

# Microstructure of two-phase random media. II. The Mayer–Montroll and Kirkwood–Salsburg hierarchies

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It is shown that the Mayer–Montroll (MM) and Kirkwood–Salsburg (KS) hierarchies of equilibrium statistical mechanics for a binary mixture under certain limits become equations for the  $n$ -point matrix probability functions  $S_n$  associated with two-phase random media. The MM representation proves to be identical to the  $S_n$  expression derived by us in a previous paper, whereas the KS representation is different and new. These results are shown to illuminate our understanding of the  $S_n$  from both a physical and quantitative point of view. In particular rigorous upper and lower bounds on the  $S_n$  are obtained for a two-phase medium formed so as to be in a state of thermal equilibrium. For such a medium consisting of impenetrable-sphere inclusions in a matrix, a new exact expression is also given for  $S_n$  in terms of a two-body probability distribution function  $\rho_2$  as well as new expressions for  $S_3$  in terms of  $\rho_2$  and  $\rho_3$ , a three-body distribution function. Physical insight into the nature of these results is given by extending some geometrical arguments originally put forth by Boltzmann.

## I. INTRODUCTION

The resurgence of interest in the determination of bulk properties of two-phase random media<sup>1,2</sup> has led to the need to further develop the precise characterization of the microstructure of such media. This series of papers addresses this need. In the first of the series<sup>3</sup> we showed for the first time the general relationship between so-called  $n$ -point matrix probability functions  $S_n$  and the  $n$ -body distribution functions  $\rho_n$ . (The  $S_n$  give the probability of simultaneously finding  $n$  points in the matrix phase.) It is the purpose of this paper to further elucidate the nature of the  $S_n$  by showing how the Mayer–Montroll (MM)<sup>4</sup> and Kirkwood–Salsburg (KS) hierarchies<sup>5</sup> of equilibrium statistical mechanics for a binary mixture under certain limits, specified below, become equations for the  $S_n$ . The MM representation proves to be identical to the  $S_n$  expression previously derived by us,<sup>3</sup> whereas the KS representation is different and new. The MM and KS representations of the  $S_n$  are shown to illuminate our understanding of the  $S_n$  from both a physical and quantitative point of view. In particular we show that the nature of the expressions for the  $S_n$  allows us to rigorously bound them as well as to get closed-form relations among the  $S_n$  and  $\rho_n$  for impenetrable-sphere inclusions in a homogeneous matrix. We illustrate our results with a new expression for  $S_2$  in terms of  $\rho_2$  and new expressions for  $S_3$  involving  $\rho_2$  and  $\rho_3$ , as well as some rigorous bounds on the  $S_2$  and  $S_3$  that can be exactly evaluated.

## II. THE MM AND KS HIERARCHIES FOR MIXTURES

We have shown in Ref. 3 that the probability of simultaneously finding  $n$  points with position vectors  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$  in the matrix phase of a statistically homogeneous two-phase medium composed of spheres of radius  $R$  and number density  $\rho$  embedded in the matrix is given by

$$S_n(\mathbf{r}_{12}, \mathbf{r}_{13}, \dots, \mathbf{r}_{1n}) = 1 + \sum_{s=1}^{\infty} (-1)^s \frac{\rho^s}{s!} \iint \dots \int g^{(s)}(\mathbf{r}_{n+1}, \mathbf{r}_{n+2}, \dots, \mathbf{r}_{n+s}) \times \prod_{j=1}^{n+s} \left\{ 1 - \prod_{i=1}^n [1 - m(r_{ij})] \right\} d\mathbf{r}_j, \quad (1)$$

where

$$m(r) = \begin{cases} 1, & \text{if } r < R \\ 0, & \text{if } r > R \end{cases},$$

$$r_{ij} \equiv |\mathbf{r}_{ij}| \equiv \mathbf{r}_j - \mathbf{r}_i.$$

Here  $g^{(s)}$  is the  $s$ -body distribution function defined below. We proceed now to state certain known results and definitions which we shall use to demonstrate that the MM equations reduce to Eq. (1) for certain binary mixtures, while the KS equations reduce to an equivalent but different set of equations.

Consider a macroscopic system of particles which constitute a mixture with  $\omega$  species at the respective fugacities  $z_\sigma$  ( $\sigma = 1, 2, \dots, \omega$ ) in the absence of external fields. It is assumed that the particles interact with pairwise potentials  $\phi_{\sigma_i\sigma_j}(\mathbf{r}_{ij})$  between every two particles of species  $\sigma_i$  and  $\sigma_j$  which are at position  $\mathbf{r}_i$  and  $\mathbf{r}_j$ , respectively. Working in the canonical ensemble<sup>6</sup> Mayer and Montroll<sup>4</sup> and Mayer<sup>5</sup> were able to obtain general sets of equations for  $n$ -body distribution functions  $\rho^{(n)}$  for the multicomponent system. Baer and Lebowitz<sup>7</sup> subsequently extended that work somewhat, using the grand ensemble.<sup>6</sup> The quantity

$$\rho_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) d\mathbf{r}_1, d\mathbf{r}_2, \dots, d\mathbf{r}_n$$

gives the probability of simultaneously finding the center of exactly one (unspecified) particle of species  $\sigma$  in the volume  $d\mathbf{r}_1$ , the center of exactly one other (unspecified) particle of species  $\sigma$  in the volume  $d\mathbf{r}_2, \dots$  and the cen-

ter of exactly one other (unspecified) particle of species  $\sigma$  in the volume  $d\mathbf{r}_n$ . For brevity we shall at times denote  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$  by  $\mathbf{r}^n$ . Setting  $k=0$  in Eq. (3.10) of Ref. 7 gives, in our notation,

$$\frac{\rho_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}^n)}{[\prod_{i=1}^n z_{\sigma_i}] e_n^{\sigma_1, \sigma_2, \dots, \sigma_n}(\mathbf{r}^n)} = \sum_{s=0}^{\infty} \frac{1}{s!} \int' \dots \int' \rho_{\sigma_{n+1}, \dots, \sigma_{n+s}}^{(s)}(\mathbf{r}_{n+1}, \dots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} \left\{ \prod_{i=1}^n [1 + f_{\sigma_i \sigma_j}(\mathbf{r}_i, \mathbf{r}_j)] - 1 \right\} d\mathbf{r}_j, \quad (2)$$

which is the MM hierarchy<sup>4</sup> of equations. Setting  $s=1$  in Eq. (3.10) gives instead the KS hierarchy,<sup>5</sup>

$$\frac{\rho_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}^n)}{z_{\sigma_1} \prod_{i=2}^n e_2^{\sigma_i}(\mathbf{r}_1, \mathbf{r}_i)} = \sum_{s=0}^{\infty} \frac{1}{s!} \int' \dots \int' \rho_{\sigma_2, \dots, \sigma_{n+s}}^{(n+s-1)}(\mathbf{r}_2, \dots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} f_{\sigma_1 \sigma_j}(\mathbf{r}_1, \mathbf{r}_j) d\mathbf{r}_j. \quad (3)$$

Here  $f_{\sigma_i \sigma_j}(\mathbf{r}_i, \mathbf{r}_j) \equiv f_{\sigma_i \sigma_j}(\mathbf{r}_{ij}) \equiv \exp[-\beta \phi_{\sigma_i \sigma_j}(r_{ij})] - 1$ . (4)

This is the Mayer- $f$  function. We have also introduced  $e_n^{\sigma_1, \sigma_2, \dots, \sigma_n}(\mathbf{r}^n) = \exp\left[-\beta \sum_{i < j}^n \phi_{\sigma_i \sigma_j}(r_{ij})\right]$ ,

where  $\int'(\ ) d\mathbf{r}_j$  stands for  $\sum_{\sigma} \int(\ ) d\mathbf{r}_j$ .

It is convenient to define the  $n$ -body distribution functions  $g_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}$  which are related to the  $\rho_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}$  such that

$$g_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}^n) = \frac{\rho_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}^n)}{\prod_{i=1}^n \rho_{\sigma_i}^{(1)}(\mathbf{r}_i)}. \quad (5)$$

For a statistically homogeneous system  $\rho_{\sigma}^{(1)}(\mathbf{r})$  is independent of position and is simply equal to the number density of species  $\sigma$  or  $\rho_{\sigma}$ . We shall use the definitions

$$\rho^{(0)} \equiv 1, \quad g^{(0)} \equiv 1, \quad (6)$$

which are consistent with our equations.

III. RELATION BETWEEN THE MM EQUATIONS AND THE  $S_n$

Consider a statistically homogeneous and isotropic binary mixture of species  $U$  and species  $V$ . Setting  $n=1$  in Eq. (3) and using Eqs. (5) and (6) gives

$$\frac{\rho_{\sigma_1}^{(1)}}{z_{\sigma_1}} = \sum_{s=0}^{\infty} \frac{1}{s!} \int' \dots \int' \prod_{k=2}^{1+s} \rho_{\sigma_k}^{(1)} \times g_{\sigma_2, \dots, \sigma_{1+s}}^{(s)}(\mathbf{r}_2, \dots, \mathbf{r}_{1+s}) \prod_{j=2}^{1+s} f_{\sigma_1 \sigma_j}(r_{1j}) d\mathbf{r}_j. \quad (7)$$

Letting  $\sigma_1 = U$ , the series in Eq. (7) up to the term  $s=2$  is equal to

$$\begin{aligned} \frac{\rho_U}{z_U} &= 1 + \sum_{\sigma_2} \rho_{\sigma_2} f_{U\sigma_2}(r_{12}) d\mathbf{r}_2 + \sum_{\sigma_2} \sum_{\sigma_3} \frac{1}{2!} \iint \rho_{\sigma_2} \rho_{\sigma_3} g_{\sigma_2 \sigma_3}^{(2)}(r_{23}) f_{U\sigma_2}(r_{12}) f_{U\sigma_3}(r_{13}) d\mathbf{r}_2 d\mathbf{r}_3 + \dots \\ &= 1 + \rho_U \int f_{UU}(r_{12}) d\mathbf{r}_2 + \rho_V \int f_{UV}(r_{12}) d\mathbf{r}_2 + \frac{1}{2} \rho_U^2 \iint g_{UU}^{(2)}(r_{23}) f_{UU}(r_{12}) f_{UU}(r_{13}) d\mathbf{r}_2 d\mathbf{r}_3 \\ &\quad + \frac{1}{2} \rho_U \rho_V \iint g_{UV}^{(2)}(r_{23}) f_{UU}(r_{12}) f_{UV}(r_{13}) d\mathbf{r}_2 d\mathbf{r}_3 + \frac{1}{2} \rho_U \rho_V \iint g_{VV}^{(2)}(r_{23}) f_{UV}(r_{12}) f_{UV}(r_{13}) d\mathbf{r}_2 d\mathbf{r}_3 \\ &\quad + \frac{1}{2} \rho_V^2 \iint g_{VV}^{(2)}(r_{23}) f_{UV}(r_{12}) f_{UV}(r_{13}) d\mathbf{r}_2 d\mathbf{r}_3 + \dots \end{aligned} \quad (8)$$

So far in this section the solute and solvent particles could be defined by an arbitrary interparticle potential. Let us now consider the special case of a mixture of hard-sphere particles characterized by the radii  $R_U$  and  $R_V$ . As the size of  $U$  particles goes to zero ( $R_U \rightarrow 0$ ) and the density of  $U$  particles goes to zero (infinite dilution limit;  $\rho_U \rightarrow 0$ ), Eq. (8) becomes

$$\begin{aligned} \frac{\rho_U}{z_U} &= 1 + \rho_V \int f_{UV}(r_{12}) d\mathbf{r}_2 \\ &\quad + \frac{\rho_V}{2!} \iint g_{VV}^{(2)}(r_{23}) f_{UV}(r_{12}) f_{UV}(r_{13}) d\mathbf{r}_2 d\mathbf{r}_3 + O(\rho_V^3) \\ &= 1 + \text{diagram 1} + \text{diagram 2} + O(\rho_V^3), \end{aligned} \quad (9)$$

since terms on the right-hand side involving  $\rho_U$  are identically zero and since  $f_{UU}(r) = 0$  as a result of  $\phi_{UU}(r_{12})$  being zero for all  $r_{12}$ . The second line of Eq. (9) is the diagrammatic equivalent of the first line.<sup>8</sup> Here ---- is an  $f_{UV}$  bond and ——— is a  $g_{VV}^{(2)}$  bond. Associated with each black circle is a factor in the number density of the solvent species  $\rho_V$  and associated with each point particle is a factor of unity. Comparison of the general term of Eq. (9) with that of Eq. (1) with  $n=1$  reveals that the former is precisely the expression for the 1-point matrix function,  $S_1$ , since  $f_{UV}(r) = -m(r)$ . Thus

$$\lim_{\substack{\rho_U \rightarrow 0 \\ R_U \rightarrow 0}} \left[ \frac{\rho_U}{z_U} \right] = S_1 = \phi, \quad (10)$$

where  $\phi$  is the volume fraction of the matrix phase. The result given by Eq. (10) is interesting from the standpoint that it relates a purely thermodynamic quantity on the left-hand side to a geometric quantity on the right-hand side. This equality is consistent with the interpretation of the fugacity as an "effective density" for a hard-sphere system.

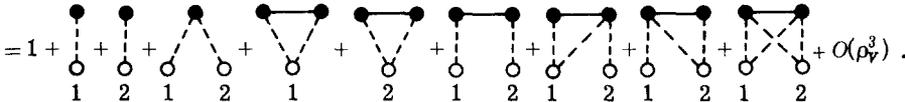
Let us now consider Eq. (5) when  $n=2$ , which gives for a homogeneous and isotropic system

$$\frac{\rho_{\sigma_1} \rho_{\sigma_2} g_{\sigma_1 \sigma_2}^{(2)}(r_{12})}{z_{\sigma_1} z_{\sigma_2} e_2^{U \dots U}(r_{12})} = \sum_{s=0}^{\infty} \frac{1}{s!} \int \int' \dots \int' \prod_{k=3}^{2+s} \rho_{\sigma_k} g_{\sigma_3, \dots, \sigma_{2+s}}^{(s)}(\mathbf{r}_3, \dots, \mathbf{r}_{2+s}) \times \prod_{j=3}^{2+s} [f_{\sigma_1 \sigma_j}(r_{1j}) + f_{\sigma_2 \sigma_j}(r_{2j}) + f_{\sigma_1 \sigma_j}(r_{1j}) f_{\sigma_2 \sigma_j}(r_{2j})] d\mathbf{r}_j. \tag{11}$$

Setting  $\sigma_1 = U$  and  $\sigma_2 = U$ , the series given by Eq. (11) up through terms for  $s=2$  is equal to

$$\frac{\rho_U^2 g_{UU}^{(2)}(r_{12})}{z_U^2 e_2^{UU}(r_{12})} = 1 + \sum_{\sigma_3} \int \rho_{\sigma_3} [f_{U\sigma_3}(r_{13}) + f_{U\sigma_3}(r_{23}) + f_{U\sigma_3}(r_{13}) f_{U\sigma_3}(r_{23})] d\mathbf{r}_3 + \sum_{\sigma_3} \sum_{\sigma_4} \iint \rho_{\sigma_3} \rho_{\sigma_4} g_{\sigma_3 \sigma_4}^{(2)}(r_{34}) [f_{U\sigma_3}(r_{13}) + f_{U\sigma_3}(r_{23}) + f_{U\sigma_3}(r_{13}) f_{U\sigma_3}(r_{23})] [f_{U\sigma_4}(r_{14}) + f_{U\sigma_4}(r_{24}) + f_{U\sigma_4}(r_{14}) f_{U\sigma_4}(r_{24})] d\mathbf{r}_3 d\mathbf{r}_4 + \dots \tag{12}$$

Expanding Eq. (12) and taking the limits  $\rho_U \rightarrow 0$  and  $R_U \rightarrow 0$  gives

$$\frac{\rho_U^2 g_{UU}^{(2)}(r_{12})}{z_U^2 e_2^{UU}(r_{12})} = 1 + \rho_U \int [f_{UV}(r_{13}) + f_{UV}(r_{23}) + f_{UV}(r_{13}) f_{UV}(r_{23})] d\mathbf{r}_3 + \frac{\rho_U^2}{2!} \iint g_{VV}^{(2)}(r_{34}) [f_{UV}(r_{13}) + f_{UV}(r_{23}) + f_{UV}(r_{13}) f_{UV}(r_{23})] [f_{UV}(r_{14}) + f_{UV}(r_{24}) + f_{UV}(r_{14}) f_{UV}(r_{24})] d\mathbf{r}_3 d\mathbf{r}_4 + O(\rho_U^3) \tag{13}$$


Going on to arbitrary order in  $\rho$ , we find that Eq. (13) is precisely the expression for the 2-point matrix function given by Eq. (1); i.e.,

$$\lim_{\substack{\rho_U \rightarrow 0 \\ R_U \rightarrow 0}} \left[ \frac{\rho_U^2 g_{UU}^{(2)}(r_{12})}{z_U^2 e_2^{UU}(r_{12})} \right] = S_2(r_{12}). \tag{14}$$

More generally, for any  $n$ , one finds

$$\lim_{\substack{\rho_U \rightarrow 0 \\ R_U \rightarrow 0}} \left[ \frac{\rho_U^n g_{UU \dots U}^{(n)}(r_{12}, r_{13}, \dots, r_{1n})}{z_U^n e_n^{U \dots U}(r_{12}, \dots, r_{1n})} \right] = \sum_{s=0}^{\infty} \frac{\rho_U^s}{s!} \int \dots \int g_{V \dots V}^{(s)}(\mathbf{r}_{n+1}, \dots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} \left\{ \prod_{i=1}^n [1 + f_{UV}(r_{ij})] - 1 \right\} d\mathbf{r}_j = S_n(r_{12}, r_{13}, \dots, r_{1n}), \tag{15}$$

i.e., there is a one-to-one mapping between the  $n$ -point matrix-function equations and the MM binary-mixture equations in the limit of infinite dilution of the point-particle species (the solute species). Note that in this limit  $e_n^{U \dots U}(r_{12}, \dots, r_{1n})$  is always unity. In addition, it is seen that the solute particles are always associated with the labelings  $1, 2, \dots, n$  while the solvent particles of radius  $R_V = R$  are associated with the labelings  $n+1, n+2, \dots$ . Consequently, every  $g^{(s)}$  in the MM equations is a pure solvent quantity and every  $f$  is a solute-solvent  $f$ . We can therefore suppress the  $U$ 's and  $V$ 's and write the MM relations, without misunderstanding, as

$$S_n(r_{12}, r_{13}, \dots, r_{1n}) = \phi^n g^{(n)}(r_{12}, r_{13}, \dots, r_{1n}), \tag{16a}$$

$$S_n(r_{12}, r_{13}, \dots, r_{1n}) = \sum_{s=0}^{\infty} \frac{\rho_U^s}{s!} \int \dots \int g^{(s)}(\mathbf{r}_{n+1}, \mathbf{r}_{n+2}, \dots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} \left\{ \prod_{i=1}^n [1 + f(r_{ij})] - 1 \right\} d\mathbf{r}_j, \tag{16b}$$

if it is kept in mind that the labelings  $1, 2, \dots, n$  are associated with the point particles of infinite dilution while  $n+1, n+2, \dots$  are associated with the "full-blown" solvent particles of radius  $R$ . Apart from the constant factor  $\phi^n$  the binary-mixture  $n$ -body correlation function for point particles of infinite dilution is the  $n$ -point matrix probability function  $S_n$ . It is instructive to recast Eq. (16a) as

$$g^{(n)}(r_{12}, r_{13}, \dots, r_{1n}) = \frac{S_n(r_{12}, r_{13}, \dots, r_{1n})}{S_1^n}. \tag{17}$$

We note that as the mutual distances between the  $n$  points increase, the  $S_n$  (assuming no long range order) may be written in terms of a product of  $n$  1-point matrix functions; that is

$$\lim_{\substack{r_i \rightarrow \infty \\ 1 \leq i < j \leq n}} S_n(r_{12}, r_{13}, \dots, r_{1n}) = S_1(\mathbf{r}_1) \dots S_1(\mathbf{r}_n) = S_1^n. \tag{18}$$

Under these conditions Eq. (17) becomes

$$g^{(n)}(r_{12}, r_{13}, \dots, r_{1n}) = 1$$

for all  $n$ , which is the correct normalization for  $g^{(n)}$ .

**IV. RELATION BETWEEN THE KS EQUATIONS AND THE  $S_n$**

Let us again consider a statistically homogeneous and isotropic binary mixture of solute species  $U$  and solvent species  $V$ . Setting  $n=1$  in the KS hierarchy, Eq. (6), gives

$$\frac{\rho_{\sigma_1}}{z_{\sigma_1}} = \sum_{s=0}^{\infty} \frac{1}{s!} \int' \cdots \int' \prod_{k=2}^{1+s} \rho_{\sigma_k} g_{\sigma_2 \cdots \sigma_{1+s}}^{(s)}(\mathbf{r}_2, \dots, \mathbf{r}_{1+s}) \times \prod_{j=2}^{1+s} f_{\sigma_1 \sigma_j}(\mathbf{r}_{1j}) d\mathbf{r}_j. \tag{19}$$

This equation is exactly equivalent to the corresponding MM binary mixture equation for  $n=1$ , Eq. (7). Let us again consider the special case of a mixture of hard-sphere particles characterized by the radii  $R_U$  and  $R_V$ . It is clear that if we set  $\sigma_1$  equal to  $U$  and take the limits  $\rho_U \rightarrow 0$  and  $R_U \rightarrow 0$ , in Eq. (19), we have

$$\lim_{\substack{\rho_U \rightarrow 0 \\ R_U \rightarrow 0}} \left[ \frac{\rho_U}{z_U} \right] = 1 + \rho_V \int f_{UV}(\mathbf{r}_{12}) d\mathbf{r}_2 + \frac{\rho_V^2}{2!} \iint g_{VV}^{(2)}(\mathbf{r}_{23}) f_{UV}(\mathbf{r}_{12}) f_{UV}(\mathbf{r}_{13}) d\mathbf{r}_2 d\mathbf{r}_3 + O(\rho_V^3) = S_1 = \phi, \tag{20}$$

which is the result already obtained from the MM representation, Eq. (9). The case  $n=1$ , however, is the only instance for which these two hierarchies reduce to precisely the same functional form.

Letting  $n=2$  in Eq. (6) gives for a homogeneous system

$$\frac{\rho_{\sigma_1} \rho_{\sigma_2} g_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_{12})}{z_{\sigma_1} e_2^{(1)\sigma_2}(\mathbf{r}_{12})} = \sum_{s=0}^{\infty} \frac{1}{s!} \int' \cdots \int' \prod_{k=2}^{2+s} \rho_{\sigma_k} g_{\sigma_2 \cdots \sigma_{2+s}}^{(1+s)}(\mathbf{r}_2, \dots, \mathbf{r}_{2+s}) \prod_{j=3}^{2+s} f_{\sigma_1 \sigma_j}(\mathbf{r}_{1j}) d\mathbf{r}_j. \tag{21}$$

Setting  $\sigma_1 = U$  and  $\sigma_2 = U$ , the series given by Eq. (21) up through terms for  $s=2$  is equal to

$$\begin{aligned} \frac{\rho_U^2 g_{UU}^{(2)}(\mathbf{r}_{12})}{z_U e_2^{(1)U}(\mathbf{r}_{12})} &= \rho_U + \sum_{\sigma_3} \int \rho_U \rho_{\sigma_3} g_{U\sigma_3}^{(2)}(\mathbf{r}_{23}) f_{U\sigma_3}(\mathbf{r}_{13}) d\mathbf{r}_3 + \sum_{\sigma_3} \sum_{\sigma_4} \frac{1}{2!} \iint \rho_U \rho_{\sigma_3} \rho_{\sigma_4} g_{U\sigma_3 \sigma_4}^{(3)}(\mathbf{r}_{23}, \mathbf{r}_{24}) f_{U\sigma_3}(\mathbf{r}_{13}) f_{U\sigma_4}(\mathbf{r}_{14}) d\mathbf{r}_3 d\mathbf{r}_4 + \cdots \\ &= 1 + \rho_U \int g_{UU}^{(2)}(\mathbf{r}_{23}) f_{UU}(\mathbf{r}_{13}) d\mathbf{r}_3 + \rho_V \int g_{UV}^{(2)}(\mathbf{r}_{23}) f_{UV}(\mathbf{r}_{13}) d\mathbf{r}_3 + \frac{\rho_U^2}{2!} \iint g_{UUU}^{(3)}(\mathbf{r}_{23}, \mathbf{r}_{24}) f_{UU}(\mathbf{r}_{13}) f_{UU}(\mathbf{r}_{14}) d\mathbf{r}_3 d\mathbf{r}_4 \\ &\quad + \frac{\rho_U \rho_V}{2!} \iint g_{UVU}^{(3)}(\mathbf{r}_{23}, \mathbf{r}_{24}) f_{UV}(\mathbf{r}_{13}) f_{UV}(\mathbf{r}_{14}) d\mathbf{r}_3 d\mathbf{r}_4 + \frac{\rho_V \rho_U}{2!} \iint g_{UVU}^{(3)}(\mathbf{r}_{23}, \mathbf{r}_{24}) f_{UV}(\mathbf{r}_{13}) f_{UV}(\mathbf{r}_{14}) d\mathbf{r}_3 d\mathbf{r}_4 \\ &\quad + \frac{\rho_V^2}{2!} \iint g_{UVV}^{(3)}(\mathbf{r}_{23}, \mathbf{r}_{24}) f_{UV}(\mathbf{r}_{13}) f_{UV}(\mathbf{r}_{14}) d\mathbf{r}_3 d\mathbf{r}_4 + \cdots \end{aligned} \tag{22}$$

Equation (22) in the limits  $\rho_U \rightarrow 0$  and  $R_U \rightarrow 0$  becomes

$$\lim_{\substack{\rho_U \rightarrow 0 \\ R_U \rightarrow 0}} \left[ \frac{\rho_U g_{UU}^{(2)}(\mathbf{r}_{12})}{z_U e_2^{(1)U}(\mathbf{r}_{12})} \right] = 1 + \rho_V \int g_{UV}^{(2)}(\mathbf{r}_{23}) f_{UV}(\mathbf{r}_{13}) d\mathbf{r}_3 + \frac{\rho_V^2}{2!} \iint g_{UVV}^{(3)}(\mathbf{r}_{23}, \mathbf{r}_{24}) f_{UV}(\mathbf{r}_{13}) f_{UV}(\mathbf{r}_{14}) d\mathbf{r}_3 d\mathbf{r}_4 + O(\rho_V^3) = 1 + \text{graph 1} + \text{graph 2} + O(\rho_V^3), \tag{23}$$

where  is now a  $g_{UV}^{(2)}$  bond and  is a  $g_{UVV}^{(3)}$  bond. Note the difference between Eq. (23) and the MM counterpart Eq. (13). The graphs are topologically different in these two instances. All of the correlation functions on the right-hand side of Eq. (13) involve only "full blown" solvent particles while those of Eq. (23) involve, in addition to the solvent particles, a point particle. For example, the two-body distribution function appearing in the MM version is a "solvent-solvent"  $g_{VV}^{(2)}(\mathbf{r})$  while the two-body function appearing in the KS counterpart is a "solute-solvent"  $g_{UV}^{(2)}(\mathbf{r})$ . Multiplying Eq. (24) by

$$\phi = \lim_{\substack{\rho_U \rightarrow 0 \\ R_U \rightarrow 0}} \left[ \frac{\rho_U}{z_U} \right]$$

gives

$$\lim_{\substack{\rho_U \rightarrow 0 \\ R_U \rightarrow 0}} \left[ \frac{\rho_U^2 g_{UU}^{(2)}(\mathbf{r}_{12})}{z_U^2 e_2^{(1)U}(\mathbf{r}_{12})} \right] = \phi \left[ 1 + \rho_V \int g_{UV}^{(2)}(\mathbf{r}_{23}) f_{UV}(\mathbf{r}_{13}) d\mathbf{r}_3 + \frac{\rho_V^2}{2!} \iint g_{UVV}^{(3)}(\mathbf{r}_{23}, \mathbf{r}_{24}) f_{UV}(\mathbf{r}_{13}) f_{UV}(\mathbf{r}_{14}) d\mathbf{r}_3 d\mathbf{r}_4 + O(\rho_V^3) \right]. \tag{24}$$

On comparing the left-hand side of Eq. (24) to Eq. (14) we find that

$$S_2(\mathbf{r}_{12}) = \phi \left[ 1 + \rho_V \int g_{UV}^{(2)}(\mathbf{r}_{23}) f_{UV}(\mathbf{r}_{13}) d\mathbf{r}_3 + \frac{\rho_V^2}{2!} \iint g_{UVV}^{(3)}(\mathbf{r}_{23}, \mathbf{r}_{24}) f_{UV}(\mathbf{r}_{13}) f_{UV}(\mathbf{r}_{14}) d\mathbf{r}_3 d\mathbf{r}_4 + O(\rho_V^3) \right]. \tag{25}$$

In general, for any  $n$  we have

$$\lim_{\rho_U \rightarrow 0} \left[ \frac{\rho_U^n g_{UU \dots U}^{(n)}(\mathbf{r}_{12}, \mathbf{r}_{13}, \dots, \mathbf{r}_{1n})}{z_U \prod_{j=2}^n e_{2U}^{(j)}(\mathbf{r}_{1j})} \right] = \rho_U^{n-1} \sum_{s=0}^{\infty} \frac{\rho_V^s}{s!} \iint \dots \int g_{UU \dots UV \dots V}^{(n-1+s)}(\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{n+s}) \prod_{j=n+1}^{n+s} f_{UV}(\mathbf{r}_{1j}) d\mathbf{r}_j. \quad (26)$$

We then have, on comparing Eq. (26) to the left-hand side of Eq. (15),

$$\begin{aligned} \phi g_{UU \dots U}^{(n)}(\mathbf{r}_{12}, \dots, \mathbf{r}_{1n}) &= \sum_{s=0}^{\infty} \frac{\rho_V^s}{s!} \iint \dots \int g_{UU \dots UV \dots V}^{(n-1+s)}(\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{n+s}) \prod_{j=n+1}^{n+s} f_{UV}(\mathbf{r}_{1j}) d\mathbf{r}_j \\ &= S_n(\mathbf{r}_{12}, \dots, \mathbf{r}_{1n}) / \phi^{n-1}. \end{aligned} \quad (27)$$

Note that the correlation function  $g^{(n-1+s)}$  on the right-hand side of Eq. (27) contains  $n-1$  subscripted  $U$ 's and  $s$  subscripted  $V$ 's. Since the point particles are associated with the labels  $1, 2, \dots, n$  and the solvent particles of radius  $R$  are associated with the labels  $n+1, n+2, \dots$ , we may suppress the  $U$ 's and  $V$ 's without loss of information and write

$$\begin{aligned} S_n(\mathbf{r}_{12}, \mathbf{r}_{13}, \dots, \mathbf{r}_{1n}) &= \phi^{n-1} \sum_{s=0}^{\infty} \frac{\rho_V^s}{s!} \int \dots \int g^{(n-1+s)}(\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{n+s}) \\ &\quad \times \prod_{j=n+1}^{n+s} f(\mathbf{r}_{1j}) d\mathbf{r}_j, \end{aligned} \quad (28)$$

which is the KS representation of the  $S_n$ . Although in the context of the statistical mechanics of mixtures, both the KS and MM representations have been considered, the KS representation of the matrix functions  $S_n$  has not heretofore been given.

## V. DISCUSSION OF EQS. (15) AND (16)

We have shown in Secs. III and IV the mathematical correspondence between the  $n$ -point matrix functions  $S_n$  and the  $n$ -point solute functions in the case of point-particle solute molecules in the limit of infinite solute dilution. The question remains: In physical terms *why* is there this remarkable correspondence? The solute functions are (except for normalization) probability densities that give the probability that solute particle 1 will be centered at  $\mathbf{r}_1$ , solute particle 2 at  $\mathbf{r}_2, \dots$ , and solute particle  $n$  at  $\mathbf{r}_n$ , in the presence of solvent particles as well as the other solute particles. When we take the limit of infinite solute dilution there are no "other" solute particles; only the  $n$  solute particles directly described by the  $g^{(n)}$  are retained in the equations. When the  $n$  solute particles are point particles of zero radius, it is clear that for hard-sphere solvent particles that are impenetrable to the solute particles (whether or not they are penetrable to each other) the solute particles will only be found in the matrix. Thus the probability that point solute particle 1 will be centered at  $\mathbf{r}_1$ , point solute particle 2 at  $\mathbf{r}_2$ , etc., is strictly proportional to the probability that point 1 is in the matrix at  $\mathbf{r}_1$ , point 2 is in the matrix at  $\mathbf{r}_2$ , etc. Thus,  $g^{(n)}$  is proportional to  $S_n$ . Since  $g^{(n)}$  is normalized to go to 1 for  $\mathbf{r}_i$  all widely separated and  $S_n$  defined so that it goes to a product of  $n S_1$ 's, we have finally

$$g_n(\mathbf{r}_1, \dots, \mathbf{r}_n) = S_n(\mathbf{r}_1, \dots, \mathbf{r}_n) / S_1(\mathbf{r}_1) S_1(\mathbf{r}_2), \dots, S_1(\mathbf{r}_n). \quad (29)$$

The left-hand sides of the MM equations [Eq. (15)]

are the full  $S_n(\mathbf{r}_1, \dots, \mathbf{r}_n)$ . It is equally easy to characterize the left-hand sides of the KS equations Eq. (27); they are the conditional probabilities  $S_n(\mathbf{r}_1/\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n)$  of finding point 1 in the matrix at  $\mathbf{r}_1$ , given that point 2 is in the matrix at  $\mathbf{r}_2$ , point 3 is in the matrix at  $\mathbf{r}_3$ , etc. We have

$$S_2(\mathbf{r}_1, \mathbf{r}_2) = S_2(\mathbf{r}_1/\mathbf{r}_2) S_1(\mathbf{r}_2)$$

$$S_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = S_3(\mathbf{r}_1/\mathbf{r}_2, \mathbf{r}_3) S_1(\mathbf{r}_2) S_1(\mathbf{r}_3)$$

etc.

We note that if the solvent particles are wholly or partially penetrable to each other, none of the previous considerations of this paper are changed, as long as they remain impenetrable to the point particles that represent the solute.

Clearly, if the solute particles do not become point particles, but remain hard-sphere particles of finite diameter  $\sigma$  then the KS and MM representations of the  $g^{(n)}$  still have a well-defined meaning as solute probability distribution functions and  $\rho_U/z_U$  as a solute density/fugacity ratio. We note that the  $S_n(\rho_U/z_U)^n g^{(n)}/e_n$  also continue to have meaning as matrix functions; they give the probability that spheres of diameter  $\sigma$  centered at  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$ , respectively, will all be found to be wholly in the matrix.

From the KS equations it easily follows that for a single-species hard-sphere system

$$g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) / e_n = (z/\rho)^{n-1}, \quad (30)$$

as  $\mathbf{r}_{i1} \rightarrow 0$  for  $i=2, \dots, n$ . [Hoover and Poirier<sup>9</sup> proved Eq. (30) for  $n=2$  by different means.] We note that the analogous statement for  $S_n$  is

$$S_n(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_1) = S_1(\mathbf{r}_1),$$

which is wholly obvious—essentially by definition—in the language of the matrix functions.

We wish to point out that there is nothing that limits the medium under consideration to a fluid of hard spheres. In the  $g^{(n)}$  language both the solute and solvent can have arbitrary interparticle potentials as is clear from the development of Secs. I and II. Matrix functions, on the other hand, only make sense (as they are usually defined, at least) for media consisting of particles that are wholly impenetrable to the points  $\mathbf{r}_i$  that give the arguments of the  $S_n$  (although not necessarily to each other), so that there is no ambiguity in what constitutes matrix and particle phases. But even within the context of this restriction, the media particles need not be taken to be hard spheres with respect to the argu-

ments of the  $S_n$ ; they can be hard particles of any sort. For example, they can be parallel cubes impenetrable to each other. For such particles the coefficients of the density expansions of the  $g^{(n)}$  and  $S_n$  can be analytically determined to any order<sup>10</sup> if the  $g^{(n)}$  are assumed to be those of the grand canonical ensemble.

An interesting conceptual point is brought out by the following observation. Equation (1) was derived in our previous work<sup>3</sup> under the very general assumption that the  $g^{(n)}$  are those of a distribution of included spheres that is statistically homogeneous and isotropic but otherwise arbitrary. In particular, they need not be the  $g^{(n)}$  associated with a system in thermal equilibrium. On the other hand, our rederivation here starting with the MM or KS equations and using Eqs. (15) or (16a) is in the context of the  $g^{(n)}$  that characterize thermal equilibrium. It appears that for hard-sphere systems, Eq. (16), which expresses the zero-density "point solute"  $g_{U...V}^{(n)}$  (or equivalently, the  $S_n$ ) in terms of the pure-solvent  $g_{V...V}^{(n)}$ , has a far wider domain of validity than that of thermal equilibrium. It is only when one takes the full set of MM equations for a particular system (which include the equations expressing the  $g_{V...V}^{(n)}$  and  $g_{U...V}^{(n)}$  as well as the  $g_{V...V}^{(n)}$  in terms of sums of integrals involving these same functions) that one can solve for the  $g^{(n)}$ , i. e., the equations become a closed set. One then finds that the  $g^{(n)}$  are those of thermal equilibrium. In contrast, the partial set of MM equations we work with here simply give the set of  $S_n$  that are compatible with a prescribed set of  $\rho_V$  and  $g_{V...V}^{(s)}$  without prescribing the latter. The status of the KS Eqs. (28) in the nonequilibrium case is less clear; here we have established the equivalence of Eqs. (16) and (28) only in the case of thermal equilibrium. We hope to return to this fascinating question in subsequent work.

In the case of a system of hard spheres all of equal diameter, Boltzmann<sup>11</sup> considered the first two members of the KS hierarchy (in the context of a canonical ensemble) long before the work of Mayer or Kirkwood and Salsburg. He recognized that  $V\rho/z$  is the average space available to the center of a sphere inserted into a system of  $N$  spheres (except for boundary effects that become negligible in the thermodynamic limit,  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V$  finite) and gave a means of constructing this average; it is the hard-sphere KS equation for  $n=1$  for a homogeneous, isotropic system. He also demonstrated a similar geometric significance for the hard-sphere KS equation for  $n=2$  and  $r_{12}=\sigma$ . We use Boltzmann's language in Sec. IX.

## VI. BOUNDING PROPERTY OF SUCCESSIVE PARTIAL SUMS OF THE MM AND KS SERIES

In this section we note an important bounding property enjoyed by the partial sums of both the MM and KS series for the  $S_n$ . In Sec. VII we further note that in the case of impenetrable-sphere inclusions in thermal equilibrium both series consist of only a finite number of terms, thus yielding closed-form expressions for the  $S_n$  in terms of the  $g^{(s)}$ . In Sec. VIII we show explicitly how these results of Secs. VI and VII yield a new expression for  $S_2$  as a function of  $g^{(2)}$  and new expressions

for  $S_3$  as a function of  $g^{(2)}$  and  $g^{(3)}$ , as well as various rigorous bounds on the  $S_2$  and  $S_3$  that can be exactly evaluated.

We begin with the MM and KS equations for a statistically homogeneous and isotropic mixture with  $\omega$  species at the respective fugacities  $z_\sigma$  ( $\sigma=1, 2, \dots, \omega$ ) written in a form that explicitly exhibits remainder terms

$$\frac{[\prod_{i=1}^n \rho_{\sigma_i}^{(1)}] g_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}^n)}{[\prod_{i=1}^n z_{\sigma_i}] e_n^{\sigma_1, \sigma_2, \dots, \sigma_n}(\mathbf{r}^n)} = Q_n^{\text{MM}(l)} + R_n^{\text{MM}(l)}, \quad (31)$$

$$\frac{[\prod_{i=1}^n \rho_{\sigma_i}^{(1)}] g_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}^n)}{z_{\sigma_1} \prod_{i=1}^n e_2^{\sigma_i}(\mathbf{r}_i, \mathbf{r}_i)} = Q_n^{\text{KS}(l)} + R_n^{\text{KS}(l)}, \quad (32)$$

where

$$Q_n^{\text{MM}(l)} = \sum_{s=0}^l \frac{1}{s!} \int' \dots \int' \int' \left[ \prod_{i=1}^{n+s} \rho_{\sigma_i}^{(1)} \right] g_{\sigma_{n+1} \dots \sigma_{n+s}}^{(s)}(\mathbf{r}_{n+1}, \dots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} \left\{ \prod_{i=1}^n [1 + f_{\sigma_i \sigma_j}(\mathbf{r}_i, \mathbf{r}_j)] - 1 \right\} d\mathbf{r}_j, \quad (33)$$

$$Q_n^{\text{KS}(l)} = \sum_{s=0}^l \frac{1}{s!} \int' \dots \int' \int' \left[ \prod_{i=2}^{n+s} \rho_{\sigma_i}^{(1)} \right] g_{\sigma_2 \dots \sigma_{n+s}}^{(n+s-1)}(\mathbf{r}_2, \dots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} f_{\sigma_1 \sigma_j}(\mathbf{r}_1, \mathbf{r}_j) d\mathbf{r}_j. \quad (34)$$

Here  $R_n^{\text{MM}(l)}$  and  $R_n^{\text{KS}(l)}$  are the MM and KS remainder terms, respectively. (Their explicit form can be found in Ref. 7 and will not be needed by us in what follows.)

The first observation to make about these hierarchies is that they are alternating series for a positive interaction potential, i. e.,  $\phi_{\sigma_i \sigma_j}(r_{ij}) > 0$ . This is true by virtue of the fact that for such a potential we have  $-1 \leq f_{\sigma_i \sigma_j}(r_{ij}) \leq 0$  and  $g_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}^n) > 0$  for all  $\mathbf{r}^n$ . Baer and Lebowitz<sup>7</sup> have noted that the remainder terms given in Eqs. (31) and (32) satisfy the following bounds:

$$R_n^{(l)} \begin{cases} \geq 0 & \text{for } l \text{ odd} \\ \leq 0 & \text{for } l \text{ even} \end{cases}, \quad (35)$$

which implies that

$$\frac{[\prod_{i=1}^n \rho_{\sigma_i}^{(1)}] g_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}^n)}{[\prod_{i=1}^n z_{\sigma_i}] e_n^{\sigma_1, \sigma_2, \dots, \sigma_n}(\mathbf{r}^n)} \begin{cases} \geq Q_n^{\text{MM}(l)} & \text{for } l \text{ odd} \\ \leq Q_n^{\text{MM}(l)} & \text{for } l \text{ even} \end{cases}, \quad (36)$$

$$\frac{[\prod_{i=1}^n \rho_{\sigma_i}^{(1)}] g_{\sigma_1, \sigma_2, \dots, \sigma_n}^{(n)}(\mathbf{r}^n)}{z_{\sigma_1} \prod_{i=1}^n e_2^{\sigma_i}(\mathbf{r}_i, \mathbf{r}_i)} \begin{cases} \geq Q_n^{\text{KS}(l)} & \text{for } l \text{ odd} \\ \leq Q_n^{\text{KS}(l)} & \text{for } l \text{ even} \end{cases}, \quad (37)$$

which are successive rigorous upper and lower bounds on the left-hand sides of Eqs. (31) and (32), respectively. Since the left-hand sides of Eqs. (36) and (37) become equations for the MM and KS representations of the  $n$ -point matrix probability functions  $S_n$  (apart from trivial constants) we also have successive upper and lower bounds on the  $S_n$ . To our knowledge such rigorous bounds on the  $S_n$  have never been demonstrated before.

In the case of a binary mixture in which one of the two species, the solute species,  $U$  consists of point particles of infinite dilution of the point-particle species while the other species, the solvent  $V$ , consists of particles

of radius  $R$ , we have, from the inequalities of Eqs. (36) and (37) and Eqs. (16b) and (28):

$$S_n \begin{cases} \geq Q_n^{MM(l)} & \text{for } l \text{ odd} \\ \leq Q_n^{MM(l)} & \text{for } l \text{ even} \end{cases}, \quad (38)$$

where

$$S_n = \sum_{s=0}^{\infty} (-1)^s S_n^{MM(s)}, \quad (39)$$

$$Q_n^{MM(l)} = \sum_{s=0}^l (-1)^s S_n^{MM(s)}, \quad (40)$$

$$S_n^{MM(s)} = \frac{\rho^s}{s!} \int \dots \int g^{(s)}(\mathbf{r}_{n+1}, \dots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} \left\{ 1 - \prod_{i=1}^n [1 - m(r_{ij})] \right\} d\mathbf{r}_j \quad (41)$$

$$S_n^{MM(0)} \equiv 1,$$

which is the MM result. Similarly,

$$S_n \begin{cases} \geq Q_n^{KS(l)} & \text{for } l \text{ odd} \\ \leq Q_n^{KS(l)} & \text{for } l \text{ even} \end{cases}, \quad (42)$$

where

$$S_n = \sum_{s=0}^{\infty} (-1)^s S_n^{KS(s)}, \quad (43)$$

$$Q_n^{KS(l)} = \sum_{s=0}^l (-1)^s S_n^{KS(s)}, \quad (44)$$

$$S_n^{KS(s)} = \phi^{n-1} \frac{\rho^s}{s!} \int \dots \int g^{(n+s-1)}(\mathbf{r}_2, \dots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} m(r_{1j}) d\mathbf{r}_j, \quad (45)$$

$$S_n^{(0)} \equiv \phi^{n-1} g^{(n-1)}(\mathbf{r}_2, \dots, \mathbf{r}_n), \quad (46)$$

which is the KS result. Since the point particles are associated with the labels  $1, 2, \dots, n$  and the solvent particles of radius  $R$  are associated with the labels  $n+1, n+2, \dots$ , we suppress the  $U$ 's and the  $V$ 's. Here we have made use of the relationship between the "solute-solvent" Mayer- $f$  function and the indicator function  $m$ , namely,

$$f_{UV}(r) = -m(r) = \begin{cases} -1 & r < R \\ 0 & r > R \end{cases}.$$

We now make the observation that the product  $\phi^{n-1} g^{n-1}$  of Eq. (46) is equal to  $S_{n-1}$ , according to Eq. (16a). Thus

$$S_n^{(0)} = S_{n-1}(r_{23}, r_{24}, \dots, r_{2n}). \quad (47)$$

That is, the first term of the KS representation of the  $n$ -point function is precisely the  $(n-1)$ -point function. This important result will prove to be quite useful in obtaining specific bounds on  $S_n$ .

**VII. TRUNCATION OF THE MM AND KS SERIES FOR MUTUALLY IMPENETRABLE SPHERES**

We first consider a pure system of hard spheres with radius  $R$  and then discuss a binary system of hard

spheres where one species is made up of infinitely dilute point particles while the other is composed of solvent particles of radius  $R$ .

To begin with, let us consider the MM and KS equations when  $n=1$  for a pure and isotropic system of hard spheres. From Eqs. (31) and (32) we see that these representations are identical (where, since we are dealing with a pure solvent, all quantities are pure-solvent quantities):

$$\frac{\rho}{z} = 1 + \int f(r_{12}) d\mathbf{r}_2 + \frac{\rho^2}{2!} \int g^{(2)}(r_{23}) f(r_{12}) f(r_{13}) d\mathbf{r}_2 d\mathbf{r}_3 + \frac{\rho^3}{3!} \int g^{(3)}(r_{23}, r_{24}) f(r_{12}) f(r_{13}) f(r_{14}) d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 + O(\rho^4) \quad (48)$$

where ---- is an  $f$  bond ( $f = -1$  for  $r < 2R$  and  $f = 0$  otherwise), ——— is a  $g^{(2)}$  bond and represents  $g^{(3)}$ . For a system of mutually impenetrable spheres,  $g^{(s)}(\mathbf{r}^s) = 0$  for  $r_{ij} < 2R$  for any  $i$  and  $j$  such that  $1 \leq i < j \leq s$  whereas  $f(r_{ij}) = 0$  for any  $r_{ij} > 2R$  and thus the terms in the series of Eq. (48) are identically zero for  $s > 12$ . In other words, these series are finite series and hence no question of convergence can arise.

Now let the particles labeled  $1, 2, \dots, n$  be solute species and those labeled  $n+1, n+2, \dots$  be the solvent species. If the particles of the solute species are allowed to become infinitely dilute and infinitesimally small, Eq. (48) becomes the 1-point matrix function or the volume fraction of the matrix phase<sup>3</sup>:

$$S_1 = 1 + \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + O(\rho^4), \quad (49)$$

(where now  $f = -1$  for  $r < R$  and  $f = 0$  otherwise). Since  $g^{(s)}(\mathbf{r}^s) = 0$  for  $r_{ij} < 2R$  if  $i$  and  $j$  represent solvent species, and  $f(r_{ij}) = 0$ , and  $r_{ij} > R$ , any term containing the subgraph (where represents either a  $g^{(2)}$  bond or an edge of a  $g^{(s)}$  polyhedron,  $s > 2$ )



will be identically zero. It is clear that all terms beyond the second contain such graphs. Note that this is consistent with our geometrical interpretation of the  $S_n$  given elsewhere.<sup>3</sup> In this case,  $S_1$  is seen to be the probability that no sphere centers are inside a region  $\Omega^{(1)}$ , the volume of a sphere. The region  $\Omega^{(1)}$  is large enough to accommodate one sphere center but not large enough to accommodate two or more centers of impenetrable spheres; any integral including correlations between two or more particles must be zero. We have

$$S_1 = 1 + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} = 1 - \frac{4\pi}{3} R^3 \rho = \frac{V - N \cdot (4\pi/3)R^3}{V}, \quad (50)$$

which states the simple result that the volume fraction of matrix  $\phi$  is the volume not occupied by spheres divided by the total volume of the system  $V$ .

Consider the MM and KS equations when  $n=2$  for a pure and isotropic system of hard spheres. By letting the particles labeled  $1, 2, \dots, n$  be solute species and those labeled  $n+1, n+2, \dots$  be solvent species and allowing the particles of the solute species to become infinitely dilute and infinitesimally small, we have from Eqs. (31) and (32), respectively,

$$\frac{\rho^2 g_{UV}^{(2)}(r_{12})}{z^2 e_2(r_{12})} = S_2(r_{12}) = 1 + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} + O(\rho^3), \quad (51)$$

$$\frac{\rho g_{UV}^{(2)}(r_{12})}{z e_2(r_{12})} = \frac{S_2(r_{12})}{S_1} = 1 + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} + O(\rho^3). \quad (52)$$

Equation (51) is the MM representation of  $S_2$  and Eq. (52) is the corresponding KS representation. Here  $\text{---}$  represents  $g^{(2)}$  and  $\triangle$  represents  $g^{(3)}$ . Black and white circles are associated with solvent and solute, respectively. As in the previous case (when  $n=1$ ), any term containing the graph  is identically zero for impenetrable spheres and therefore gives

$$S_2(r_{12}) = 1 + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array}, \quad (53)$$

$$S_2(r_{12}) = \phi \left( 1 + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 1 \end{array} + \begin{array}{c} \bullet \\ | \\ \circ \\ | \\ 2 \end{array} \right), \quad (54)$$

which are the exact expressions for the  $S_2$  in the MM and KS representations, respectively.

In general, for an isotropic system of hard spheres and infinitely dilute point particles, the MM representation of  $S_n$  requires knowledge of the spatial correlations between  $n$  solvent particles and all lower order correlations and is, therefore, a finite series containing  $n+1$  terms. The KS representation of  $S_n$ , on the other hand requires knowledge of the spatial correlation between one solvent particle and point particles, and proves to be a finite series containing only two terms. [It is to be noted that for spheres which are penetrable by one another, all terms in Eqs. (31) and (32) will, in general, be nonzero.]

VIII. EXACT EXPRESSIONS FOR  $S_2$  AND  $S_3$  AND SOME SPECIFIC RIGOROUS BOUNDS THAT FOLLOW

As a result of Eqs. (38) and (42) there exists a variety of upper and lower bounds on  $S_n$ :

$$S_n \leq S_n^{(0)}, \quad (55a)$$

$$S_n \geq S_n^{(0)} - S_n^{(1)}, \quad (55b)$$

$$S_n \leq S_n^{(0)} - S_n^{(1)} + S_n^{(2)}, \quad (55c)$$

$$S_n \geq S_n^{(0)} - S_n^{(1)} + S_n^{(2)} - S_n^{(3)} \\ \vdots \quad (55d)$$

where the  $S_n^{(s)}$  are given by Eqs. (41) and (45), the MM and KS representations of  $S_n$ , respectively. We shall examine the above inequalities for lower order  $n$ -point matrix functions in both the MM and KS forms for a particle phase consisting of hard spheres. In what follows, it will be convenient to replace  $f(r)$  with the function  $-m(r)$ .

Letting  $n=1$ , we have in either representation that

$$S_1 \leq 1, \quad (56)$$

$$S_1 = \phi = 1 - \rho V_1. \quad (57)$$

The inequality in Eq. (56) states that  $S_1$ , the volume fraction of the matrix phase  $\phi$  must be less than or equal to one; a result applicable to penetrable spheres as well. The result of Eq. (57) is an exact result for hard spheres only. As aforementioned, for  $n > 1$  the MM and KS representations of  $S_n$  are different. To avoid ambiguity, therefore, in the following discussion, we shall denote the MM and KS representations of  $S_n$  as  $S_n^{MM}$  and  $S_n^{KS}$ , respectively. We shall also use the subscripts  $U$  and  $V$  on the  $g^{(s)}$  to distinguish pure-solvent distributions from mixed solute-solvent distributions.

Letting  $n=2$  in the inequalities of Eqs. (38) and (42) gives, in the MM and KS representations, respectively, for impenetrable spheres,

$$S_2^{MM}(r_{12}) \leq 1, \quad (58)$$

$$S_2^{MM}(r_{12}) \geq 1 - \rho V_2(r_{12}), \quad (59)$$

$$S_2^{MM}(r_{12}) = 1 - \rho V_2(r_{12}) + \rho^2 \iint g_{UV}^{(2)}(r_{34}) m(r_{13}) m(r_{24}) d\mathbf{r}_3 d\mathbf{r}_4, \quad (60)$$

where

$$V_2(r_{12}) = 2 \int m(r) d\mathbf{r} - \int m(r_{13}) m(r_{23}) d\mathbf{r}_3 = \begin{cases} \frac{4\pi}{3} R^3 \left[ 1 + \frac{3}{4} \left( \frac{r}{R} \right) - \frac{1}{16} \left( \frac{r}{R} \right)^3 \right], & r < 2R \\ \frac{8}{3} \pi R^3, & r > 2R \end{cases}$$

and

$$S_2^{KS}(r_{12}) \leq \phi \quad (61)$$

$$S_2^{KS}(r_{12}) = \phi \left[ 1 - \rho \int g_{UV}^{(2)}(r_{23}) m(r_{13}) d\mathbf{r}_3 \right]. \quad (62)$$

Here  $V_2(r)$  is the union volume of two spheres of radius

$R$  whose centers are separated by distance  $r$ .<sup>3</sup> Note that the KS inequality of Eq. (61) is a better upper bound on  $S_2$  than the corresponding MM inequality of Eq. (58). (We have shown elsewhere that the maximum value of  $S_2$  is simply the matrix volume fraction.<sup>3</sup>) The inequalities of Eqs. (58), (59), and (61) are applicable to penetrable spheres, while the equalities of Eqs. (60) and (62) are exact expressions for the two-point function for hard spheres as discussed in the previous section. (More generally, it will be true throughout the rest of this section that all inequalities for the  $S_n$  hold for both penetrable and impenetrable spheres whereas the equalities hold only for impenetrable spheres.)

We obtain better bounds on  $S_2$  than provided by the inequalities of Eqs. (59) and (61) by bounding the  $g_{VV}^{(2)}$ ,<sup>s</sup> appearing in Eqs. (60) and (62). Recall that the  $g^{(2)}$  appearing in Eqs. (60) and (62) are the solvent-solvent and solute-solvent two-body functions, respectively. The solvent-solvent  $g^{(2)}$  may be bounded using the inequality of Eq. (37) for a pure and isotropic hard-sphere system:

$$g_{VV}^{(2)}(r_{12}) \leq \frac{z}{\rho} e_2(r_{12}), \quad (63)$$

$$g_{VV}^{(2)}(r_{12}) \geq \frac{z}{\rho} e_2(r_{12}) \left[ 1 - \rho \int g_{VV}^{(2)}(r_{23}) m(r_{13}) d\mathbf{r}_3 \right]. \quad (64)$$

We also have from Eq. (37) that

$$\frac{\rho}{z} \leq 1, \quad (65)$$

$$\frac{\rho}{z} \geq 1 - \rho V_1(2R), \quad (66)$$

where

$$V_1(2R) = \int m(r) d\mathbf{r} = \frac{4\pi}{3} (2R)^3.$$

The quantity  $V_1$  is simply the volume of a sphere of radius  $2R$ . Combining Eqs. (63) and (66) with Eq. (60) gives the upper bound

$$S_2^{\text{MM}}(r_{12}) \leq 1 - \rho V_2(r_{12}) + z\rho \iint e_2(r_{34}) m(r_{13}) m(r_{24}) d\mathbf{r}_3 d\mathbf{r}_4 \quad (67)$$

and the weaker upper bound

$$S_2^{\text{MM}}(r_{12}) \leq 1 - \rho V_2(r_{12}) + \frac{\rho^2}{1 - \rho V_1(2R)} \times \iint e_2(r_{34}) m(r_{13}) m(r_{24}) d\mathbf{r}_3 d\mathbf{r}_4, \quad (68)$$

where it is to be recalled that in the impenetrable-sphere case

$$e_2(r_{34}) = \begin{cases} 0, & r_{34} < 2R \\ 1, & r_{34} > 2R \end{cases},$$

since particles labeled 3, 4, ... are solvent particles. In a similar manner we may obtain a lower bound on  $S_2^{\text{MM}}$  by substituting Eq. (64) into Eq. (60).

A rigorous bound on the solute-solvent  $g_{VV}^{(2)}$  may be obtained from the inequality of Eq. (37) by allowing the particle labeled 1 to be a point particle. We find

$$g_{VV}^{(2)}(r_{12}) \leq \frac{1}{S_1} e_2(r_{12}) = \frac{1}{\phi} e_2(r_{12}). \quad (69)$$

Inserting the right-hand side of Eq. (69) into Eq. (62) yields the lower bound

$$S_2^{\text{KS}}(r_{12}) \geq \phi \left[ 1 - \frac{\rho}{\phi} \int e_2(r_{23}) m(r_{13}) d\mathbf{r}_3 \right], \quad (70)$$

where here  $e_2(r)$  is a solute-solvent quantity

$$e_2(r) = \begin{cases} 0, & r < R \\ 1, & r > R \end{cases}$$

for both penetrable and impenetrable sphere-solvent particles. Since  $e_2 = 1 - m$  we also have

$$S_2^{\text{KS}}(r_{12}) \geq \phi \left\{ 1 - \frac{\rho}{\phi} [V_1(R) - V_2^I(r_{12}; R)] \right\}, \quad (71)$$

where

$$V_1(R) = \frac{4\pi}{3} R^3,$$

$$V_2^I(r_{12}; R) = \int m(r_{13}) m(r_{23}) d\mathbf{r}_3$$

$$= \begin{cases} \frac{4\pi}{3} R^3 \left[ 1 - \frac{3}{4} \frac{r}{R} + \frac{1}{16} \left( \frac{r}{R} \right)^3 \right], & r_{12} < 2R \\ 0, & r_{12} > 2R \end{cases}.$$

Here  $V_2^I(r; R)$  is the intersection volume of two spheres of radius  $R$  whose centers are separated by distance  $r$ . This lower bound on  $S_2(r)$  goes to  $S_1 = \phi$  for small  $r$  just as the exact  $S_2$  does.

Setting  $n=3$  in the inequalities of Eqs. (38) and (42) gives, in the MM and KS representations, respectively, for impenetrable spheres,

$$S_3^{\text{MM}}(r_{12}, r_{12}) \leq 1, \quad (72)$$

$$S_3^{\text{MM}}(r_{12}, r_{13}) \geq 1 - \rho V_3(r_{12}, r_{13}), \quad (73)$$

$$S_3^{\text{MM}}(r_{12}, r_{13}) \leq 1 - \rho V_3(r_{12}, r_{13}) + \frac{\rho^2}{2!} \iint g_{VV}^{(2)}(r_{45}) m^{(3)}(r_{14}, r_{24}, r_{34}) m^{(3)}(r_{15}, r_{25}, r_{35}) d\mathbf{r}_4 d\mathbf{r}_5, \quad (74)$$

$$S_3^{\text{MM}}(r_{12}, r_{13}) = 1 - \rho V_3(r_{12}, r_{13}) + \frac{\rho^2}{2!} \iint g_{VV}^{(2)}(r_{45}) m^{(3)}(r_{14}, r_{24}, r_{34}) m^{(3)}(r_{15}, r_{25}, r_{35}) d\mathbf{r}_4 d\mathbf{r}_5 - \frac{\rho^3}{3!} \iiint g_{VVV}^{(3)}(r_{45}, r_{46}) m^{(3)}(r_{14}, r_{24}, r_{34}) m^{(3)}(r_{15}, r_{25}, r_{35}) m^{(3)}(r_{16}, r_{26}, r_{36}) d\mathbf{r}_4 d\mathbf{r}_5 d\mathbf{r}_6, \quad (75)$$



tract the expected overlap volume between all indistinguishable pairs of covering spheres:

$$\frac{N(N-1)}{2} \int m(r_{12}) m(r_{13}) P_N^{(2)}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_2 d\mathbf{r}_3, \quad (89)$$

where  $P_N^{(2)}(\mathbf{r}_2, \mathbf{r}_3)$  is the probability of finding particle 2 in volume  $d\mathbf{r}_2$  about  $\mathbf{r}_2$  and particle 3 in volume  $d\mathbf{r}_3$  about  $\mathbf{r}_3$ . But now we have overestimated this overlapping since we have overcounted the overlap whenever three or more covering spheres happen to simultaneously overlap. This line of reasoning can be continued until we obtain an expression for  $A/V$ , denoted by  $W$ :

$$W = 1 - W^{(1)} + W^{(2)} - W^{(3)} + \dots, \quad (90)$$

where

$$W^{(n)} = \frac{\rho^n}{n!} \int \left\{ \prod_{i=1}^n d\mathbf{r}_i m(r_{1i}) \right\} g_N^{(n)}(\mathbf{r}_2, \dots, \mathbf{r}_{n+1}), \quad (91)$$

$$W_0 \equiv 1,$$

and where we have taken the thermodynamic limit. Equation (90) is precisely the MM or KS equation when  $n=1$ . That is,  $A/V$  is equal to  $\rho/z$ . It should be geometrically clear from the way in which the series for  $W$  is built up that in the limit as  $V \rightarrow \infty$ ,  $W=1$  is an upper bound to  $W$  and that  $W=1 - W^{(1)}$  is a lower bound. Moreover, when we add  $W_2$  we are clearly adding on too much, so that  $1 - W^{(1)} + W^{(2)}$  is again an upper bound. To summarize, we can say that the remainder

$$W - \left[ \sum_{s>0} (-1)^s W^s \right]$$

alternates in sign, and thus we have a succession of upper and lower bounds. From these arguments, however, it is not immediately clear that  $W_l$  uniformly decreases in absolute value as  $l$  increases, i.e., that the bounds are successively better and better, although, as we have seen, there are instances in which the series will be truncated [i.e., for certain interparticle potentials there exists some  $l > k > 0$  such that  $W^{(l)} = 0$  for all  $l > k$ ]. Using the same reasoning, we may use similar geometrical arguments to show that the higher order MM and KS equations (i.e.,  $n > 1$ ) are alternating series that satisfy the conditions of Eqs. (36) and (37) and thus may be expressed as successive lower and upper bounds. The arguments given here for the pure-system case may be easily extended to the multicomponent case.

We may apply the above geometrical arguments to the case where some of the particles are infinitesimally small. We may regard the 1-point function,

$$S_1 = \lim_{\substack{\rho_U \rightarrow 0 \\ R_U \rightarrow 0}} \left[ \frac{\rho_U}{z_U} \right]$$

as the space available for a point in a system of spheres of radius  $R$  divided by the total volume of the system  $V$ . It is clear that this is simply the matrix volume fraction. The space available, again denoted by  $A$ , will be  $V$  minus at most the volume taken up by the interaction spheres of the  $N$  molecules, which in this case is

$$N \int m(\mathbf{r}) d\mathbf{r} = N \cdot \frac{4\pi}{3} R^3, \quad (92)$$

where  $m$  equals 1 for  $r < R$  and equals zero otherwise.

However, there is expected overlapping of the covering spheres that must be considered when the spheres are not totally impenetrable. We must subtract the expected overlap volume between all indistinguishable pairs of covering spheres:

$$\frac{N(N-1)}{2} \iint m(r_{12}) m(r_{13}) P_N^{(2)}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_2 d\mathbf{r}_3. \quad (93)$$

But, as before, we have overestimated this overlapping since we have overcounted the overlap whenever three or more covering spheres happen to simultaneously overlap. This line of reasoning can be continued until we obtain an expression for  $A/V = S_1$ :

$$S_1 = 1 - S_1^{(1)} + S_1^{(2)} - S_1^{(3)} + \dots, \quad (94)$$

where

$$S_1^{(n)} = \frac{\rho^n}{n!} \int \dots \int g^{(n)}(\mathbf{r}_2, \dots, \mathbf{r}_{n+1}) \left\{ \prod_{i=1}^n d\mathbf{r}_i m(r_{1i}) \right\}. \quad (95)$$

It is again geometrically clear that we have a succession of upper and lower bounds on  $S_1$ . We may apply similar reasoning to higher order  $n$ -point matrix functions to give similar physical insight to the bounds given by Eqs. (36) and (37).

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