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Structure and effective interactions in three-component hard sphere liquids

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Complete and simple analytical expressions for the partial structure factors of the ternary hard sphere mixture are obtained within the Percus-Yevick approximation and presented as functions of relative packing fractions and relative hard sphere diameters. These solutions follow from the Laplace transform method as applied to multicomponent systems by Lebowitz [Phys. Rev. **133**, A895 (1964)]. As an important application, we examine effective interactions in hard sphere liquid mixtures using the microscopic information contained in their partial structure factors. Thus the ensuring pair potential for an effective one-component system is obtained from the correlation functions by using an approximate inversion, and examples of effective potentials for three-component hard sphere mixtures are given. These mixtures may be of particular interest for the study of the packing aspects of melts that form glasses or quasicrystals, since noncrystalline solids often emerge from melts with at least three atomic constituents.

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I. INTRODUCTION

The starting point of this paper is the determination of the partial structure factors for the three-component hard sphere liquid in the Percus-Yevick approximation, obtained using the Laplace transform methods of Wertheim [1], Thiele [2], and Lebowitz [3]. The corresponding total correlation functions then follow by direct Fourier transformation. Full knowledge of the analytical partial structure factors and the corresponding correlation functions is the foundation upon which our subsequent investigations of *effective potentials* in ternary hard sphere mixtures (Secs. IV and V) rest. The notion of an effective potential in a classical system follows the familiar corresponding quantum mechanical concept, which arises from tracing out ''fast'' degrees of freedom in a system with components of different scales, for example, systems of electrons and ions. The principle can be transferred to classical systems, and might be referred to as ''classical screening;'' it is familiar from the concept of screening in quantum systems, for example, in metals. An immediate application is therefore to the idea of effective potentials as they may arise in the ternary hard sphere mixture. In particular we show that the presence of three components can lead to effective potentials whose shape may even favor the emergence of unusual solids from the melt. This may occur for an effective potential with flat well regions that allow a continuous positioning of particles, or for a potential with double wells of comparable depth, or even with peaks in the potential that are positioned at separations where they can inhibit standard crystalline arrangements from forming upon freezing.

The paper is therefore arranged as follows: Section II presents the solution of the Percus-Yevick equation for the three-component hard sphere liquid and gives simple closed-form analytical expressions for the partial structure factors, Sec. III briefly discusses the concept of effective attraction and its entropic origin [4], Sec. IV introduces our method for calculating effective potentials in hard sphere mixtures, and Sec. V presents examples of effective potentials in three-component hard sphere mixtures, the choices of parameters being motivated, in particular, by the observation that noncrystalline solids may often emerge from melts where at least three atomic constituents are present.

II. THE PARTIAL STRUCTURE FACTORS FOR THE TERNARY HARD SPHERE LIQUID

The derivation of the analytical partial structure factors for the three-component hard sphere liquid in the Percus-Yevick approximation extends the Laplace transform methods of Wertheim and Thiele for the one-component hard sphere liquid, and of Lebowitz for the binary mixture. Wiener-Hopf transformation methods have been used successfully by Baxter [5] and for the multicomponent liquid by Blum and Stell [6]. Paschinger, Reiner, and Kahl [7] have specifically treated the three-component system by this approach for the real-space structure. In what follows, the focus will be on the reciprocal-space structure as manifested through the partial structure factors, these generally being the quantities most directly related to scattering experiments.

The three diameters in the mixture will be taken as σ_1 for the smallest species, σ_2 for the intermediate sized species, and σ_3 for the largest species: $\sigma_1<\sigma_2<\sigma_3$. The additive mixture has contact distances $\sigma_{ij}=\frac{1}{2}(\sigma_i+\sigma_j)$, and the Ornstein-Zernike (OZ) equation for the homogeneous ternary mixture is then

$$[g_{ij}(r)-1]=c_{ij}(r)+\rho_i\sum_{l=1,2,3}\int_V[g_{il}(|\mathbf{r}'-\mathbf{r}|)-1]\times c_{lj}(r')d\mathbf{r}'. \tag{1}$$

In fluid mixtures the Percus-Yevick closure is given by

$$g_{ij}(r)(e^{-\beta\Phi_{ij}(r)}-1)=e^{-\beta\Phi_{ij}(r)}c_{ij}(r) \tag{2}$$

for corresponding pair potentials Φ_{ij}. For hard sphere potentials the Percus-Yevick (PY) approximation then reduces to

$$g_{ij}(r)=0 \quad \text{for } r<\sigma_{ij}, \tag{3a}$$

and

$$c_{ij}(r)=0 \quad \text{for } r>\sigma_{ij}. \tag{3b}$$

The Percus-Yevick equation [after insertion of Eqs. (2) and (3) into Eq. (1)] can be solved with Laplace transform techniques following Lebowitz's solution for the binary hard sphere mixture [3]. The essential steps to the analytical solution to the Percus-Yevick equations are (i) the use of the PY statements (3) to define an auxiliary function that is proportional to the direct correlation function inside the core, proportional to the pair distribution function outside, and continuous at contact, (ii) a rewriting of the OZ equation (1) in terms of an auxiliary function and a rewriting of the integrals using bipolar coordinates, (iii) the Laplace transform of the OZ equation in this form, (iv) the use of Liouville's theorem and Watson's lemma to solve the OZ equation for the Laplace transform of the auxiliary function, and finally (v) an inverse Laplace transformation to obtain the auxiliary functions and thus also the direct correlation functions in real space. (Extensive details of the calculation for the ternary hard sphere mixture can be found in Ref. [8].) The manipulations largely follow those presented in Lebowitz's solution for the binary mixture [3], but the solutions do differ, importantly, in the form of the coefficients for the cubic polynomial direct correlation functions.

The direct correlation functions of the ternary hard sphere mixture, with the definitions $x_{ij}=r-\lambda_{ij}$ and $\lambda_{ij}=\frac{1}{2}|\sigma_i-\sigma_j|$, are then found to be, for species $i=1,2,3$,

$$\begin{aligned}
-c_{ii}(r)&=a_i+b_ir+dr^3, \quad r<\sigma_i,\\
-c_{ij}(r)&=-c_{ji}(r)=a_i, \quad r<\lambda_{ij},\\
&=a_i+(b_{ij}x_{ij}^2+4\lambda_{ij}dx_{ij}^3+dx_{ij}^4)/r,\\
&\quad \lambda_{ij}<r<\sigma_{ij},
\end{aligned} \tag{4}$$

with the coefficients defined below. The pressure p^c via the compressibility, is given by

$$\begin{aligned}
\beta p^c(\rho_1,\rho_2,\rho_3)=\Big\{&(\rho_1+\rho_2+\rho_3)(1+\xi+\xi^2)\\
&-(18/\pi)\sum_{i<j}(\sigma_i-\sigma_j)^2[2\sigma_{ij}+\sigma_i\sigma_j(\epsilon_1\sigma_1^2\\
&+\epsilon_2\sigma_2^2+\epsilon_3\sigma_3^2)]\Big\}(1-\xi)^{-3},
\end{aligned} \tag{5}$$

with $\rho_i=\rho_i^{(1)}=N_i/V$ as the average one-particle density of species i. The ϵ_i's are the reduced partial packing fractions, $\epsilon_i=\pi\rho_i/6$, and simply introduced for calculational ease. The usual dimensionless definition of the partial packing fraction is in terms of the number density and the diameter of a sphere of species i, namely,

$$\eta_i=\frac{\pi}{6}\rho_i\sigma_i^3=\epsilon_i\sigma_i^3, \tag{6}$$

and $\xi=\epsilon_1\sigma_1^3+\epsilon_2\sigma_2^3+\epsilon_3\sigma_3^3$ is the conventional total packing fraction.

The coefficients (with $\sigma_{ij}=\sigma_{ji}$ and $\sigma_{ii}=\sigma_i$) are then

$$a_i=\frac{\partial[\beta p(\rho_1,\rho_2,\rho_3)]}{\partial\rho_i},$$

$$b_i=-6\sum_{l=1}^{3}\epsilon_lD_{il}^2g_{il}^2(\sigma_{il}),$$

$$b_{ij}=-6\sum_{l=1}^{3}\epsilon_l\sigma_{il}\sigma_{lj}g_{il}(\sigma_{il})g_{lj}(\sigma_{lj}),$$

and

$$d=\tfrac{1}{2}(\epsilon_1a_1+\epsilon_2a_2+\epsilon_3a_3). \tag{7}$$

Correspondingly the pair distribution functions at contact are given by

$$g_{ii}(\sigma_i)=[(1-\xi)+\tfrac{3}{2}\sigma_i(\epsilon_1\sigma_1^2+\epsilon_2\sigma_2^2+\epsilon_3\sigma_3^2)]/(1-\xi)^2$$

and

$$g_{ij}(\sigma_{ij})=[\sigma_jg_{ii}(\sigma_i)+\sigma_ig_{jj}(\sigma_j)]/2\sigma_{ij}. \tag{8}$$

These contact values are readily obtained from the required continuity of the direct correlation function and the pair distribution function at contact, that is, $-c_{ij}(\sigma_{ij})=g_{ij}(\sigma_{ij})$. They are an important thermodynamical corroboration, since they are related to the pressure (in the exact case) and to the virial pressure in the PY approximation. The virial pressure p^v can be found from the contact values through the virial theorem, as generalized to ternary mixtures [3], namely,

$$\beta p^v=\rho_1+\rho_2+\rho_3+\tfrac{2}{3}\pi\sum_{i,j=1,2,3}\rho_i\rho_j\sigma_{ij}^2g_{ij}(\sigma_{ij}). \tag{9}$$

The partial structure factors can be expressed in terms of the Fourier transforms of the direct correlation functions, and the Fourier transformations of these finite range polynomials can all be expressed in terms of Bessel functions. For the simpler diagonal cases we have

$$\begin{aligned}
-c_{ii}(k)&=\int_V d\mathbf{r}c_{ii}(r)e^{i\mathbf{k}\cdot\mathbf{r}}\\
&=\frac{4\pi}{k}\int_0^{\sigma_i}dr\,\sin(kr)(a_ir+b_ir^2+dr^4),
\end{aligned} \tag{10}$$

and performing the integral over r we get

$$\rho_i c_{ii}(k) = -\frac{24\epsilon_1}{k^3}\Big(a_i[\sin(k\sigma_i) - k\sigma_i\cos(k\sigma_i)] + \frac{b_i}{k}\{2k\sigma_i\sin(k\sigma_i) - [(k\sigma_i)^2 - 2]\cos(k\sigma_i) - 2\} + \frac{d}{k^3}\{[4(k\sigma_i)^3 - 24k\sigma_i]\sin(k\sigma_i) - [(k\sigma_i)^4 - 12(k\sigma_i)^2 + 24]\cos(k\sigma_i)\}\Big). \tag{11}$$

Taking an off-diagonal case we have

$$-c_{ij}(k) = \frac{4\pi}{k}\left(\int_0^{\sigma_{ij}} dr\,\sin(kr)a_i r + \int_{\lambda_{ij}}^{\sigma_{ij}} dr\,\sin(kr) \times [b_{ij}(r-\lambda_{ij})^2 + 4\lambda_{ij}d(r-\lambda_{ij})^3 + d(r-\lambda_{ij})^4]\right), \tag{12}$$

with the result that for $i<j$

$$\sqrt{\rho_i\rho_j}c_{ij}(k) = -\frac{24\sqrt{\epsilon_1\epsilon_2}}{k^3}\Bigg[a_i[\sin(k\sigma_{ij}) - k\sigma_{ij}\cos(k\sigma_{ij})] + \frac{b_{ij}}{k}\{2k\sigma_i\sin(k\sigma_{ij}) + [2-(k\sigma_i)^2]\cos(k\sigma_{ij}) - 2\cos(k\lambda_{ij})\} + \frac{4d\lambda_{ij}}{k^2}\{3[(k\sigma_i)^2 - 2] \times \sin(k\sigma_{ij}) + k\sigma_i[6-(k\sigma_i)^2]\cos(k\sigma_{ij}) + 6\sin(k\lambda_{ij})\} + \frac{d}{k^3}\{4k\sigma_i[(k\sigma_i)^2 - 6] \times \sin(k\sigma_{ij}) - [(k\sigma_i)^4 - 12(k\sigma_i)^2 + 24]\cos(k\sigma_{ij}) + 24\cos(k\lambda_{ij})\}\Bigg]. \tag{13}$$

We use the definitions of Ref. [9] for the partial structure factors of a mixture, namely,

$$S_{ij}(k) = \delta_{ij} + \sqrt{\rho_i\rho_j}\int_V d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}[g_{ij}(r) - 1] = \delta_{ij} + \sqrt{\rho_i\rho_j}\int_V d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}h_{ij}(r). \tag{14}$$

These definitions incorporate the standard expectation that the diagonal entries S_{ii} should approach unity for large k, and the cross terms S_{ij}, $i\neq j$ (for unlike species), should approach zero in the same limit.

Using the Ornstein-Zernike equation in reciprocal space we can now rewrite the partial structure factors [9] in terms of the direct correlation functions, namely,

$$\tilde{S}_{ij}(k) = \sqrt{\rho_i\rho_j}c_{ij}(k) + \sum_l \sqrt{\rho_l\rho_j}\tilde{S}_{il}(k)c_{lj}(k), \tag{15}$$

with the structure factors themselves given by $S_{ij}(k) = \tilde{S}_{ij}(k) + \delta_{ij}$. An example for the solution of a diagonal case is then

$$S_{11}(k) = \{1 - \rho_2 c_{22}(k) - \rho_3 c_{33}(k) + \rho_2\rho_3 \times [c_{22}(k)c_{33}(k) - c_{23}(k)^2]\}/D(k) \tag{16}$$

with the denominator

$$D(k) = 1 - \rho_1 c_{11}(k) - \rho_2 c_{22}(k) - \rho_3 c_{33}(k) + \rho_1\rho_2 c_{11}(k)c_{22}(k) + \rho_1\rho_3 c_{11}(k)c_{33}(k) + \rho_2\rho_3 c_{22}(k)c_{33}(k) - \rho_1\rho_2 c_{12}(k)^2 - \rho_1\rho_3 c_{13}(k)^2 - \rho_2\rho_3 c_{23}(k)^2 + \rho_1\rho_2\rho_3[c_{12}(k)^2 c_{33}(k) + c_{13}(k)^2 c_{22}(k) + c_{23}(k)^2 c_{11}(k) - 2c_{12}(k)c_{13}(k)c_{23}(k) - c_{11}(k)c_{22}(k)c_{33}(k)]. \tag{17}$$

As an example for the off-diagonal case we may give

$$S_{12}(k) = \sqrt{\rho_1\rho_2}\{c_{12}(k)[1 - \rho_3 c_{33}(k)] + \rho_3 c_{13}(k)c_{23}(k)\}/D(k) \tag{18}$$

and it is clear that the complete set of partial structure factors $S_{ij}(k)$ is now straightforwardly evaluated using as input just the five parameters of the three-component hard sphere liquid (the two relative sizes of the hard spheres σ_1/σ_3 and σ_2/σ_3 and the three partial packing fractions η_1, η_2, and η_3). This set of closed-form functions constitutes a primary result of the present paper; they are the direct parallels of Eq. (6) of Ashcroft and Langreth (Ref. [9]) for the two-component case, and direct comparison immediately reveals the degree of complexity introduced by an additional component. Figures 1 and 2 show, respectively, diagonal $[S_{ii}(k)]$ and off-diagonal $[S_{ij}(k)]$ examples of partial structure factors for relative diameters $\sigma_3=1$, $\sigma_2=0.6$, and $\sigma_3=0.2$ (and for packing fractions $\eta_3=0.47$, $\eta_2=0.05$, and $\eta_1=0.05$).

III. APPLICATION TO ENTROPIC FORCES: CLASSICAL SCREENING AND THE NOTION OF THE DEPLETION POTENTIAL

In metallic systems ionic interactions are often described by effective (and state dependent) potentials; for structural purposes the electrons are neglected in all but their screening effect on the interaction between the ions. In the free energy of a classical system the momenta can be traced over trivially since all momenta are permitted classically. Nevertheless, because of the differing set of initial interactions the concept of effective potentials can still remain applicable to classical systems. In the classical hard sphere liquids discussed below, we integrate out the degrees of freedom of the smaller spe-

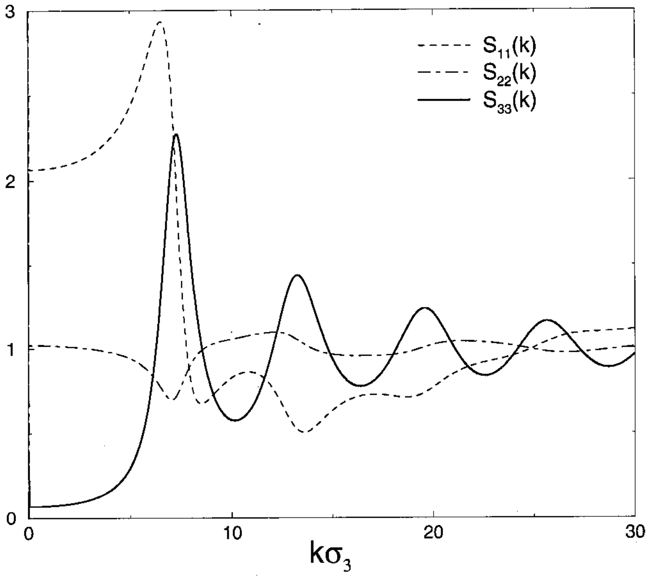

FIG. 1. Diagonal structure factors for the ternary hard sphere mixture as a function of $k\sigma_3$ for diameters $\sigma_1=0.2$, $\sigma_2=0.6$, $\sigma_3=1$ and packing fractions $\eta_1=0.05$, $\eta_2=0.05$, $\eta_3=0.47$.

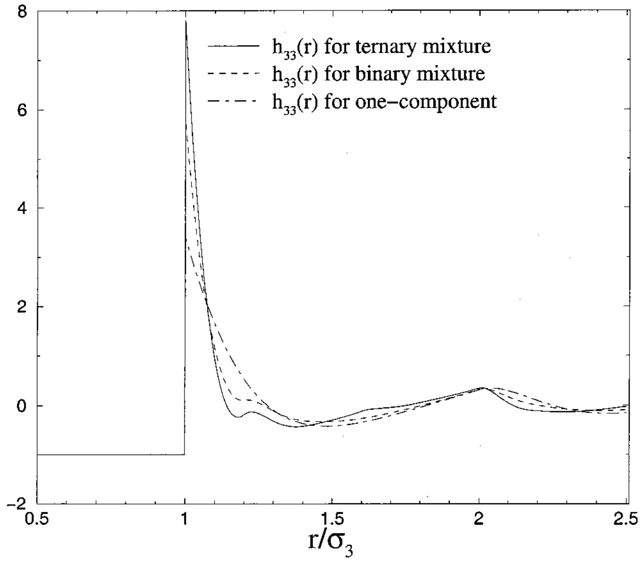

FIG. 3. Total correlation function $h(r)=g(r)-1$ of the large spheres with packing fraction $\eta=0.47$, in a one-component, a binary ($\sigma_1/\sigma_3=0.2$, $\eta_1=0.05$, $\eta_3=0.47$), and a ternary ($\sigma_1/\sigma_3=0.2$, $\sigma_2/\sigma_3=0.6$, $\eta_1=\eta_2=0.05$, $\eta_3=0.47$) liquid. These are obtained by direct Fourier inversion of the partial structure factors.

cies and subsume their effects in the structure of the system through the introduction of an effective interaction between the remaining larger particles. This effective interaction or effective potential is also referred to as a *depletion potential* in the literature on liquid mixtures and colloid suspensions [10–14]. We base our investigation of effective interactions on the microscopic structure of the mixture, and in the hard sphere liquid mixtures investigated here the partial structure factor of the larger spheres is to be reinterpreted as the structure factor of an effective one-component system consisting *only* of those larger spheres. The presence of the small spheres is then expressed only in its effect on the structure of the larger [15] As Fig. 3 demonstrates, the structure of the effective one-component system differs from the structure of a pure one-component hard sphere liquid at the same packing fraction, and corresponds to an effective pair potential between the spheres deviating from the pure hard sphere potential. It will be seen below that there are important differences between the two- and three-component cases.

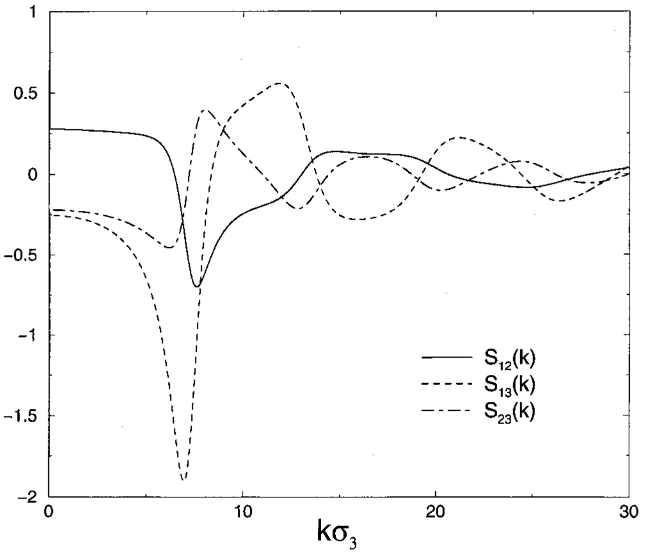

FIG. 2. Off-diagonal partial structure factors for the ternary hard sphere mixture (and for the parameter set given in Fig. 1).

To review the concept of effective potentials in the classical context consider a one-component hard sphere liquid of unit diameter with packing fraction $\eta=0.47$. To this system hard spheres of smaller diameters are now added, and it is interesting to ask how the structure factor and correlation function of the spheres of unit size change after addition of the smaller spheres. Figure 3 actually answers this question by comparing the total correlation function for a one-component liquid of hard spheres of diameter σ_3 and packing fraction $\eta_3=0.47$ with the total correlation function of those spheres in a *binary* mixture after small spheres of diameter $\sigma_1=0.2$ and packing fraction $\eta_1=0.05$ have been added, and finally in a *three-component* mixture where small spheres of diameter $\sigma_1=0.2$ and packing fraction $\eta_1=0.05$ as well as intermediate spheres of diameter $\sigma_2=0.6$ and $\eta_2=0.05$ have been added. The required total correlation functions of the mixtures are obtained from the partial structure factors in Sec. II by direct Fourier transformation.

The presence of the smaller spheres is seen to be expressed in the total correlation function of the large spheres by the presence of additional peaks or shoulders, and as physically expected these fall at separations roughly corresponding to the diameter of the smaller species. They also lead to a higher contact value of the pair distribution function of the large species. The length scale of both the small and the medium spheres is clearly revealed in the total correlation function of the large spheres. If we now ignore the smaller spheres in all but their effect on the arrangement of

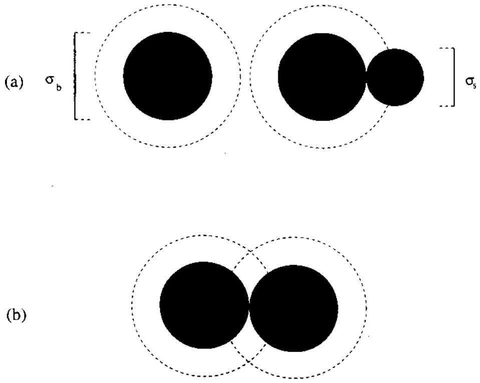

FIG. 4. (a) Shown is a configuration with the larger spheres separated by more than a small sphere diameter: the excluded volume for the small spheres is maximal. (b) Shown is a configuration where the larger spheres are in contact: the excluded volume is minimal.

the larger by regarding the latter as an effective one-component system, then the higher contact value can be interpreted as arising from an effective attraction between the large spheres. The presence of the small spheres evidently drives the larger spheres together at small separations; the effective potential will extend outside the core region, exhibiting an attractive or ''sticky'' tail. Interesting regions in this effective potential that may initiate the formation of unusual solids from the melt might well include double wells at incommensurate separations and flat valleys or humps that suppress normally favored crystalline phases.

In seeking the physical origin of the effective attraction between the large spheres in a hard sphere liquid mixture, we may appeal to a binary hard sphere mixture with large diameters σ_3 and small diameters σ_1 (the notation echoes the previous case of a ternary mixture). We neglect the effect of the mutual exclusion of small spheres arising from their hard core interactions, since we are interested in the regime where the large spheres fill most of space, this being most relevant to mixtures close to freezing. The volume from which the small spheres are excluded is then determined purely by the density and average arrangement of the larger spheres. For a particular configuration the volume forbidden to the small spheres (because of the presence of the larger spheres) is additive, provided the separation of the large spheres is larger than the diameter of the small spheres. The excluded volume per large sphere is just $(4\pi/3)(\sigma_1+\sigma_3)^3/8$. Figure 4(a) shows a fragment of a configuration where two large spheres are separated by a distance larger than the diameter of the small spheres, and where the total excluded volume is the sum of excluded volumes per large sphere. Should the distance between the large spheres be smaller than the diameter of the small spheres then the total excluded volume will be reduced. Figure 4(b) shows the case where the large spheres are in contact and the total excluded volume is minimal. A configuration in which the large spheres are closer together reduces the excluded volume for the small spheres and by this elementary argument therefore leads to an increase in their entropy. A smaller mean separation between large spheres is entropically favored, and this can be viewed on average as an effective attraction between the large spheres at small separations.

For a more quantitative argument, we begin again with the example of a binary liquid mixture; assume the system contains N_1 small particles and N_3 large particles in a volume V and has partial average number densities $\rho_1 = N_1/V$ and $\rho_3 = N_3/V$. The goal is to formally eliminate the small particles from the description of the mixture. The coordinates and momenta of the particles are given by $\{\mathbf{r}_{i,\mu}\}$, and $\{\mathbf{p}_{i,\mu}\}$, $\mu = 1,2,\ldots,N_i$, for the small and large species $i = 1,3$. In the canonical ensemble the classical trace with respect to the coordinates and momenta of species i over any function $\hat{O}$ of all coordinates and momenta is defined as

$$\mathrm{Tr}_i[\hat{O}] = \frac{h^{-3N_i}}{N_i!}\int d\mathbf{p}_{i,1}\cdots d\mathbf{p}_{i,N_i}\int d\mathbf{r}_{i,1}\cdots d\mathbf{r}_{i,N_i}\hat{O} \times(\mathbf{r}_{s,1},\ldots,\mathbf{p}_b,N_3), \quad i=1,3. \tag{19}$$

In particular, the Helmholtz free energy of the binary mixture is then

$$\mathcal{F} = -k_B T \ln \mathrm{Tr}_3 \mathrm{Tr}_1 e^{-\beta\hat{H}}, \tag{20}$$

where the Hamiltonian contains the kinetic energies of the two species $i,j = 1,3$, and their interactions, i.e.,

$$\hat{H}_{ij} = \sum_{i=1,3}\left(\sum_{\mu=1}^{N_i}\frac{\mathbf{p}_{i,\mu}^2}{2m_i} + \frac{1}{2}\sum_{j=1,3}\int_V d\mathbf{r}\int_V d\mathbf{r}'\,\hat{\rho}_{ij}^{(2)} \times(\mathbf{r},\mathbf{r}')\Phi_{ij}(|\mathbf{r}-\mathbf{r}'|)\right). \tag{21}$$

In Eq. (21), m_i is the mass of the particles of species i, and $\Phi_{ij}(r)$ is the potential energy between two particles of species i and j at separation $\mathbf{r}$. The two-particle density operators for the small and large species $i,j = 1,3$ are given in terms of the one-particle density operator $\hat{\rho}_i^{(1)}(\mathbf{r}) = \Sigma_{\mu}^{N_i}\delta(\mathbf{r}-\mathbf{r}_{i,\mu})$:

$$\hat{\rho}_{ij}^{(2)}(\mathbf{r},\mathbf{r}') = \hat{\rho}_i^{(1)}(\mathbf{r})\hat{\rho}_j^{(1)}(\mathbf{r}') - \delta_{ij}\delta(\mathbf{r}-\mathbf{r}')\hat{\rho}_i^{(1)}(\mathbf{r}). \tag{22}$$

Integration over the momentum variables is again trivial, and we trace out the coordinates of the small species to define

$$\exp\{-\beta\hat{H}_{\mathrm{eff}}\} = \mathrm{Tr}_1 \exp\{-\beta\hat{H}\}. \tag{23}$$

The free energy can therefore be expressed formally as a trace only over the coordinates and momenta of the large species, namely,

$$\mathcal{F} = -k_B T \ln \mathrm{Tr}_3 \exp\{-\beta\hat{H}_{\mathrm{eff}}\}. \tag{24}$$

The effective Hamiltonian $\hat{H}_{\mathrm{eff}}$ is itself a trace and therefore intermediate between a pure Hamiltonian and a free energy of the small particles in the instantaneous environment of the large ones. An immediate consequence is that the resulting formal effective potential in $\hat{H}_{\mathrm{eff}}$ is state dependent, and, as with the electron case described above, is generally expected to possess many-particle terms; the ensuing effective interactions between the large particles will depend on the temperature and density of the small particles.

By construction, the effective Hamiltonian $\hat{H}_{\text{eff}}$ preserves the partition function. The reduction to an effective Hamiltonian also preserves the thermal average $\langle \hat{O} \rangle$ of any operator $\hat{O}(\{\mathbf{p}_3\},\{\mathbf{r}_3\})$ whose value depends only on the momenta and coordinates of the large particles, such as, most importantly, the two-particle density operator, whose average is the pair correlation function. This is clear from the definition of the thermal average in the original system:

$$\langle \hat{O} \rangle = \frac{\text{Tr}_3\text{Tr}_1[\hat{O}(\{\mathbf{p}_3\},\{\mathbf{r}_3\})\exp\{-\beta\hat{H}\}]}{\text{Tr}_3\text{Tr}_1[\exp\{-\beta\hat{H}\}]} = \frac{\text{Tr}_3[\hat{O}(\{\mathbf{p}_3\},\{\mathbf{r}_3\})\exp\{-\beta\hat{H}_{\text{eff}}\}]}{\text{Tr}_3[\exp\{-\beta\hat{H}_{\text{eff}}\}]}. \tag{25}$$

The trace over the small subsystem in Eq. (25) may be carried out first, since the operator depends only on the coordinates and positions of the large spheres. This allows us to write the expression as an average in the effective system without loss of information: in particular, tracing out the small spheres does not affect the pair correlation function of the large spheres.

The Hohenberg-Kohn-Mermin (HKM) theorem [16] in density functional theory guarantees a unique relationship between the one-particle density and an external potential. This can be extended [17] to links between the average two-particle density $\rho_{ij}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=\langle\hat{\rho}_{ij}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\rangle$ (and thus the pair distribution function) and the pair potential $\Phi_{ij}(\mathbf{r}_1,\mathbf{r}_2)$ via the Helmholtz free energy for the equilibrium one-particle density. Multicenter interactions are included in this argument; the issue of the uniqueness of the relationship between the two-particle density and the pair potential is discussed in Ref. [18] (this is sometimes referred to as the ''classical inverse problem''). Using this extended HKM approach on the two-particle density of the large spheres in a mixture leads to an effective pair potential that is *state dependent* and thus formally incorporates the higher-body terms that are generated by tracing out the coordinates of the smaller species in the mixture.

The relationship between pair potential and pair distribution function is maintained for state dependent pair potentials, such as our effective potential. The reason for this is that the volume dependent terms in the effective Hamiltonian (those depending only on the total density but not on particle coordinates) cancel from the expectation values such as the pair correlation function, since they appear in both the numerator and denominator of Eq. (25). For the thermodynamics, especially the value of the free energy, the volume dependent terms cannot be neglected. In our case, however, we are concerned only with the *structure* of the system as expressed in the pair correlation function, for which the volume terms play no role, and the Hohenberg-Kohn-Mermin theorem and its extensions to the pair potential remain valid.

IV. STRUCTURE FACTORS, CORRELATION FUNCTIONS, AND EFFECTIVE POTENTIALS

The analytical partial structure factors for a three-component mixture obtained in the PY approximation have been given in Sec. II. They are closed-form expressions requiring, as noted, only the five parameters of packing fractions and diameter ratios. The six partial structure factors for the three-component hard sphere liquid are the equivalents of the three partial structure factors for the binary hard sphere mixture under the PY approximation as noted earlier in Ref. [9]. The microscopic view of the origin of the depletion potential therefore proceeds from the partial structure factor $S_{33}(k)$ of the large species and reinterprets it as an effective (now no longer hard sphere) one-component structure factor [19]. $S_{\text{eff}}(k)=S_{33}(k)$. The corresponding pair distribution function is reinterpreted as the pair distribution function of the effective one-component liquid, i.e., $g_{\text{eff}}(r)=g_{33}(r)$. The correlation function and the structure factor are connected by a Fourier transform, the Fourier transform pairs being $\rho[g(r)-1]$ and $S(k)-1$, and related by

$$\rho_3[g_{\text{eff}}(r)-1]=\int\frac{d\mathbf{k}}{8\pi^3}[S_{\text{eff}}(k)-1]e^{i\mathbf{r}\cdot\mathbf{k}}, \tag{26}$$

with $h_{\text{eff}}(r)=g_{\text{eff}}(r)-1$ as the *effective total* correlation function.

As discussed in the previous section, the pair distribution function of the effective one-component system is linked to its corresponding effective pair potential through the free energy. In practice it is difficult to determine the potential from a given pair distribution function (the classical inverse problem [18]), since in dense fluids very different pair potentials can often lead to quite similar structure factors and thus correlation functions. Here we turn to approximate inversions to obtain an expression for the effective potential, the simplest and most straightforward inversion approximation following from the very closure relation that led to the solution of the OZ equation in the first place. The closure equations can then be directly solved with respect to the pair potential. Two straightforward closure relations offer themselves as inversion approximations: the Percus-Yevick and the hypernetted chain (HNC) closure. In addition to the pair correlation function, knowledge of the direct correlation function of the effective one-component system is also required.

The one-component OZ equation links the structure factor and the Fourier transform of the direct correlation function:

$$S_{\text{eff}}(k)=\frac{1}{1-\rho c_{\text{eff}}(k)}, \tag{27}$$

where ρ will now be the number density of the large species. In just this way one might measure experimentally the structure factor of a liquid, calculate from it the direct and pair correlation functions, and draw conclusions on the nature of the underlying interaction in the liquid. The effective hard sphere mixture could be a model, for example, for a colloid suspension where only the interaction between the large colloid particles is of interest and the presence of the solvent is neglected in all but its modification of the bare colloid potential to an effective, screened interaction.

The effective one-component pair and direct correlation functions obtained from the partial structure factors via Eqs. (26) and (27) can now be used in an inversion approximation to calculate their corresponding effective potential. As just noted, an obvious choice for an inversion is to apply the one-component Percus-Yevick approximation in order to extract the effective potential from the effective correlation functions (these were originally obtained from the structure factors in the PY approximation). The PY closure statement for a one-component liquid is given by

$$c(r)=g(r)(1-e^{\beta\phi(r)}). \tag{28}$$

The one-component Percus Yevick closure, Eq. (28), can be solved for the pair potential, using the pair distribution and direct correlation functions of the effective one-component liquid, which will produce an effective potential deviating from the hard sphere potential, namely,

$$\beta\Phi_{\text{eff}}^{\text{PY}}(r)=\ln\left(1-\frac{c_{\text{eff}}(r)}{g_{\text{eff}}(r)}\right). \tag{29}$$

Observe that the pure hard sphere potential is recovered for the case that the correlation functions are actually those of the pure one-component hard sphere liquid.

A second elementary inversion procedure uses the hypernetted chain closure, and this could also be considered appropriate, since the effective potential is expected to differ from the pure hard sphere potential through the presence of a longer range tail. The HNC closure for a one-component liquid is:

$$g(r)=e^{-\beta\Phi(r)+h(r)-c(r)}. \tag{30}$$

Solving the one-component HNC closure (30) for the pair potential using the pair distribution and direct correlation functions of the effective one-component liquid, we find the effective potential under the HNC approximation to be

$$\beta\Phi_{\text{eff}}^{\text{HNC}}(r)=g_{\text{eff}}(r)-1-c_{\text{eff}}(r)-\ln[g_{\text{eff}}(r)]. \tag{31}$$

Note that the HNC inversion does not recover the pure hard sphere potential even if the correlation functions are purely hard sphere correlation functions [the terms $g(r)-1-\ln g(r)$ fail to vanish outside the core]. Thus the HNC inversion introduces longer range structure outside the core artificially, and, as is well known, is less appropriate for short range potentials of the hard sphere class. Our effective potential is expected, however, to be longer ranged than the pure hard sphere potential, and it is thus instructive to use both the PY and HNC inversion approximations for comparison.

V. EFFECTIVE POTENTIALS AND THE STRUCTURE OF TERNARY HARD SPHERE MIXTURES

Consider once again a ternary mixture with large, medium, and small diameters $\sigma_3>\sigma_2>\sigma_1$ and packing fractions η_3,η_2,η_1. As discussed in Sec. IV, we may formally subsume the effects of the smaller spheres and examine the resulting effective interaction between the larger spheres. In a three-component mixture we now have the freedom either to integrate out only the smallest spheres and regard the resulting system as an effective binary mixture, or to integrate out both the small and medium sized spheres and regard the system as effectively one component. In the latter case the effective potential reveals the length scales of both smaller species, σ_1 and σ_2, and therefore can significantly differ from effective potentials in binary mixtures.

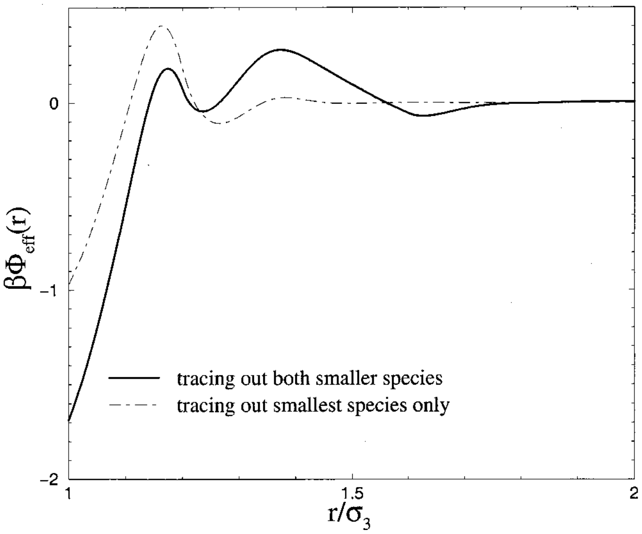

FIG. 5. Effective potentials $\beta\Phi_{\text{eff}}(r)$ between the large spheres obtained after tracing out the coordinates of the small spheres and after tracing out the coordinates of both the small and medium spheres in a three-component hard sphere mixture with $\sigma_1/\sigma_3=0.2$, $\sigma_2/\sigma_3=0.6$ and packing fractions $\eta_1=\eta_2=0.05$ and $\eta_3=0.47$; PY inversion was used in both cases.

Figure 5 compares the effective potential between spheres of the largest species for the case of an effective binary mixture (i.e., after tracing out just variables of the smallest species) with their pair potential in an effective one-component liquid (i.e., after tracing out the variables of both small and medium spheres) for a ternary mixture. The PY inversion has been used in both cases. The effective potential displays an attractive tail outside the core, as anticipated from the high contact values of the total correlation function for the large spheres in the three-component mixture. Figure 5 also shows that the elimination of the intermediate species after the smallest deepens the attractive tail even further and also leads to a more pronounced structure in the shape of the effective potential. Eliminating both smaller species leads to a description of the effective potential where the uniqueness of the three-component mixture appears most clearly in comparison to the binary mixture. The three-component mixture offers five parameters (the small and medium relative diameters and the three partial packing fractions), which can be adjusted with considerable flexibility to produce physically interesting potential shapes. It is the behavior of the largest spheres at relatively high packing in a sea of two smaller species that is considered as perhaps the most relevant to the question of the structure of a liquid mixture close to freezing.

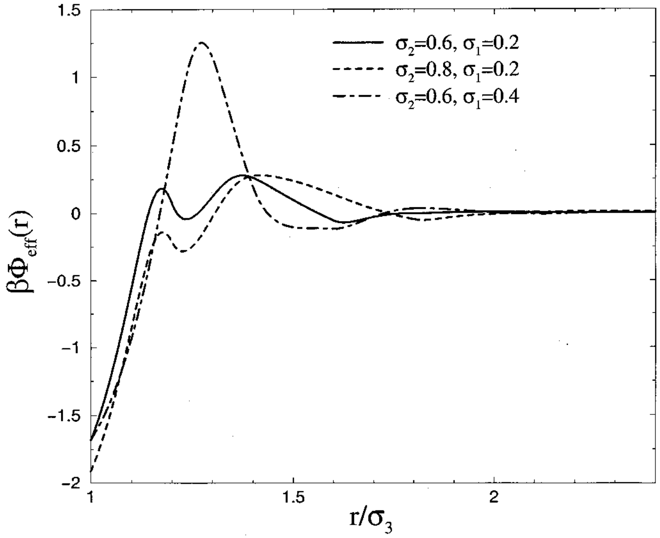

FIG. 6. Effective potential $\beta\Phi_{\text{eff}}(r)$ between the large spheres, after tracing out the coordinates of both smaller species; shown are the results for three different ternary mixtures all at packing $\eta_1 = \eta_2 = 0.05$ and $\eta_3 = 0.47$ and with varying diameters.

For some examples of effective potentials in three-component hard sphere mixtures, we start with a system with diameter ratios $\sigma_1/\sigma_3 = 0.2$, $\sigma_2/\sigma_3 = 0.6$ and packing fractions $\eta_1 = \eta_2 = 0.05$ and $\eta_3 = 0.47$. Figure 6 compares the effective potential of that mixture to those of ternary mixtures with the same partial packing fractions but different diameters. Only the results of the PY inversion are shown, but the PY and HNC approximations agree extremely well (for a comparison between HNC and PY effective potentials, see Fig. 8 below). Note the rich structure of the effective potentials, and especially the appearance of a flat potential well for the mixture with $\sigma_1/\sigma_3 = 0.4$ and $\sigma_2/\sigma_3 = 0.6$, which will be examined more closely below. If we vary the relative packing fractions but keep the sizes σ_i fixed we can also influence the depth of the valleys and the height of the peaks in the effective potential. Figure 7 shows a mixture with diameters $\sigma_1 = 0.2$ and $\sigma_2 = 0.6$ and compares the effective potential for the situation $\eta_1 = \eta_2 = 0.05$ and $\eta_3 = 0.47$ with a situation where the medium spheres are more prominent at the cost of fewer large spheres with $\eta_1 = 0.05$, $\eta_2 = 0.1$, and $\eta_3 = 0.41$. The total packing fraction is 0.57 in all cases. State dependence of the effective potentials (for example, the dependence on relative densities of the smaller species) is evident in both Figs. 6 and 7.

Finally, Fig. 8 shows the excellent agreement of the results for the effective potential for a mixture where both PY and HNC inversions have been used. For this case the parameters are $\alpha_1/\alpha_3 = 0.4$, $\alpha_2/\alpha_3 = 0.6$, $\eta_1 = \eta_2 = 0.05$, and $\eta_3 = 0.47$. The effective potential displays a flat region lacking a clear minimum. All separations within this flat section may be seen as energetically equivalent and upon freezing could give rise to the kind of structural uncertainty that might permit, at least in terms of packing, the formation of noncrystalline solids from the melt.

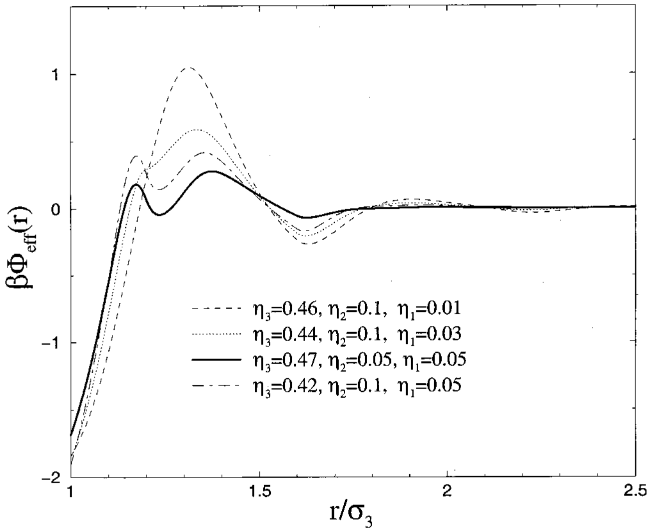

FIG. 7. Effective potential $\beta\Phi_{\text{eff}}(r)$ between the large spheres, after tracing out the coordinates of both smaller species; shown are the results for three different ternary mixtures all with sizes $\sigma_1/\sigma_3 = 0.2$, $\sigma_2/\sigma_3 = 0.6$, with varying packing fractions.

Note that the size ratios for all the examples above are moderate, which leads us to expect the systems to be in a region of fluid mixture (and away from instabilities). Extrapolating from the phase diagrams for binary mixtures in Ref. [4] we expect demixing to occur for considerably more extreme size ratios. But until phase diagrams for three-component hard sphere mixtures are available, the possibility of demixing in the above examples cannot be completely ruled out.

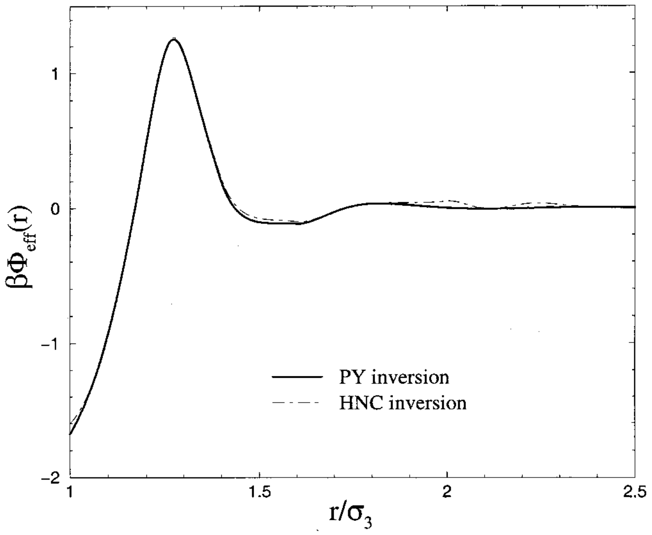

FIG. 8. Effective potential $\beta\Phi_{\text{eff}}(r)$ between the large spheres, after tracing out the coordinates of both smaller species in a mixture with diameter ratios $\sigma_1/\sigma_3 = 0.4$ and $\sigma_2/\sigma_3 = 0.6$, and packing fractions $\eta_1 = \eta_2 = 0.05$ and $\eta_3 = 0.47$. The results of PY and HNC inversions agree very well. The effective potential displays a flat region (see text).

VI. DISCUSSION

Hard spheres represent possibly the simplest model of a fluid, neglecting all but the repulsion at short range deemed largely responsible for packing effects in condensed matter. Multicomponent mixtures of hard spheres thus serve as important reference systems in the investigation of the short range correlation in the thermodynamics and structure of melts of noncrystalline solids, specifically glasses and quasicrystals. These special states of condensed matter appear to arise as stable or near stable phases only from melts with more than one atomic constituent, and often more than two; thermodynamically stable quasicrystals seem to require at least three atomic constituents. A plausible assumption is that for appropriate concentrations and microscopic length scales a third component introduces into the structure of the melt the additional complexity necessary to allow the formation of these ‘‘nontraditional’’ solids. Since the structure factors are given analytically in the Percus-Yevick approximation for hard sphere mixtures (as for the one-component liquid), the hard sphere model is also especially appealing as a reference model for thermodynamic perturbation theories, using, for example, the Gibbs-Bogoliubov inequality to obtain bounds on the free energy of a more realistic system.

Hard sphere mixtures are also a sufficiently simple model to permit exact solutions of the Ornstein Zernike equation in the PY approximation, but, as was shown, sufficiently complex to show special structural features in their correlation functions that may well be consistent with the formation of noncrystalline solids. It has also been demonstrated that from the point of view of the effective potential the ternary mixture is quite distinct from the binary mixture. Tracing out the variables of both the small and medium spheres evidently affords sufficient additional freedom of parameter choice to result in a potential with considerable complexity of structure.

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