11} + \int g_{X'_{21}}(X_{21}) e^{-\beta E_{j2}} dX_{21} \quad (23b)$$

Clearly,

$$E'_{j2} = \begin{cases} 0 & |r_{11}| > 2b_1; \\ \infty & |r_{11}| \leq 2b_1; \end{cases} \quad E''_{j2} = \begin{cases} 0 & |r_{21}| > b_1 + b_2 \\ \infty & |r_{21}| \leq b_1 + b_2 \end{cases}$$

$$E'''_{j2} = \begin{cases} 0 & |r_{11}| > b_1 + b_2; \\ \infty & |r_{11}| \leq b_1 + b_2; \end{cases} \quad E''''_{j2} = \begin{cases} 0 & |r_{21}| > 2b_2 \\ \infty & |r_{21}| \leq 2b_2 \end{cases}$$

Hence, eqs 23 yield

$$p_1(X'_{11}, V) = \alpha_1 e^{-[4(\eta_1/\alpha_1)]} + \alpha_2 e^{-[(1/2)\eta_1(1+\beta_{21})^3/\alpha_1]}$$

$$p_2(X'_{21}, V) = \alpha_2 e^{-[4(\eta_2/\alpha_2)]} + \alpha_1 e^{-[(1/2)\eta_2(1+\beta_{12})^3/\alpha_2]}$$

$$\alpha_1 = \frac{\rho_1}{\rho}; \quad \alpha_2 = \frac{\rho_2}{\rho}; \quad \eta_1 = \frac{4}{3}\pi b_1^3 \rho_1; \quad \eta_2 = \frac{4}{3}\pi b_2^3 \rho_2;$$

$$\beta_{12} = \beta_{21}^{-1} = \frac{b_1}{b_2}$$

At low densities, eq 9 is written as

$$\epsilon \left[ 1 - \frac{\rho_1}{\epsilon} \frac{\partial \epsilon}{\partial \rho_1} - \frac{\rho_2}{\epsilon} \frac{\partial \epsilon}{\partial \rho_2} \right] = \alpha_1 p_1(X'_{11}, V) e^{-(\rho/\epsilon)(\partial \epsilon / \partial \rho_1)} + \alpha_2 p_2(X'_{21}, V) e^{-(\rho/\epsilon)(\partial \epsilon / \partial \rho_2)} = [\alpha_1^2 e^{-[4(\eta_1/\alpha_1)]} + \alpha_1 \alpha_2 e^{-[(1/2)\eta_1(1+\beta_{21})^3/\alpha_1]}] e^{-((\rho_1+\rho_2)/\epsilon)(\partial \epsilon / \partial \rho_1)} + [\alpha_2^2 e^{-[4(\eta_2/\alpha_2)]} + \alpha_1 \alpha_2 e^{-[(1/2)\eta_2(1+\beta_{12})^3/\alpha_2]}] e^{-((\rho_1+\rho_2)/\epsilon)(\partial \epsilon / \partial \rho_2)} \quad (24)$$

At low densities, we may also write:  $\epsilon = 1 + (\text{terms of order } \eta_1, \eta_2, \text{ and higher})$

Hence

$$\frac{(\rho_1 + \rho_2)}{\epsilon} \frac{\partial \epsilon}{\partial \rho_1} = \eta_1 \frac{\partial \epsilon}{\partial \eta_1} + \beta_{12}^3 \eta_2 \frac{\partial \epsilon}{\partial \eta_1} + (\text{terms of order } \eta_1^2, \eta_2^2, \eta_1 \eta_2, \text{ and higher})$$

and

$$\frac{(\rho_1 + \rho_2)}{\epsilon} \frac{\partial \epsilon}{\partial \rho_2} = \eta_2 \frac{\partial \epsilon}{\partial \eta_2} + \beta_{21}^3 \eta_1 \frac{\partial \epsilon}{\partial \eta_2} + (\text{terms of order } \eta_1^2, \eta_2^2, \eta_1 \eta_2, \text{ and higher})$$

Substituting these results in eq 24 and expanding exponentials gives some interesting cancellation of terms. We, thus, are able to obtain a rigorous expression for  $\epsilon$  up to terms of order  $\eta_1, \eta_2$  after a very lengthy set of algebraic manipulations as

$$\epsilon(\eta_1, \eta_2) \cong$$

$$1 - \left[ 4\eta_1 \alpha_1 + \frac{1}{2} \eta_1 \alpha_2 (1 + \beta_{21})^3 + 4\eta_2 \alpha_2 + \frac{1}{2} \eta_2 \alpha_1 (1 + \beta_{12})^3 \right]$$

(The result  $\alpha_1^2 + 2\alpha_1 \alpha_2 + \alpha_2^2 = (\alpha_1 + \alpha_2)^2 = 1$  has been employed). Note that besides  $\eta_1, \eta_2 \ll 1$ , the density  $\rho$  is assumed so low that  $(4/3)\pi b_1^3 \rho, (4/3)\pi b_2^3 \rho \ll 1$  and, thus,  $\eta_1/\alpha_1, \eta_2/\alpha_2 \ll 1$ . Note also that  $\alpha_1, \alpha_2$  must also be thought of as functions of  $\eta_1, \eta_2$  in the expression for  $\epsilon(\eta_1, \eta_2)$ . (Also,  $\epsilon$  may be alternatively written as  $\epsilon(\rho_1, \rho_2)$ ). Noting that

$$\frac{\partial \alpha_1}{\partial \eta_1} = \frac{\partial}{\partial \eta_1} \left( \frac{\eta_1}{\eta_1 + \beta_{12}^3 \eta_2} \right) = \frac{\alpha_1 \alpha_2}{\eta_1}, \text{ and}$$

$$\frac{\partial \alpha_2}{\partial \eta_1} = \frac{\partial}{\partial \eta_1} \left( \frac{\eta_2}{\eta_2 + \beta_{21}^3 \eta_1} \right) = -\frac{\alpha_1 \alpha_2}{\eta_1}$$

we obtain

$$\frac{\partial \epsilon}{\partial \eta_1} = - \left( 4\alpha_1 + 4\alpha_1 \alpha_2 + \frac{1}{2} \alpha_1^2 (1 + \beta_{21})^3 \right) + \left( \frac{\eta_2}{\eta_1} \right) \left( 4\alpha_1 \alpha_2 - \frac{1}{2} \alpha_1 \alpha_2 (1 + \beta_{12})^3 \right)$$

Similarly,

$$\frac{\partial \epsilon}{\partial \eta_2} = - \left( 4\alpha_2 + 4\alpha_1 \alpha_2 + \frac{1}{2} \alpha_2^2 (1 + \beta_{12})^3 \right) + \left( \frac{\eta_1}{\eta_2} \right) \left( 4\alpha_1 \alpha_2 - \frac{1}{2} \alpha_1 \alpha_2 (1 + \beta_{21})^3 \right)$$

Hence, using eq 12 and approximating

$$\frac{1}{\epsilon} \approx 1 + \left[ 4\eta_1 \alpha_1 + \frac{1}{2} \eta_1 \alpha_2 (1 + \beta_{21})^3 + 4\eta_2 \alpha_2 + \frac{1}{2} \eta_2 \alpha_1 (1 + \beta_{12})^3 \right],$$

we obtain the equation of state up to terms of order  $\eta_1, \eta_2$  for the low-density binary mixture of hard spheres as

$$\phi = 1 - \frac{1}{\epsilon} \left( \rho_1 \frac{\partial \epsilon}{\partial \rho_1} + \rho_2 \frac{\partial \epsilon}{\partial \rho_2} \right) = 1 - \frac{1}{\epsilon} \left( \eta_1 \frac{\partial \epsilon}{\partial \eta_1} + \eta_2 \frac{\partial \epsilon}{\partial \eta_2} \right) \cong$$

$$1 + \rho \left[ \frac{\eta_1}{\rho} 4\alpha_1 + \frac{\eta_1}{\rho} 4\alpha_1 \alpha_2 + \frac{1}{2} \frac{\eta_1}{\rho} \alpha_2^2 (1 + \beta_{21})^3 - \frac{\eta_2}{\rho} 4\alpha_1 \alpha_2 + \frac{1}{2} \frac{\eta_2}{\rho} \alpha_1 \alpha_2 (1 + \beta_{12})^3 \right] + \rho \left[ \frac{\eta_2}{\rho} 4\alpha_2 + \frac{\eta_2}{\rho} 4\alpha_1 \alpha_2 + \frac{1}{2} \frac{\eta_2}{\rho} \alpha_1^2 (1 + \beta_{12})^3 - \frac{\eta_1}{\rho} 4\alpha_1 \alpha_2 + \frac{1}{2} \frac{\eta_1}{\rho} \alpha_1 \alpha_2 (1 + \beta_{21})^3 \right] =$$

$$1 + \rho \left[ \frac{16}{3} \pi b_1^3 \alpha_1^2 + \frac{16}{3} \pi b_2^3 \alpha_2^2 + \frac{4}{3} \pi \alpha_1 \alpha_2^2 (b_2 + b_1)^3 + \frac{4}{3} \pi \alpha_1^2 \alpha_2 (b_2 + b_1)^3 \right] = 1 + \rho \left[ \frac{2}{3} \pi (2b_1)^3 \alpha_1^2 + \frac{2}{3} \pi (2b_2)^3 \alpha_2^2 + \frac{4}{3} \pi (b_1 + b_2)^3 \alpha_1 \alpha_2 \right] \quad (25)$$

In the literature,<sup>6</sup> it is known that the equation of state of an equilibrium multicomponent system may be written as

$$\phi = \sum_{k=1}^{\infty} \rho^{k-1} B_k$$

( $B_1 = 1$ ). The virial coefficients  $B_k$  (being more complicated than those in the single-component system) are made up of sub-coefficients as

$$B_n = \sum_{i_1=1}^m \dots \sum_{i_n=1}^m \alpha_{i_1} \alpha_{i_2} \dots \alpha_{i_n} B_{i_1 i_2 \dots i_n}$$

( $B_{i_1 i_2 \dots i_n}$ 's are sub-coefficients which are invariant with respect to the permutation of indices;  $m$  is the number of components). From eq 25, we see that our sub-coefficients are

$$B_{11} = \frac{2}{3} \pi (2b_1)^3; \quad B_{22} = \frac{2}{3} \pi (2b_2)^3; \\ B_{12} = B_{21} = \frac{2}{3} \pi (b_1 + b_2)^3$$

and these are in agreement with known<sup>6</sup> results.

From the above developments, general expressions for thermodynamic functions as Gibbs free energy, activity function, excess Gibbs free energy, etc. (as well as their limiting behavior) can be derived in terms of the newly defined variables as  $\epsilon$ ,  $\Omega_i$ , etc. Results for the thermodynamic functions for specific systems (as the binary mixture of hard particle fluids) may then be obtained rigorously using exact values for the new variables. Such calculations are very elaborate, and their developments are deferred for a later investigation.

## V. Conclusions and Remarks

The notion of “generalized order” has once again been employed, this time to obtain a new formalism for investigating the statistical thermodynamics of classical multicomponent systems. The approach involved employing statistical arguments to develop an integral equation incorporating the statistical parameters  $\langle p_j \rangle$ . By invoking yet another concept (the concept of the reduced one-particle phase space), it was possible to give an adequate functional form for partition functions which then led to a suitable nonlinear partial differential equation from which partition functions could be deduced. To help the reader, a brief summary of the corresponding formulation for pure systems (which is relatively simpler) is outlined in the Appendix.

Application of the above formalism to the binary mixture of hard particles in the low-density limit was demonstrated. Self-consistency arguments have also been provided in various limiting conditions (see Appendix). Just as in the single-component case, it is expected that progressive application to more complex systems will vindicate the suitability of the scheme of this paper for general multicomponent systems. Currently, work is under way in (a) obtaining exact expressions for PNPDF's, (b) implementing the present scheme to its fullness for simple systems, such as the 1-D case (as has been done for single-component 1-D systems), and (c) developing the numerical method for computing  $\langle p_j \rangle$ , which is an inevitable aspect of the new scheme for obtaining the *exact* statistical thermodynamic properties of more realistic 3-D material systems.

## Appendix

**A. Brief Summary of the New Approach for Pure Systems (from Refs 1 and 8).** It is shown in ref 8 that the joint pdf for  $n$  nearest neighbors of a particle situated at the origin in

equilibrium pure systems is

$$g_{1,\dots,n}(\vec{r}_1, \dots, \vec{r}_n) = h_n \exp \left[ -\frac{4}{3} \pi r_n^3 \rho \left( 1 - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho} \right) \right] e^{-\beta U_{n+1}} \quad (\text{A1})$$

The variables and parameters in the expression are largely as defined in this paper, except that all particles are assumed to be of a single species (hence, for instance,  $\vec{r}_{ki}$  is written as  $\vec{r}_i$ ), while  $h_n$  is introduced for normalization.  $U_{n+1}$  is the potential energy of  $n + 1$  particles involving the particle at the origin and its  $n$  nearest neighbors.

For the general point process where the origin does not necessarily coincide with a particle center,  $U_{n+1}$  is replaced by  $U_n$ , and for the case where the origin coincides with the boundary of  $V$ , the factor of  $4/3$  is replaced by  $2/3$  if the boundary of  $V$  is everywhere “smooth”. It is argued that eq A1 and similar equations are valid (and, thus, sufficiently accurate) when  $n$  becomes a few tens or so.

Using the NNPDF for the general point process with origin at the boundary of  $V$ , a numerical scheme (for instance) may be used to determine the average of the energy function  $e^{-\beta E_2}$ .  $E_2$  is the energy contribution to the system for a given configuration of particles in the system when the energy of interaction between a particle placed at the origin (on one hand), and the rest ( $N - 1$ ) particles in the system (on the other hand) is “turned on”. The average in question is referred to as the parameter  $p$ . If the boundary of  $V$  is not smooth “often enough”, then  $p$  will vary with the position of the origin at the boundary, and  $p$  must be replaced by its average  $\langle p \rangle$  over the boundary of  $V$ .

The statistical parameter  $\langle p \rangle$  is then used in the following nonlinear differential equation

$$\epsilon \left( 1 - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho} \right) = \langle p \rangle \exp \left( -\frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho} \right) \quad (\text{A2})$$

$\epsilon$ , which provides a measure of the free energy of the system, may be initially guessed in an iterative scheme. A good initial guess may be expected to be  $\epsilon = 1$ , which applies for the noninteracting poisson point process. This is used to formulate the relevant NNPDF used to evaluate  $\langle p \rangle$ , which in turn is used in eq A2 to solve for a new  $\epsilon$ , etc.

**B. The New Theory in Some Limiting Conditions.** A limiting condition for multicomponent systems is briefly investigated here for our scheme. Interaction between particles of different species is assumed to be nonexistent, while intraspecies interaction may exist. It is clear from eq 5 that  $p_j$  will be a function only of  $\rho_j$  in this case; ie,  $p_j = p_j(\rho_j)$ , and this will be applicable for a single-component system involving particles of only type species  $j$  at density  $\rho_j$ . Equation 9 therefore may be written for a single-component system involving particles of only type species  $j$  as

$$\epsilon_j(\rho_j) \left( 1 - \frac{\rho_j}{\epsilon_j(\rho_j)} \frac{\partial \epsilon_j(\rho_j)}{\partial \rho_j} \right) = \langle p_j(\rho_j) \rangle \exp \left( \frac{-\rho_j}{\epsilon_j(\rho_j)} \frac{\partial \epsilon_j(\rho_j)}{\partial \rho_j} \right) \quad (\text{B1})$$

The partition function is assumed of the form

$$Z(N_j) = \frac{1}{N_j!} (\epsilon_j \Omega_j V)^{N_j}$$

where  $\epsilon_j = \epsilon_j(\rho_j)$ . On the other hand, eq 9 may be written for the multicomponent system as

$$\epsilon \left( 1 - \sum_{i=1}^n \frac{\rho_i}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right) = \sum_{i=1}^n \alpha_i \langle p_i \rangle \exp \left( - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right) \quad (\text{B2})$$

We will now show that the solution to eq B2 is the following required expression

$$\epsilon = \epsilon_1^{\alpha_1} \epsilon_2^{\alpha_2} \dots \epsilon_n^{\alpha_n} \quad (\text{B3})$$

Using eq B3, we may write

$$- \rho \frac{\partial \ln \epsilon}{\partial \rho_i} = - \rho \frac{\partial}{\partial \rho_i} (\ln \prod_{j=1}^n \epsilon_j^{\alpha_j}) = \sum_{j=1}^n - \rho \frac{\partial (\alpha_j \ln \epsilon_j)}{\partial \rho_i}$$

Hence

$$\exp \left( - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right) = \prod_{j=1}^n \exp \left( - \rho \frac{\partial (\alpha_j \ln \epsilon_j)}{\partial \rho_i} \right)$$

We have that

$$\frac{\partial (\alpha_j \ln \epsilon_j)}{\partial \rho_i} = \alpha_j \frac{\partial \ln \epsilon_j}{\partial \rho_i} + \frac{\partial \alpha_j}{\partial \rho_i} \ln \epsilon_j = \begin{cases} \frac{\alpha_i}{\epsilon_i} \frac{\partial \epsilon_i}{\partial \rho_i} + \frac{(1 - \alpha_i)}{\rho} \ln \epsilon_i & (i = j) \\ - \frac{\alpha_j}{\rho} \ln \epsilon_j & (i \neq j) \end{cases}$$

Hence

$$\exp \left( - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right) = \exp \left[ - \rho \left( \alpha_i \frac{\partial \ln \epsilon_i}{\partial \rho_i} + \frac{(1 - \alpha_i)}{\rho} \ln \epsilon_i \right) \right] \prod_{j=1(j \neq i)}^n \exp(\alpha_j \ln \epsilon_j) = \epsilon \exp \left[ - \rho \left( \alpha_i \frac{\partial \ln \epsilon_i}{\partial \rho_i} + \frac{1}{\rho} \ln \epsilon_i \right) \right] \quad (\text{B4})$$

Substituting eq B4 in eq B2 yields

$$\left( 1 - \sum_{i=1}^n \frac{\rho_i}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right) = \sum_{i=1}^n \alpha_i \langle p_i \rangle \exp \left[ - \rho \left( \alpha_i \frac{\partial \ln \epsilon_i}{\partial \rho_i} + \frac{1}{\rho} \ln \epsilon_i \right) \right] = \sum_{i=1}^n \frac{\alpha_i \langle p_i \rangle}{\epsilon_i} \exp \left( - \frac{\rho_i}{\epsilon_i} \frac{\partial \epsilon_i}{\partial \rho_i} \right) \quad (\text{B5})$$

Substituting eq B1 in eq B5 then yields

$$\left( 1 - \sum_{i=1}^n \frac{\rho_i}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right) = \sum_{i=1}^n \alpha_i \left( 1 - \frac{\rho_i}{\epsilon_i} \frac{\partial \epsilon_i}{\partial \rho_i} \right) \quad (\text{B6})$$

$$\begin{aligned} \frac{1}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} &= \sum_{j=1}^n \frac{\partial \ln \epsilon_j^{\alpha_j}}{\partial \rho_i} = \frac{\partial \ln \epsilon_i^{\alpha_i}}{\partial \rho_i} + \sum_{j=1(j \neq i)}^n \frac{\partial \alpha_j}{\partial \rho_i} \ln \epsilon_j = \\ &= \alpha_i \frac{\partial \ln \epsilon_i}{\partial \rho_i} + \frac{1}{\rho} (1 - \alpha_i) \ln \epsilon_i - \sum_{j=1(j \neq i)}^n \frac{\alpha_j}{\rho} \ln \epsilon_j = \\ &= \alpha_i \frac{\partial \ln \epsilon_i}{\partial \rho_i} + \frac{1}{\rho} \ln \epsilon_i - \frac{1}{\rho} \sum_{j=1}^n \ln \epsilon_j^{\alpha_j} = \alpha_i \frac{\partial \ln \epsilon_i}{\partial \rho_i} + \frac{1}{\rho} \ln \frac{\epsilon}{\epsilon} \end{aligned}$$

Hence we have

$$\begin{aligned} \sum_{i=1}^n \frac{\rho_i}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} &= \sum_{i=1}^n \alpha_i \rho_i \frac{\partial \ln \epsilon_i}{\partial \rho_i} + \sum_{i=1}^n \ln \left( \frac{\epsilon_i}{\epsilon} \right)^{\alpha_i} = \\ &= \sum_{i=1}^n \alpha_i \rho_i \frac{\partial \ln \epsilon_i}{\partial \rho_i} + \ln \left( \frac{\epsilon}{\epsilon^{\sum_i \alpha_i}} \right) = \sum_{i=1}^n \alpha_i \rho_i \frac{\partial \ln \epsilon_i}{\partial \rho_i} \end{aligned}$$

Hence, this shows eq B6 is a correct equality, thus proving the limiting case in question.

Next, we consider another limiting condition. Using eqs 8 and 12, we readily obtain

$$\left( 1 + V \frac{\partial \ln \epsilon}{\partial V} \right) = \sum_{i=1}^n \frac{\alpha_i}{\epsilon} \langle p_i \rangle \exp \left( - N \frac{\partial \ln \epsilon}{\partial N_i} \right) \quad (\text{B7})$$

Since  $\epsilon$  may be written as a function of only the  $\rho_i$ 's, we readily observe the lhs of eq B7 as  $\phi$ . The rhs of eq B7 may also be re-expressed (yielding the same result as solving eqs 9 and 12) to get

$$\phi = \sum_{i=1}^n \frac{\alpha_i}{\epsilon} \langle p_i \rangle \exp \left( - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho_i} \right) \quad (\text{B8})$$

Hence, if  $\epsilon$  and  $\langle p_i \rangle$  may be known,  $\phi$  will also be known. In the non-interaction limit, we already showed that  $\epsilon = \langle p_i \rangle = 1$ ; hence, (B8) yields  $\phi = \sum_{i=1}^n \alpha_i = 1$ , which is correct. This fact is also deducible from eq 12.

The Helmholtz free energy may be written as

$$F = -k_B T \ln \left[ \frac{1}{N_1! \dots N_n!} \prod_{i=1}^n \left( \frac{\epsilon \Omega_i V}{h^{c_i}} \right)^{N_i} \right] = F_{\text{id}} - N k_B T \ln \epsilon \quad (\text{B9})$$

where  $F_{\text{id}}$  is the free energy for the noninteracting (ideal) mixture. However, we may write  $F = U - TS$ , where  $U$  and  $S$  are the internal energy and entropy of the system, respectively. In the neighborhood of the low-temperature limit, we may, therefore, write  $F \approx U$ . However, we also have that  $F_{\text{id}} \rightarrow 0$  as  $T \rightarrow 0$  (since  $T \ln T \rightarrow 0$ ); hence, we may use eq B9 in the low- $T$  (crystalline) limit as  $F \approx U \approx -N k_B T \ln (\epsilon)$ . Hence, we have that

$$\epsilon \approx \exp \left( - \frac{U}{N k_B T} \right) \quad (\text{low } T) \quad (\text{B10})$$

This is the low- $T$  behavior for  $\epsilon$ . In the neighborhood of the low- $T$  limit, we may therefore write

$$\phi = \left( 1 + V \frac{\partial \ln \epsilon}{\partial V} \right) \approx \left( 1 - \frac{V}{N k_B T} \frac{\partial U}{\partial V} \right)$$

Hence we get

$$P = \rho k_B T - \frac{\partial U}{\partial V} \quad (\text{B11})$$

We have as an independent result,  $\partial U / \partial V \rightarrow 0$  for  $P, T \rightarrow 0$  since particle motion is completely lost and particles simply occupy their respective potential energy minima, thus providing insignificant change in  $U$  for slight changes in  $V$ . Since the first term on the rhs of eq B11 also tends to zero, eq B11 is, therefore, a self-consistent equation in the limit  $P, T \rightarrow 0$ . The magnitude of the second term on the rhs of eq B11 may, however, be made

to dominate the first term by subjecting the system in question to stresses under equilibrium at low  $T$ . This then yields:  $P \approx -\partial U/\partial V$  (which is the result for the first law of thermodynamics for a pure mechanical system with thermal motion ignored. This result is obviously obtained classically using the original equation  $P = -(\partial F/\partial V)_{T,N}$ , and  $F \approx U$ ).

Observe that eq B11 shows that, near  $T = 0$ , the “ideal gas” term ( $\rho k_B T$ ) provides a competing term in the expression for  $P$  for low  $P$ .

Alternatively, if we substitute the expression of eq B10 for  $\epsilon$  into eq B8, we find we will need to know how  $\epsilon$  (or  $U$ ) varies for small changes in  $\rho_i$  or  $N_i$  in the low- $P$ ,  $T$  limit to be able to reproduce the self-consistency argument of eq B11. The investigation into the microscopic nature of solids which yields the behavior of  $(\partial\epsilon/\partial\rho_i)$ ,  $\epsilon$ ,  $U$ , etc. at low  $P$ ,  $T$  is very involved. Hence, we do not carry out such investigation at this time.

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**Note Added after ASAP Posting.** The ASAP version of this paper, published on 8/12/2004, contained typographical errors

in eqs 17 and 20–22. The corrections were reported on 8/19/2004. The corrected version was reposted on 8/19/2004.

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