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Theoretical studies of the correlations in moderately asymmetric binary hard-sphere solid mixtures

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A theoretical approach to calculate the correlation functions in binary hard-sphere (HS) solid mixtures is developed. The method is motivated by the theory of correlations in one-component HS solids [Rascon *et al.*, Phys. Rev. E **54**, 1261 (1996)] and the Kirkwood-Buff theory for solutions. Combined with the fundamental measure density functional theory the approach provides correlation functions in good agreement with the numerical simulations results for the moderately asymmetric mixtures.

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I. INTRODUCTION

Density functional theories (DFT) have become a very useful tool in the description of thermodynamics and structure of solid and liquid phases of hard spheres (HS) [1]. In general, the results obtained by the DFT are very accurate, usually within a few percent when compared with the ones from computer simulations. To describe the properties of more realistic systems perturbative theories for free energies have been widely used [2–4]. Within this approach the free energy is computed as a sum of the free energy of a reference system plus a perturbative term, which is calculated from correlation functions of the reference system. Typically, the HS system is chosen as a reference system, as it describes many properties of the reference repulsive potentials accurately. The perturbative theory used for single-component systems became especially reliable with the combination of the fundamental measure (FM) DFT [5,6] and the Rascon-Mederos-Navascues (RMN) theory for correlation functions in solids [7–9]. The essential inputs of these theories are the solid lattice type and the choice of single particle density distribution. In the widely used Gaussian model the inhomogeneous density profile of a crystal is expressed as a sum of normalized Gaussian functions centered at the crystal lattice sites. In the framework of FM DFT, which is based on the geometrical properties of hard aspheres, the free energy is a functional of weighted densities obtained as integral convolutions of a density profile with density-independent weight functions. This type of DFT provides accurate predictions of the solid equation of state and also the Lindemann parameters [10,11]. The RMN approach for correlation functions in solids parametrizes the HS radial distribution function as a summation from various coordination shells; the contributions from the second and higher-order coordination shells are treated in a mean-field fashion whereas the contribution from the nearest neighbors are corrected using essentially exact sum rules. In our previous study [9] we have shown that the single-component HS correlation functions obtained with the theory of Ref. [7] using the fundamental measure density functional led to accurate free energies of Lennard-Jones systems. Within a single theoretical framework phase diagrams of the Lennard-Jones system can be obtained accurately without inputs from computer simulations [9].

In this paper we extend the RMN approach to the hard-sphere solid mixtures as the correlation functions of HS mix-

tures are essential inputs to the calculations of thermodynamic properties of mixtures with realistic interactions within the perturbative approach [12,13]. For HS liquid mixtures the free energy is given by the very accurate Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) formula [14,15] and there are a few theoretical approaches [16,17] and computer simulations [18,19] for the correlation functions of HS liquid mixtures. Previously several types of DFT have been generalized to the binary HS solid mixture systems [20–23]. For such systems the densities of two species are also approximated by Gaussian profiles with different widths. The stable equilibrium free energy for given mixture parameters is then determined by the minimization of the free energy functional as a function of the widths of the Gaussian profiles. On the other hand, the correlation function calculations of the hard-sphere solid mixtures are much more demanding. To our knowledge only two computer simulations were performed [24,25] and no theoretical approaches have been reported yet. In the present study we have extended the theory of Ref. [7] for the correlations in single-component HS solids to the case of binary HS solid mixtures. In the mixtures there is a set of the distribution functions, describing the correlations between different mixture species unlike the one component system with a single pair distribution function. Therefore the main task is to find enough sum rules for the parametrization of the correlation functions. In this work a set of the Kirkwood-Buff (KB) equations [26], which connect the volume integrals of correlation functions to the thermodynamical parameters in the mixture, will be used to motivate the calculation of correlation functions in solid HS mixtures.

We use FM DFT to obtain the contact values of correlation functions and Gaussian widths as essential inputs to our theory for correlation functions. In the case of homogeneous binary liquid the FM free energy functional [10,11] reduces to the accurate BMCSL free energy; accurate correlation functions in the HS liquid mixture can be found from the solution of integral equations based on the FM free energy functional [16]. Therefore the calculation of the solid and liquid properties based on the same theoretical formulation may lead to the cancellation of a similar source of errors both for the liquid and solid phases, thus more accurate liquid-solid coexistence results. In this work we considered a single perfect fcc lattice with all the particles randomly distributed

over the lattice sites, i.e., a disordered fcc solid solution, although our method can be generalized to other types of crystal lattice as well.

It should be noted that such theoretical approaches are essential for the study of phase behaviors of more realistic systems, such as alloys. For example, when the concentration of one type of atoms is small, simulations of correlation functions become computationally prohibitive, on the other hand the theoretical approaches have no such limitations.

The rest of the paper is organized as follows. In Sec. II we briefly outline the fundamental measure density functional theory for the solid mixtures, the conditions at contact for correlation functions, the Kirkwood-Buff theory for solutions, and describe a theoretical method to calculate the correlation functions in solid mixtures. In Sec. III we present the results for the correlation functions, which are compared with the corresponding ones from numerical simulations. Some concluding remarks are given in Sec. IV.

II. THEORY

We consider a binary solid mixture composed of two types of hard spheres with diameters d_{ii} and bulk number densities ρ_i ($i=1,2$). The index 2 denotes the larger sphere, thus $d_{11} < d_{22}$. The collision diameter for the additive mixture is $d_{ij} = d_{ji} = (d_{ii} + d_{jj})/2$, and the intermolecular pair potential of interactions of hard spheres being

$$u_{ij}(r) = \begin{cases} +\infty, & r < d_{ij} \\ 0, & r \geq d_{ij}. \end{cases} \quad (1)$$

The concentration of the i component is $x_i = \rho_i / \rho$ ($\rho = \rho_1 + \rho_2$), so $x_1 + x_2 = 1$. The total packing fraction η (the fraction of volume occupied by spheres) and the densities are then simply related by

$$\eta = \frac{\pi}{6} \rho_1 d_{11}^3 + \frac{\pi}{6} \rho_2 d_{22}^3 = \frac{\pi}{6} \rho \sigma^3, \quad (2)$$

where the parameter $\sigma = (x_1 d_{11}^3 + x_2 d_{22}^3)^{1/3}$ is an effective diameter.

Thus an HS binary mixture can be uniquely characterized by three quantities: total packing fraction η , concentration of the larger particles $x = x_2$ ($0 < x < 1$), which are the thermodynamical variables, and the HS diameter ratio $\delta = d_{11}/d_{22} < 1$, which is simply a geometric parameter.

The total local number density of a binary mixture is expressed as a sum of the components $\rho(\vec{r}) = \rho_1(\vec{r}) + \rho_2(\vec{r})$, where $\rho_i(\vec{r})$ denotes the local number density of species i ($i=1,2$). We will parametrize the local one-body inhomogeneous density in a solid by a sum of Gaussian density distributions centered at the crystal lattice sites. In this study we consider only a substitutionally disordered fcc solid solution. Since for the disordered fcc HS solid solution the concentration of defects is very small we will assume a given site to be occupied by the spheres of both components with the probability being equal to the corresponding concentration x_i (the defects in the crystal are mostly vacancies as the presence of interstitials is several orders of magnitude less probable than vacancies). Thus

$$\rho_i(\vec{r}) = x_i \left(\frac{\alpha_i}{\pi} \right)^{3/2} \sum_{\vec{R}_k} e^{-\alpha_i(\vec{r} - \vec{R}_k)^2} \quad (i=1,2), \quad (3)$$

where α_1 and α_2 are the parameters of the Gaussian distributions; the sum runs over all the fcc lattice sites $\{\vec{R}_k\}$.

A. Density functional theory for HS solid mixtures

To obtain the equilibrium local density distributions the solid free-energy functional is minimized with respect to the parameters of the local densities. The Helmholtz free energy of the binary HS system F is expressed as a functional of density profiles $\{\rho_i(\vec{r})\}$,

$$F[\rho_1(\vec{r}), \rho_2(\vec{r})] = k_B T \sum_{i=1}^2 \int d\vec{r} \rho_i(\vec{r}) \{ \log[\rho_i(\vec{r}) \Lambda_i^3] - 1 \} + \tilde{F}_{ex}[\rho_1(\vec{r}), \rho_2(\vec{r})], \quad (4)$$

where the first term has the form of the ideal gas free energy, although it still depends on the interparticle interaction potentials via the density profiles $\rho_i(\vec{r})$, Λ_i is the thermal de Broglie wavelength, k_B the Boltzmann constant, T the temperature, and \tilde{F}_{ex} the excess free-energy functional. The arguments in the square brackets denote the functional dependence on the inhomogeneous densities $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$. In the applications below we will use the expression for free-energy functional in the form

$$F[\rho_1(\vec{r}), \rho_2(\vec{r})] = k_B T \sum_{i=1}^2 \int d\vec{r} \rho_i \{ \log(\rho_i \Lambda_i^3) - 1 \} + F_{ex}[\rho_1(\vec{r}), \rho_2(\vec{r})], \quad (5)$$

where the first term is the ideal gas contribution in the absence of interactions and F_{ex} the excess free-energy functional, which accounts for intermolecular interactions.

Different types of DFT were previously reported to approximate the excess part of free energy F_{ex} for HS solid mixtures [20–23]. We computed the thermodynamic properties of HS solid binary mixtures using the fundamental measure (FM) free-energy functional [10,11], because this functional is shown to be able to reliably describe the properties of a single-component solid. It is also very accurate to describe the equation of state and correlation functions of HS liquid mixtures [16]. Thus we can choose FM DFT to treat both HS binary solid and liquid phases using the same theoretical framework, which is essential for the calculation of reliable liquid-solid phase diagrams. In the framework of the FM DFT, the excess part of the free energy is written as

$$F_{ex} = k_B T \sum_{i=1}^2 \int d\vec{r} \rho_i(\vec{r}) \log[\rho_i(\vec{r}) / \rho_i] + k_B T \int d\vec{r} \Phi\{n_\alpha(\vec{r})\}, \quad (6)$$

where the expression for Φ in the right-hand side (rhs) of Eq. (6) is provided in Refs. [10,11].

$$\Phi = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \vec{n}_{v_1} \vec{n}_{v_2}}{(1 - n_3)} + \frac{1}{8\pi n_3^2} \left(\frac{n_3}{(1 - n_3)^2} \right. \\ \left. + \ln(1 - n_3) \right) \left[\vec{n}_{v_2} \hat{n} \vec{n}_{v_2} - n_2 \vec{n}_{v_2}^2 - \text{tr}(\hat{n}^3) + n_2 \text{tr}(\hat{n}^2) \right]. \quad (7)$$

The scalar n_0 , n_1 , n_2 , n_3 , vector \vec{n}_{v_1} , \vec{n}_{v_2} , and tensor \hat{n}_{ij} weighted densities in this expression are given by the following integral convolutions:

$$n_\alpha(\vec{r}) = \sum_{i=1}^2 \int d\vec{r}' \rho_i(\vec{r}') \omega_i^{(\alpha)}(\vec{r} - \vec{r}') \quad (8)$$

of the densities $\{\rho_i(\vec{r})\}$ with the corresponding density-independent weight functions $\omega_i^{(\alpha)}(r)$,

$$\omega_i^{(2)}(r) = \delta\left(\frac{d_{ii}}{2} - r\right), \quad \omega_i^{(3)}(r) = \Theta\left(\frac{d_{ii}}{2} - r\right), \\ \omega_i^{(0)}(r) = \frac{1}{\pi d_{ii}^2} \omega_i^{(2)}(r), \quad \omega_i^{(1)}(r) = \frac{1}{2\pi d_{ii}} \omega_i^{(2)}(r), \\ \vec{\omega}_i^{(v_2)}(\vec{r}) = \frac{\vec{r}}{r} \delta\left(\frac{d_{ii}}{2} - r\right), \quad \vec{\omega}_i^{(v_2)}(\vec{r}) = \frac{1}{2\pi d_{ii}} \vec{\omega}_i^{(v_2)}(\vec{r}), \\ \omega_i^{(jk)}(\vec{r}) = \frac{r_j r_k}{r^2} \delta\left(\frac{d_{ii}}{2} - r\right). \quad (9)$$

In these expressions $\delta(r)$ is the Dirac delta function, $\Theta(r)$ the Heaviside step function, and $\{r_{ij}\}$ the components of vector \vec{r} . For solid mixtures with the density distribution of Eq. (3), all the weighted densities $\{n_\alpha\}$ can be found in analytical forms from Eqs. (8) and (9). The volume integration in Eq. (6) is done over a small volume simplex reflecting the symmetry of the crystal (for details of the calculations in the single-component case see Refs. [9,28]). Thus with the density parametrization of Eq. (3) the free-energy functional $F[\rho_1(\vec{r}), \rho_2(\vec{r})]$ becomes a function of α_1 and α_2 : $F = F[\eta, x, \delta; \alpha_1, \alpha_2]$. Finally, for given values of mixture parameters η , x , and δ the minimization of the free energy with α_1 and α_2 yields the equilibrium values of the free energy F and the Gaussian parameters α_1 , α_2 of the density profile.

In Fig. 1 we show the dimensionless Gaussian localization parameters $\alpha_1 \sigma^2$, $\alpha_2 \sigma^2$ as a function of the concentration of the larger sphere x for $\delta=0.85$, 0.90, 0.95 and $\eta=0.5707$. It can be seen that for given η , x , and δ the condition $\alpha_1 \sigma^2 < \alpha_2 \sigma^2$ is always satisfied. This condition reflects the fact that the smaller particles are less localized around the fcc crystal sites compared to the larger ones, and the density distributions of the smaller spheres around the lattice sites at Eq. (3) are broader compared to the ones of the larger spheres. It also can be seen that when $x \rightarrow 1$ the values of $\alpha_2 \sigma^2$ for all the HS diameters ratios δ reduces to the same single-component limit; a similar conclusion is valid for the values of $\alpha_1 \sigma^2$ when $x \rightarrow 0$.

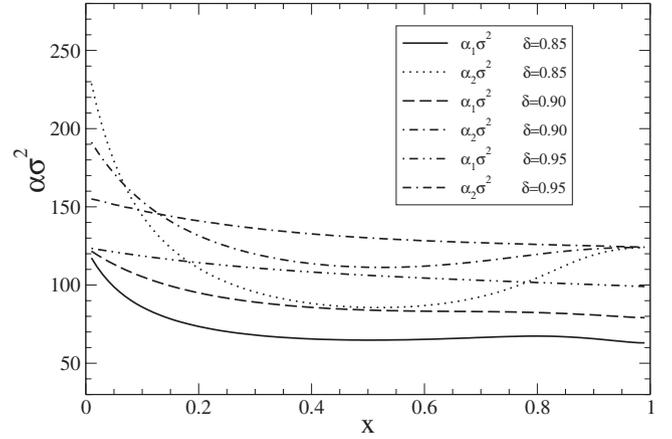


FIG. 1. Dimensionless Gaussian localization parameters $\alpha_1 \sigma^2$, $\alpha_2 \sigma^2$ vs concentration of larger spheres x for $\delta=0.85$, 0.90, 0.95 and $\eta=0.5707$.

B. Correlation functions in solid mixtures

In this section we define the correlation functions $\tilde{g}_{ij}(r)$ in solid mixtures. Let the first j -type particle be fixed at \vec{r}_1 , whereas the second i -type particle is at \vec{r}_2 ($i, j=1, 2$). In this case a pair distribution function $\rho_{ij}^{(2)}(\vec{r}_1, \vec{r}_2)$ can be expressed as a conditional density distribution of i -type particles with respect to the density distribution of j -type particles $\rho_j(\vec{r}_1)$. Instead of this pair distribution function $\rho_{ij}^{(2)}(\vec{r}_1, \vec{r}_2)$, which depends on six variables, it is convenient to introduce a pair distribution function averaged over all the locations of the first particle and the orientations of the second particle

$$\tilde{g}_{ij}(r) = \frac{1}{4\pi V \rho_i \rho_j} \int d\vec{r}_1 \int d\omega \rho_{ij}^{(2)}(\vec{r}_1, \vec{r}_1 + \vec{r}), \quad (10)$$

where V is the volume, $\rho_i = (1/V) \int d\vec{r} \rho_i(\vec{r})$ the bulk density of the i -type particles, and ω the solid angle of the direction from the first particle to the second particle. Now the correlation functions $\tilde{g}_{ij}(r)$ depend only on one variable r and is the correlation function used in the perturbative theory for free-energy calculations [12,13].

If the first particle is not fixed then the pair distribution function $\rho_{ij}^{(2)}(\vec{r}_1, \vec{r}_2)$ is equal to $\rho_j(\vec{r}_1) \rho_i(\vec{r}_2)$ and the corresponding averaged correlation function $\tilde{g}_{ij}^{(0)}(r)$ is

$$\tilde{g}_{ij}^{(0)}(r) = \frac{1}{4\pi V \rho_i \rho_j} \int d\vec{r}_1 \int d\omega \rho_j(\vec{r}_1) \rho_i(\vec{r}_1 + \vec{r}). \quad (11)$$

In this case the short-ranged correlations between the particles are not accounted for. The functions $\tilde{g}_{ij}^{(0)}(r)$ can be found analytically. Indeed, substituting Eq. (3) into Eq. (11) and some algebraic transformations lead to

$$\tilde{g}_{ij}^{(0)}(r) = \sum_{k \geq 0} \tilde{g}_{k,ij}^{(0)}(r), \quad (12)$$

where

$$\tilde{g}_{0,ij}^{(0)}(r) = \frac{1}{\rho_i} \left(\frac{\alpha_i \alpha_j}{(\alpha_i + \alpha_j) \pi} \right)^{3/2} e^{-\alpha_i \alpha_j / (\alpha_i + \alpha_j) r^2} \delta_{ij}, \quad (13)$$

$$\begin{aligned} \tilde{g}_{k,ij}^{(0)}(r) = & \frac{n_k}{4\rho\pi r R_k} \left(\frac{\alpha_i \alpha_j}{(\alpha_i + \alpha_j)\pi} \right)^{1/2} \{ e^{-\alpha_i \alpha_j (\alpha_i + \alpha_j)(r - R_k)^2} \\ & - e^{-\alpha_i \alpha_j (\alpha_i + \alpha_j)(r + R_k)^2} \} \quad (k \neq 0), \end{aligned} \quad (14)$$

where k runs over the number of the successive lattice shells, n_k is the coordination number of the k th shell, and R_k the lattice vector magnitude of the k th shell.

C. Kirkwood-Buff theory for solutions

The Kirkwood-Buff (KB) theory of solutions [26] provides the connection between the correlation functions in the form of so-called Kirkwood-Buff integrals (KBIs) $G_{ij} = \int d\vec{r} [\tilde{g}_{ij}(r) - \tilde{g}_{ij}^{(0)}(r)]$ and the thermodynamic values in an open system. Some transformations of the KB equations give us the following relations:

$$\delta_{ij} + \rho_i \int d\vec{r} [\tilde{g}_{ij}(r) - \tilde{g}_{ij}^{(0)}(r)] = G_{ij}^*, \quad (15)$$

where

$$G_{ij}^* = \rho_i \left(k_B T \kappa_T + \frac{\bar{V}_i \bar{V}_{j'}}{V \beta \mu_{i'j'}} \right) \quad (i, j = 1, 2, \quad i' \neq i). \quad (16)$$

G_{ij}^* are the dimensionless KBIs, κ_T is the isothermal compressibility, \bar{V}_i are the partial molar volumes, and μ_{ij} the derivatives of chemical potentials with respect to the numbers of particles when the pressure is fixed. Only three of these values are independent because of the additional thermodynamic conditions [26,27]: $\sum_{i=1}^2 \rho_i \bar{V}_i = 1$ and $\sum_{i=1}^2 \rho_i \mu_{ij} = 1$ (Gibbs-Duhem relation) ($j=1,2$). For the HS mixture the expressions for κ_T , \bar{V}_i , and μ_{ij} can be written as combinations of second derivatives of free energy $\frac{1}{N} \beta F(\eta, x, \delta)$ with respect to η and x . Thus if the dependence of the free energy on η , x , and δ is known all the KBIs G_{ij}^* in Eq. (16) can be calculated numerically.

The physical meaning of the KBIs G_{ij}^* in an open system can be viewed as the following. The volume integral $\rho_i \int \tilde{g}_{ij}^{(0)}(r) d\vec{r}$ is the mean number of i -type particles of the system before fixing any j -type particle at the origin, whereas the volume integral $\rho_i \int \tilde{g}_{ij}(r) d\vec{r}$ is the mean number of i -type particles of the system (minus δ_{ij} because of self-exclusion) after fixing a j -type particle at the origin. Thus the left-hand side (lhs) of Eq. (15) is the average number ΔN_{ij} of i -type particles coming into the system (plus δ_{ij}) when one j -type particle is fixed at the origin, i.e., $\Delta N_{ij} = G_{ij}^*$. The KBIs, G_{ij}^* , can be either positive or negative so the number of i -type particles in the system can increase or decrease when a j particle is fixed. The number of particles ΔN_i of i type coming into the system after fixing a particle either first or second type is $\Delta N_i = \sum_{j=1}^2 x_j \Delta N_{ij}$ (the coefficient x_j in front of ΔN_{ij} is a probability of finding a j -type particle at the origin), and the total number of particles coming into the system $\Delta N = \sum_{i=1}^2 \Delta N_i$. Now from Eqs. (15) and (16) we have

$$1 + \rho \sum_{i,j=1}^2 x_i x_j \int d\vec{r} [\tilde{g}_{ij}(r) - \tilde{g}_{ij}^{(0)}(r)] = \Delta N, \quad (17)$$

where

$$\Delta N = \rho k_B T \left(\kappa_T + \frac{(1/\rho - \bar{V}_2)^2}{V \mu_{22}} \right). \quad (18)$$

From the stability conditions of the system it follows that the values κ_T and μ_{22} are positive [27]; therefore ΔN is always positive.

Where are the ΔN particles accommodated in the crystal lattice? It is known that the equilibrium HS binary mixture crystal has a small concentration of vacancies. The probability to have a vacancy at a given lattice site in the disordered fcc HS crystal is about 10^{-5} [34], which gives the number of vacancies per lattice shell $\sim 10^{-4}$. From Eq. (18) we estimate $\Delta N \sim 10^{-2}$; therefore to accommodate ΔN particles coming into the system after fixing one particle at the origin, approximately 10^2 lattice shells are needed.

Following the arguments in Ref. [7] we note that fixing a particle at the origin introduces short-ranged correlations, which affects mostly the nearest neighbors (the particles in the first coordination shell). The contributions to the correlation functions $\tilde{g}_{ij}(r)$ from the lattice shells higher than the first shell are the same as the ones to $\tilde{g}_{ij}^{(0)}(r)$ with the only difference that no vacancies are needed to be taken into consideration. As a result, the correlation functions $\tilde{g}_{ij}(r)$ can be approximated as

$$\tilde{g}_{ij}(r) = \tilde{g}_{1,ij}(r) + \sum_{k \geq 2} \tilde{g}_{k,ij}^{(0)}(r). \quad (19)$$

Thus all of the correlations induced by fixing a particle at the origin are accounted for by the first coordination shell.

D. Conditions for the first peaks of the correlation functions

To find the first peak contribution $\tilde{g}_{1,ij}(r)$ in the above expression we propose the following function form:

$$\tilde{g}_{1,ij}(r) = A_{ij} \frac{e^{-\alpha'_{ij}/2(r-r_1)^2}}{r}, \quad r \geq d_{ij} \quad (20)$$

with $\tilde{g}_{1,ij}(r) = 0$ for $r < d_{ij}$. In the single-component case the expression for the first peak Eq. (20) reduces to the function proposed in Ref. [7]. To find the seven parameters $\{A_{ij}\}$, $\{\alpha'_{ij}\}$, and r_1 in Eq. (20) seven independent conditions are needed.

The first three conditions are from the contact values of the correlation functions. The three values of correlation functions $\{\tilde{g}_{ij}(r)\}$ at contact $\tilde{g}_{11}(d_{11})$, $\tilde{g}_{12}(d_{12})$, and $\tilde{g}_{22}(d_{22})$ [$\tilde{g}_{21}(d_{21}) = \tilde{g}_{12}(d_{12})$] can be found from the conditions for the derivatives of $\frac{1}{N} \beta F_{ex}$ with respect to HS diameters d_{11} and d_{22} , which are provided by the Hamad-Mansoori theory in Refs. [29,30].

$$\left. \frac{\partial}{\partial d_{ii}} \left(\frac{\beta F_{ex}}{N} \right) \right|_{T, \rho, x, d_{i'j'}} \Bigg|_{i=1,2} = 2\pi\rho \sum_{k=1}^2 x_i x_k d_{ik}^2 \tilde{g}_{ik}(d_{ik})$$

$$(i = 1, 2; i' \neq i). \quad (21)$$

Changing the variables d_{11} and d_{22} to $\sigma = (x_1 d_{11}^3 + x_2 d_{22}^3)^{1/3}$ and $\delta = d_{11}/d_{22}$ in the lhs of these equations yields a virial theorem for HS mixtures

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3} \rho \sum_{i,j=1}^2 x_i x_j d_{ij}^3 \tilde{g}_{ij}(d_{ij}) \quad (22)$$

and another exact condition

$$\begin{aligned} \left. \frac{\partial}{\partial \delta} \left(\frac{\beta F_{ex}}{N} \right) \right|_{\eta, x} &= \frac{2\pi \rho d_{22} x_1 x_2}{(x_1 \delta^3 + x_2)} [x_1 d_{11}^2 \tilde{g}_{11}(d_{11}) \\ &+ (x_2 - x_1 \delta^2) d_{12}^2 \tilde{g}_{12}(d_{12}) \\ &- x_2 \delta^2 d_{22}^2 \tilde{g}_{22}(d_{22})]. \end{aligned} \quad (23)$$

In Eq. (22) P is the pressure. The lhs of Eq. (22) is a compressibility factor

$$\frac{\beta P}{\rho} = 1 + \eta \frac{\partial}{\partial \eta} \left(\frac{\beta F_{ex}}{N} \right). \quad (24)$$

Equations (22) and (23) are exact, which are related to the two zero-separation theorems for the cavity functions in HS liquid mixtures [17] and to the criteria for HS mixtures [32]. An approximate closure is needed to determine the three contact values [31] and a reasonable choice is the one suggested in Ref. [24].

$$g_{12}(d_{12}) = [g_{11}(d_{11}) g_{22}(d_{22})]^{1/2}. \quad (25)$$

This closure becomes more accurate when the dissimilarity between the mixture components is not too high, i.e., for $\delta > 0.90$.

The next group of conditions are the normalization conditions for the functions $\tilde{g}_{1,ij}(r)$ to the nearest-neighbors number

$$\rho \int d\vec{r} \tilde{g}_{1,ij}(r) = n_1. \quad (26)$$

Indeed, as we discussed in the previous section we can neglect the vacancies in the first lattice shell. Therefore the functions $\tilde{g}_{1,ij}(r)$ are normalized to give the exact number of the nearest neighbors n_1 . Neglecting the vacancies in the first shell gives also the condition, which follows from the approximation for the mean location of the nearest neighbors $\langle r \rangle$,

$$\sum_{i,j=1}^2 x_i x_j \int d\vec{r} r \tilde{g}_{1,ij}(r) = \sum_{i,j=1}^2 x_i x_j \int d\vec{r} r \tilde{g}_{1,ij}^{(0)}(r) = \frac{n_1}{\rho} \langle r \rangle. \quad (27)$$

In the single-component case in the close-packing limit this condition is exact and is quite accurate over all density ranges [7].

To sum up, to find the seven parameters of the first peaks of the correlation functions $\{A_{ij}\}$, $\{\alpha'_{ij}\}$, and r_1 at Eq. (20) we have seven conditions: three equations from the contact values of the correlation functions [Eqs. (22)–(25)], three conditions for the number of nearest neighbors [Eq. (26)] and a

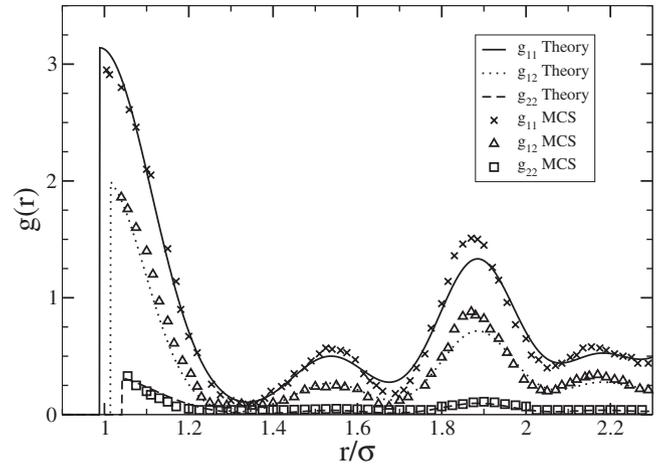


FIG. 2. The dependence of the correlation functions $(-\delta_{ij})x_i x_j \tilde{g}_{ij}$ on the scaled distance r/σ as a result of the present theory and MC simulations [24]. The mixture parameters are $\eta = 0.5707$, $x = 0.2037$, and $\delta = 0.95$.

formula for the mean location of the nearest neighbors [Eq. (27)]. These conditions are the key relations of our approach.

III. RESULTS

Using the method outlined in the previous section, results for the correlation functions $\tilde{g}_{ij}(r)$ in HS binary solid mixtures will be presented. First of all, for the given mixture parameters η , x , and δ the equilibrium values of Gaussian parameters $\alpha_1 \sigma^2$, $\alpha_2 \sigma^2$ are numerically obtained to calculate the higher number shell contributions in Eq. (14). The contact values of correlation functions $\tilde{g}_{ij}(d_{ij})$ are found from the calculated dimensionless compressibility factor $\frac{\beta P}{\rho}$, the derivative $\frac{\partial}{\partial \delta} \left(\frac{\beta F_{ex}}{N} \right)$, and the approximate closure Eq. (25). Using these data the solution of a set of algebraic equations from Eqs. (20), (26), and (27) yields all the parameters of the first peak $\{A_{ij}\}$, $\{\alpha'_{ij}\}$, and r_1 . Finally, the resulting correlation functions $\tilde{g}_{ij}(r)$ are found from Eqs. (14), (19), and (20).

Comparisons with the simulation ones [24] are shown in Figs. 2–6 for the correlation functions $\tilde{g}_{ij}(r)$ at a single packing fraction $\eta = 0.5707$ and various x and δ (we study one value of the packing fraction $\eta = 0.5707$ since the correlation functions from the numerical experiment are only available for that value [24]). It can be seen that the present theory correctly reproduces the main qualitative features of the correlation functions from simulations. In general, the quantitative differences between the results of the present theory and simulations are small, especially when δ is close to 1, i.e., $\delta = 0.95$ and 0.90 (see Figs. 2 and 3). The differences may become more pronounced for $\delta = 0.85$ (see Figs. 4–6), particularly in the first peaks.

To elucidate the sources of errors we summarize all of the approximations used in our approach. The first one is the approximate nature of FM density functional at Eq. (7), which is used to calculate $\frac{\beta P}{\rho}$ and $\frac{\partial}{\partial \delta} \left(\frac{\beta F_{ex}}{N} \right)$. The second one is the approximate closure expression of Eq. (25). Both of these approximations may result in some error for the obtained

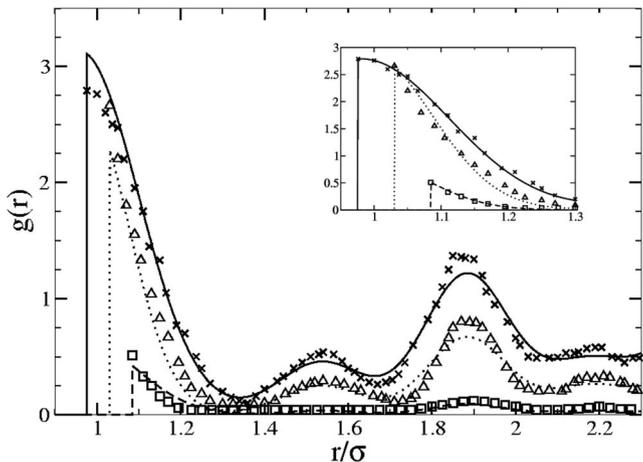


FIG. 3. The same as Fig. 2. The mixture parameters are $\eta = 0.5707$, $x = 0.2037$, and $\delta = 0.90$. The inset shows first peaks of the correlation functions obtained with contact values input from simulations [24] (see explanations in text).

contact values of the correlation functions. To eliminate this source of errors in the calculations of the first peaks we can, in our approach, directly use the contact values obtained from simulations [24]. In this case, in the set of equations for the first peaks the only approximate one is Eq. (27). We show the resulting first peaks in the insets of Figs. 3–6. It can be seen that excellent agreements in the first peaks are obtained between the theory and the simulations for all the values of the mixture parameters. Therefore the approximate condition in Eq. (27) turns out to be a very accurate one. The parametric form of the first peak in Eq. (20) is also very accurate, as it reproduces accurately the simulation results using correct parameters in Eq. (20).

We also notice that the Gaussian distributions in Eq. (3) are reasonable representations of one-body densities for the disordered fcc solid. As a matter of fact, the part of correlation functions $\tilde{g}_{ij}(r)$ in the bulk which is not affected by the short-ranged correlations is simply given by a sum of one-body density convolutions in the rhs of Eq. (19). The contri-

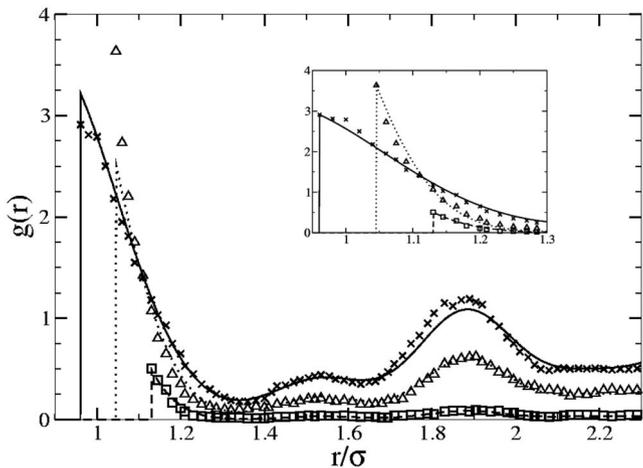


FIG. 4. The same as Fig. 2. The mixture parameters are $\eta = 0.5707$, $x = 0.2037$, and $\delta = 0.85$.

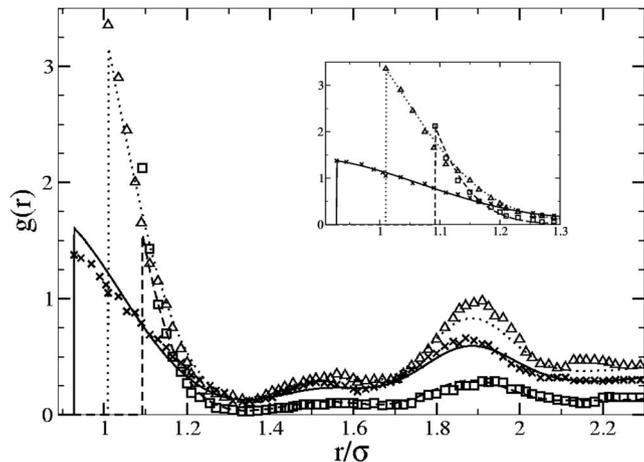


FIG. 5. Same as Fig. 4, but for $x = 0.3981$.

butions to the sum $\tilde{g}_{k,ij}^{(0)}(r)$ ($k \geq 2$) from Eq. (14) depend on the Gaussians' parameters $\alpha_1 \sigma^2$ and $\alpha_2 \sigma^2$. It can be seen in Figs. 2–6 that when $r^* = r/\sigma$ is larger than the minimum between the first and second peaks of correlation functions the agreement between the correlation functions obtained from the present theory and from the simulations is sufficiently good (for some mixture parameters the quantitative difference between the corresponding peaks with $k \geq 2$ obtained by the theory and simulations are due to the approximate α_1 and α_2 values). This conclusion is in contradiction to the DFT study of Ref. [33] where it was found that the larger particles are showing structure very similar to the one obtained using Gaussian densities, whereas the peaks of densities of smaller particles reveal a rich structure with the splitting of the major peaks at fcc lattice sites, such as the emerging multiple peaks. A possible explanation of such contradictions is that Ref. [33] used an early Ramakrishnan-Yussouff (RY) DFT and also the Percus-Yevick (PY) equations to calculate the direct correlation function in liquids which are the inputs to the RY free-energy density functional. This approach is not accurate enough to describe the highly inhomogeneous densities in crystals with high packing fractions in contrast to the fundamental measure DFT used in our study.

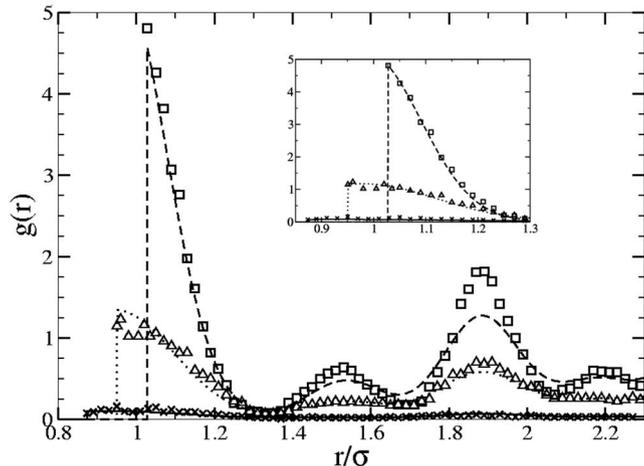


FIG. 6. Same as Fig. 4, but for $x = 0.7963$.

IV. CONCLUSIONS

A theory to study correlations in a single-component HS crystal has been developed previously by Rascon, Mederos, and Navascues in Ref. [7]. In that method the contributions to the correlation function from second and higher lattice shells are accounted for in a mean-field fashion, whereas the parameters of the first peak (contributions from nearest neighbors) are found from the sum rules. We have recently applied that method in combination with the fundamental measure free-energy functional and a perturbative theory to obtain accurate solid-liquid coexistence conditions of Lennard-Jones systems [9]. In the present study the calculation of the correlation functions is extended to binary mixtures of hard spheres. The binary system is characterized by three parameters, namely the total packing fraction η , the composition of larger spheres x , and the HS diameters ratio δ . Following Ref. [7], we consider the interaction of the fixed particle at the origin with the particles from the successive lattice shells in such a manner that the short-ranged correlations mostly affect the nearest neighbors. The method used for the calculation of the free energy is a fundamental measure DFT [10,11], although any other relevant DFT could be used [20–23]. We have considered just one type of crystal structure for the binary mixtures, namely disordered fcc structure as this is the only one with extensive studies from computer simulations. The defects were not accounted for in simulations of Ref. [24]. Thus to compare our results with the ones of Ref. [24] we did not account for defects in our theoretical calculations, though it is interesting to estimate the effects of defects on the thermodynamics and structure of solid mixture [34,35] with FM DFT [36]. In the present work the one-body density used is a sum of Gaussian distributions around crystal sites. The crystal structure and density distribution are inputs to the FM free-energy functional to provide all conditions to calculate the correlation functions. We have found that the obtained correlation functions are in good agreements with the ones from numerical simulations [24] for $\eta=0.5707$ and a variety of parameters δ and x . It will be interesting to have more extensive numerical simulations studies of the correlation functions in HS solid mixtures with various packing fraction η and different types of crystal lattice to compare with our theoretical predictions of the dependence of the correlation functions on the mixture parameters.

The quality of our theory is getting a bit worse with the increase of disparity between the two species (decreasing the parameter δ), especially for $\delta < 0.90$, this is largely due to the approximate functional in Eq. (7) and closure [Eq. (25)] used in the calculations as shown in the previous section.

We have applied our methodology to compute the free energies of liquid and solid phases of an Au-Cu alloy using a perturbative theory [37], which is the original motivation of the current work. We found that the typical range of parameters of reference HS solid mixture systems near melting temperatures are $\eta \sim 0.52\text{--}0.55$ and $\delta \sim 0.91\text{--}0.94$, i.e., the range where our theory provides the reliable results for correlation functions in HS solid mixtures. The resulting melting temperatures for different compositions are in a good agreement (within 6%) with the ones from simulations.

Our method to calculate correlation functions in binary HS solid mixtures can be straightforwardly generalized to ternary mixtures. Indeed, the Rosenfeld fundamental measure density functional theory [5], Kirkwood-Buff theory [26], and the Hamad-Mansoori theory [29], which are inputs to our approach, were initially formulated for multicomponent mixtures. It should be interesting to try to find an exact or, at least, a very accurate closure formula instead of Eq. (25) using the principles of statistical mechanics or scaled particle theory. Better closures in combination with exact equations (22) and (23) may provide more accurate contact values of correlation functions in a HS solid mixture, which are essential for the first peaks of the correlation functions. Another challenging task is to improve FM free-energy functional in Eq. (7) to have more accurate values for compressibility factor $\frac{\beta P}{\rho}$, derivative of free energy $\frac{\partial}{\partial \delta}(\frac{\beta F_{ex}}{N})$, and Gaussian parameters α_1, α_2 in HS solid mixtures. It may lead to better correlation functions, especially for largely dissimilar hard-sphere diameters.

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