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Theoretical approach to the correlations of a classical crystal

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We present a theoretical approach to the angular-average of the two-body correlation function $\tilde{g}(r)$ for simple solids. It is based on three sum rules for $\tilde{g}(r)$: the virial, compressibility, and normalization equations. We apply the theory to determine this correlation function for the case of the fcc solid phase of hard spheres. The agreement with simulation data is excellent over all the density range. The application to other simple systems is discussed. The approach opens a route to perturbation theories for simple solids. [S1063-651X(96)12108-5]

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The most important correlation function in fluid classical systems is the radial distribution function $g(r)$. Its first accurate description for a hard-sphere (HS) fluid, namely the Percus-Yevick approximation, was the starting point to the extraordinary development of the theory of simple liquids [1,2]. The analogous progress has been lacking in solids, the structured phases of these systems. In spite of the advance experimented during the past 15 years [3] in the theory of classical nonuniform systems, one of the most important theoretical objectives, correlations, has remained unapproachable.

In structured systems the most important correlation function is $\tilde{g}(r)$, the angular average of the two-particle density function $\rho^{(2)}(\mathbf{r},\mathbf{r}')$. It appears in all crucial equilibrium equations as the virial, compressibility, or energy equation [2], and it is the key of all perturbation approaches [2–4]. The $\tilde{g}(r)$ plays the same role in classical solids as $g(r)$ does in classical fluids. However, up to now, no theoretical approach to $\tilde{g}(r)$ had been reported. Here, we present a theoretical approach to this function and apply it to evaluate $\tilde{g}(r)$ for a face-centered-cubic HS solid. The agreement with simulation results is excellent over all the physical range of densities from below melting up to almost close-packing. The application to other systems is straightforward as it is discussed below.

All previous theoretical approaches reported in the literature to the correlations of classical solids have been focused on $g(\mathbf{r},\mathbf{r}')$ [defined through $\rho^{(2)}(\mathbf{r},\mathbf{r}')\equiv\rho(\mathbf{r})\rho(\mathbf{r}')g(\mathbf{r},\mathbf{r}')$] for HS and mainly in relation to perturbation schemes. They are not true approximations; rather, they are simple mappings to the radial distribution function of a uniform system at some effective density. None of these approaches can resist a direct comparison with simulation results [5]. In fact, these mappings could be done over a wide family of functions [6]. Moreover, only $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ (the probability of finding two particles at $\mathbf{r}$ and $\mathbf{r}'$) and $\rho^{(2)}(\mathbf{r},\mathbf{r}')/\rho(\mathbf{r})$ (the probability of finding a particle at $\mathbf{r}'$ provided there is another one at $\mathbf{r}$) and their angular averages involve a direct physical meaning. It is, therefore, more sensible to make approximations on these functions than on $g(\mathbf{r},\mathbf{r}')$. The function $\tilde{g}(r)$ is defined as

$$\tilde{g}(r)=\frac{1}{4\pi V\rho^2}\int d\Omega\int d\mathbf{r}_1\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_1+\mathbf{r}), \qquad (1)$$

where V is the volume, $\rho\equiv N/V$ is the mean density, and $d\Omega$ the differential solid angle aperture around $\mathbf{r}$.

To motivate the theory we shall first discuss the two types of correlations that $\tilde{g}(r)$ must account for in a solid. The long-range correlation, characteristic of structured phases, is directly due to the periodicity of the solid. If no other correlation is considered, each particle would move around a lattice site independently of each other. As the probability of finding a particle at $\mathbf{r}$ is given by the local density $\rho(\mathbf{r})$—which is a sum of Gaussian-like functions located at each lattice site— $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ is then given by the simple product of individual probabilities $\rho(\mathbf{r})\rho(\mathbf{r}')$ multiplied by a steplike function, $g(\mathbf{r},\mathbf{r}')$, to avoid double occupancy. Its proper angular average gives the long-range contribution to $\tilde{g}(r)$. So, it is convenient to define $\tilde{g}_0(r)$ as the angular average of the product $\rho(\mathbf{r})\rho(\mathbf{r}')$,

$$\tilde{g}_0(r)=\frac{1}{4\pi V\rho^2}\int d\Omega\int d\mathbf{r}_1\rho(\mathbf{r}_1)\rho(\mathbf{r}_1+\mathbf{r}), \qquad (2)$$

which has the form of a sum of Gaussian-like peaks $\tilde{g}_0{}^{(i)}$ centered around successive neighbor distances R_i, normalized to the corresponding number of neighbors n_i. If we consider only this long-range correlation, or if other kinds of correlations are dismisible, $\tilde{g}(r)$ must be given by a sum of peaks $\tilde{g}^{(i)}$ which should coincide with $\tilde{g}_0^{(i)}$ for $i>0$. The case $i=0$ has to be excluded to avoid double occupancy. For instance, this long-range correlation is the only one existing in the close-packing limit of a HS solid. In this limit $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ is exactly a sum of products of δ functions at any pair of different lattice sites multiplied by a steplike function to exclude the double occupancy. Hence, the function $\tilde{g}(r)$ will be a sum of δ functions at different neighbor distances, except at zero distance, normalized to the corresponding number of neighbors.

To take into account the other correlations, the successive peaks $\tilde{g}^{(i)}$ must be increasingly modified from the $\tilde{g}_0^{(i)}$ as i decreases to 1. The compressibility equation [2],

$$1+4\pi\rho\int drr^2[\tilde{g}(r)-\tilde{g}_0(r)]=\rho k_BT\chi_T, \qquad (3)$$

will help us to understand these modifications. The integral of $\tilde{g}_0(r)$ in Eq. (3) gives the average number of particles inside the system. The integral of $\tilde{g}(r)$ gives the average number of particles inside the system (minus one because of the self-exclusion) provided a particle is fixed at the origin. Thus, the left hand side of Eq. (3) can be understood as the average number ΔN of particles coming into the system when a particle is fixed at the origin, i.e., $\Delta N = \rho k_B T \chi_T$. For example, in the HS close-packing limit $\chi_T = 0$, the correlation reduces to the long-range one discussed above ($\tilde{g}^{(i)} \equiv \tilde{g}_0^{(i)}$) and Eq. (3) is verified identically. In other words, no HS comes into the system if it is completely packed. If we imagine a spherical system of radius R, we can estimate ΔN as $\rho 4\pi R^2 \delta R$, where δR is the displacement of the peaks at the border of the system, i.e., the displacement of $\tilde{g}^{(i)}$ with respect to $\tilde{g}_0^{(i)}$ for $R_i \approx R$. Then, $\delta R \approx \rho k_B T \chi_T / (\rho 4\pi R_i^2)$. This is a quite interesting result that shows that the differences, which should include some kind of deformation, between $\tilde{g}^{(i)}$ and $\tilde{g}_0^{(i)}$ reduce quadratically with the distance.

Up to now the discussion has been quite general, and now we apply it to the case of a HS solid (from now on all distances in HS diameter units, d_{HS}). The compressibility of the HS solid is so small that δR would be practically imperceptible in a simulation. A rough estimation of this displacement is already negligible for the first peak even at the lowest densities: taking $R \approx 1$ and $\rho k_B T \chi_T \approx 0.02$ gives $\delta R \approx 0.001$. Thus the location of the peaks of $\tilde{g}(r)$ does not differ from the location of those of $\tilde{g}_0(r)$. If the displacement of the peaks is negligible it seems quite sensible to assume that they cannot differ significantly from the peaks of $\tilde{g}_0(r)$. However, the identification of peaks cannot be done without considering the characteristic HS zero value of $\tilde{g}(r)$ at distances $r < 1$ and the fact that the nearest neighbors will bear the most important part of the short-range correlations. Therefore $\tilde{g}^{(1)}$ will be different from $\tilde{g}_0^{(1)}$ as we will see below.

To go far toward an explicit form of the peaks, we can regard the existent functional theories [3] which give an accurate description of the free energy of a HS solid and from which it is possible to determine $\rho(\mathbf{r})$. All these theories use successfully the Gaussian parametrization of $\rho(\mathbf{r})$, [7]

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_{\mathbf{R_i}} e^{-\alpha(\mathbf{r}-\mathbf{R}_i)^2}, \tag{4}$$

where α is the Gaussian width parameter. Setting Eq. (4) in Eq. (2) yields

$$\tilde{g}_0^{(i)}(r) = \frac{1}{4\pi\rho}\left(\frac{\alpha}{2\pi}\right)^{1/2} n_i \frac{e^{-\alpha(r-R_i)^2/2} + e^{-\alpha(r+R_i)^2/2}}{rR_i}, \quad i > 0. \tag{5}$$

For the sake of simplicity, we have dropped all terms which arise from the exponential products with $\mathbf{R} \neq \mathbf{R}'$ in (5). At the usual values of α they give negligible contributions because of the absence of overlapping. In accordance with the discussion above, we take $\tilde{g}^{(i)}(r) = \tilde{g}_0^{(i)}(r)$ for $i > 1$.

To find a compromise between the functional form of Eq. (5) and the mentioned features of the first peak, we propose the simple parametric form

$$\tilde{g}^{(1)}(r) = \frac{A e^{-\alpha_1(r-r_1)^2/2}}{r}, \quad r \geq 1, \tag{6}$$

with $\tilde{g}^{(1)}(r) = 0$ for $r < 1$, where A, r_1, and α_1 will be determined by the following sum rules. As the compressibility shows that even in the less favorable case the displacement of the first peak is quite small, the mean location of the nearest neighbors $\langle r \rangle$ can be approximated by the mean value obtained with the first peak of $\tilde{g}_0(r)$:

$$\frac{n_1}{\rho}\langle r \rangle \equiv \int d\mathbf{r} r \tilde{g}^{(1)}(r) = \int d\mathbf{r} r \tilde{g}_0^{(1)}(r). \tag{7}$$

This sum rule for $\tilde{g}^{(1)}(r)$ becomes more accurate as the mean density increases and it is exact in the limit of close-packing. Besides, two other *exact* sum rules must be obeyed by $\tilde{g}(r)$. The first one corresponds to the normalization of $\tilde{g}^{(1)}$ to the nearest-neighbor number:

$$4\pi\rho \int_{d_{\mathrm{HS}}}^{\infty} dr r^2 \tilde{g}^{(1)}(r) = n_1. \tag{8}$$

The virial equation is the second *exact* sum rule. It can be easily proved that, for nonuniform systems, the pressure is related to the value of $\tilde{g}(r)$ at contact exactly in the same way as it is related to the radial distribution function of uniform fluids:

$$\beta P/\rho = 1 + 4\eta \tilde{g}(d_{\mathrm{HS}}), \tag{9}$$

where $\beta = 1/k_B T$ and η is the packing fraction ($\eta = \pi\rho/6$).

All the required information to determine $\tilde{g}(r)$ (α and pressure as functions of ρ) is now provided by the minimization of any of the well known and accurate density functionals for the Helmholtz free energy of the HS solid. With these data, the three proposed sum rules form a nonlinear system of equations which is solved to find A, α_1, and r_1 at each ρ. Simultaneously, using α and Eq. (5), the successive peaks of $\tilde{g}(r)$ are obtained.

Very recent studies have shown that the equation of state of the HS solid deduced from different functional approaches agrees quite well with simulation results over all the density range [8]. For the following calculation, we use the generalized effective liquid approximation (GELA) [9] as it gives the best overall behavior. However, there are no significant differences if any other functional approach is used. If we compare the most recent Monte Carlo simulations by Choi *et al.* [10] with the predictions of the present theory for $\tilde{g}(r)$, the agreement is excellent over all densities and especially impressive at high densities. Figures 1 and 2 show $\tilde{g}(r)$ for two significant densities: $\eta = 0.52$, the lowest density below melting ($\eta_m \approx 0.54$) with available simulation data, and $\eta = 0.71$, near close-packing ($\eta_{\mathrm{cp}} \approx 0.74$), respectively. There are some differences between theoretical predictions and simulation results. Nevertheless, they are quite small and can only be appreciated easily at the lowest densities. Let us first pay attention to $\tilde{g}^{(1)}(r)$. The value at

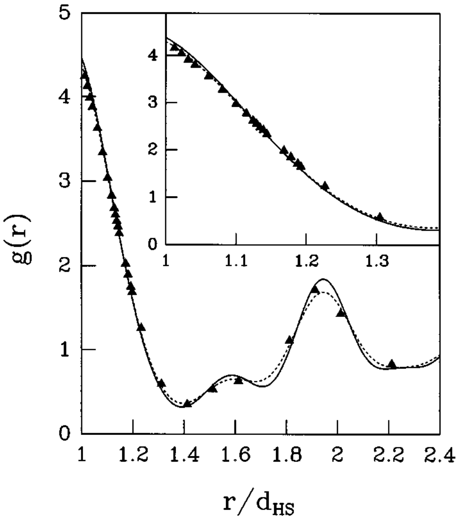

FIG. 1. $\tilde{g}(r)$ at $\eta=0.52$. Solid line is the prediction of the present theory using theoretical data from GELA functional approach. Dotted line corresponds to the theoretical predictions using data from a hypothetical exact theory. Triangles are Monte Carlo results from Choi *et al.* The inset shows details of the first peak $\tilde{g}_1(r)$.

contact differs from that of simulation. It is a direct consequence, via virial equation, of the approximate theoretical pressure. If the *exact* pressure (from simulation) is used in the theory, the agreement with simulation would be almost complete (see Fig. 1) confirming the goodness of the theory. The rest of the peaks of $\tilde{g}(r)$, which only depends on the parameter α ($\alpha=113$ for $\eta=0.54$ and $\alpha=10094$ for $\eta=0.71$), also agree quite well with the simulation results. Introducing again the *exact* α values (estimated from simulation: $\alpha=91$ for $\eta=0.54$ and $\alpha=7659$ for $\eta=0.71$) the agreement is excellent. The Gaussian parameter α_1 is approximately half that of the rest of the peaks ($\alpha_1=50$ for $\eta=0.54$ and $\alpha_1=5405$ for $\eta=0.71$). However, because of the cut, the width of this first peak is similar to the rest. The excellent agreement of the first peak showed in the inset of the figures would give an estimation of α_1 from simulation practically equal to that predicted by the theory. More interesting is the r_1 parameter which corresponds to the position where the first peak has practically its maximum value. Notice that at very low densities the real maximum is located at contact (see Fig. 1) and r_1 would be the maximum if the first peak is analytically extrapolated below $r=1$. The important point is that simulation data of this maximum have been reported (at very low densities the extrapolation has been also estimated and reported). Figure 3 shows these data for different densities together with our theoretical predictions. The parameter r_1 must always be smaller than the $\langle r\rangle$ except at the close-packing limit where both coincide. As ρ decreases from this limit, the pressure decreases rapidily from infinity and also the value of $\tilde{g}(r)$ at contact. Meanwhile, the lattice parameter hardly changes and the peak width still remains quite sharp. Under these circumstances, the only way to keep on with the normalization is increasing r_1. However, the pressure does not change too much at low ρ and the peak becomes duller as ρ decreases. Then, r_1 must recede to maintain the normalization. We mention this because the overall agreement of the peaks would not necessarily imply the nice agreement of the behavior of r_1 with the mean density. Futhermore, as Fig. 3 shows, the expression for $\langle r\rangle$, Eq. (7), which is only exact in the close-packing limit, turns out to be quite accurate over all the density range (the simulation numerical values when $\eta=0.54$ and $=0.71$ are 1.1208 and 1.0141, respectively, while the theoretical predictions are 1.1190 and 1.0142). All this proves the suitable physical description of our theoretical approach. The parameter A is a simple factor to adjust the normalization or to adjust the value at contact.

A major consequence of the theoretical knowledge of $\tilde{g}(r)$ is the possibility to develop and use proper perturbation theories for solids where the perturbative term can now use the appropriate correlation function of the reference HS system instead of the correlation function of a HS fluid at the same effective density [3]. Work along this direction is in progress. Moreover, these theories provide a way to deter-

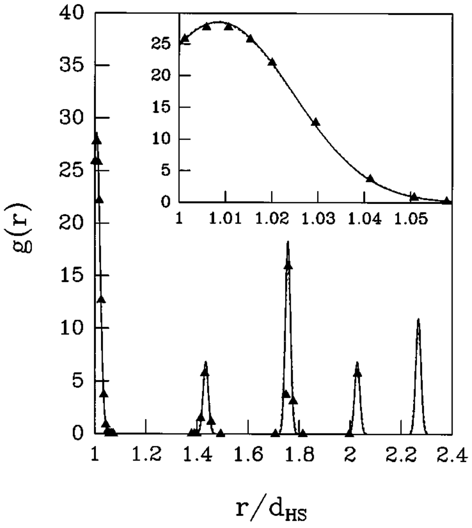

FIG. 2. As Fig. 1. but for $\eta=0.71$.

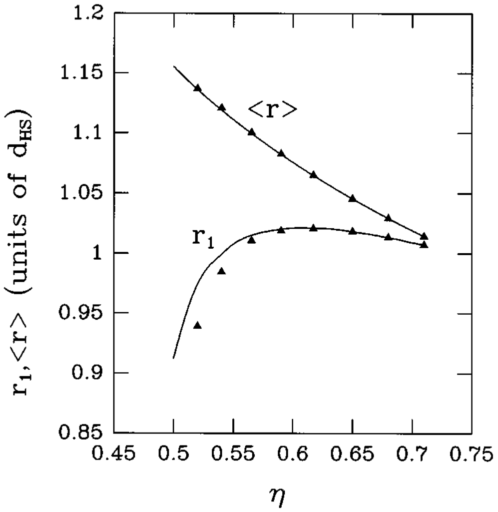

FIG. 3. Parameter r_1 (lower curve) and $\langle r\rangle$ for the first neighbour (upper curve) as a function of the mean density predicted by the theory. Triangles are simulation data from Choi *et al.*

mine $\widetilde{g}(r)$ for any simple system in the very same way as in the theory of simple liquids where the HS system is used as a reference system [2]. An alternative and fresh method is to apply the present approach directly. A parametric form of $\widetilde{g}(r)$ can be proposed which includes all the relevant physics. Extending the approach to systems with significant compressibility, the two parameters of each peak, α and R_i, should differ from their homologous of $\widetilde{g}_0(r)$ in an amount which should decrease quadratically with the distance. The normalization and equilibrium equations should be enough to determine this decrease and to describe $\widetilde{g}(r)$ reasonably. Notice that the energy equation is another sum rule which can be applied to these systems. The presence of defects, vacants, and interstitials would change the normalization of the peaks in both $\widetilde{g}(r)$ and $\widetilde{g}_0(r)$ depending on the distance. For this contribution, however, one expects an exponential decrease as defects behave as a kind of fluid inside the solid, which induces a short-range correlation.

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