Freezing of hard spheres within the modified weighted density approximation

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The real space version of the modified weighted density approximation is investigated in order to determine the effective liquid density that is used to represent a face centered cubic hard-sphere solid. It is shown that above a threshold average density of the solid the theory is unable to predict the existence of the crystal phase. [S1063-651X(97)04103-2]

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In the density functional theory of freezing [1] the Helmholtz free energy of a solid, $F[\rho]$, is a unique functional of the local density, $\rho(\mathbf{r})$, which can be split into ideal and excess contributions, $F[\rho]=F_{\mathrm{id}}[\rho]+F_{\mathrm{ex}}[\rho]$. The equilibrium local density of the solid is obtained by minimizing $F[\rho]$ at constant average density but, since only $F_{\mathrm{id}}[\rho]$ is known exactly as a functional of the local density, any implementation of density functional theory requires some explicit approximation for $F_{\mathrm{ex}}[\rho]$. In the modified weighted density approximation (MWDA) of Denton and Ashcroft [2] and in the generalized effective liquid approximation (GELA) of Lutsko and Baus [3] the excess free energy per particle of the solid $f_{\mathrm{ex}}[\rho]=F_{\mathrm{ex}}[\rho]/N$, with N the number of particles, is mapped onto that of an effective uniform fluid, i.e., $f_{\mathrm{ex}}[\rho]=f_{\mathrm{ex}}(\hat{\rho})$. Here $\hat{\rho}\equiv\hat{\rho}[\rho]$ denotes the effective liquid density which is used to represent the solid and $f_{\mathrm{ex}}(\hat{\rho})$ is the excess free energy per particle of the corresponding uniform fluid. Both approximations differ in the way the effective liquid density is found. In the GELA $\hat{\rho}$ is the unique solution of a differential equation [3], while in the MWDA $\hat{\rho}$ is defined as a doubly weighted average of the local density of the solid with respect to a weight function [2]:

$$\hat{\rho}=\frac{1}{N}\int d\mathbf{r}\ \rho(\mathbf{r})\int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|;\hat{\rho}), \tag{1}$$

where $w(|\mathbf{r}-\mathbf{r}'|;\hat{\rho})$ is the weight function.

To ensure that the MWDA becomes exact in the limit of a uniform system $\rho(\mathbf{r})\to\rho_l$, with ρ_l denoting the density of the uniform system, the weight function must satisfy the normalization condition

$$\int d\mathbf{r}'w(|\mathbf{r}-\mathbf{r}'|;\rho_l)=1, \tag{2}$$

where we have taken into account that $\hat{\rho}\to\rho_l$ when $\rho(\mathbf{r})\to\rho_l$.

A unique specification of the weight function is obtained by requiring that the second functional derivative of the excess free energy functional $-\beta F_{\mathrm{ex}}[\rho]$, with β the inverse temperature, is, in the uniform fluid limit, the direct correlation function of the uniform fluid, yielding

$$w(|\mathbf{r}|;\rho_l)=-\frac{1}{2\psi'(\rho_l)}\left[c(|\mathbf{r}|;\rho_l)+\frac{1}{V}\rho_l\psi''(\rho_l)\right], \tag{3}$$

where V is the volume, $\psi(\rho)=\beta f_{\mathrm{ex}}(\rho)$, and $c(|\mathbf{r}|;\rho)$ is the direct correlation function of the fluid. As usual, the prime denotes diferentiation with respect to the argument.

Five years ago, Kyrlidis and Brown [4] made a comparison between the MWDA and the GELA for the face centered cubic (fcc) hard-sphere solid at low densities. They found that the MWDA can possess two solutions for $\hat{\rho}$. The reason for this unphysical multiplicity of solutions for the effective liquid density was not investigated by these authors but interpreted by them as a serious defect of the theory. Very recently Likos and Ashcroft [5] concluded that the solution of the MWDA, when it exists, is always unique if proper account is taken of the boundary conditions that $\hat{\rho}$ has to satisfy for small localizations of the particles in the solid. In particular, they showed that the so-called second branch of solutions of the MWDA must be discarded since, in the uniform fluid limit, the effective liquid packing fraction of this branch $\hat{\eta}=\pi\hat{\rho}\sigma^3/6$, with σ the hard-sphere diameter, approaches unity. This value is greater than the packing fraction at close packing of the fcc crystal ($\pi\sqrt{2}/6\simeq 0.7405$) and would therefore correspond to an unphysical fluid (or even solid) phase since hard spheres cannot completely fill space without overlapping. In this paper we apply the real space version of the MWDA [6] to a fcc hard-sphere solid and determine the branches of solutions for the effective liquid density. We investigate low and high density solids, finding important qualitative differences.

Adopting the Percus-Yevick (PY) approximation to describe the fluid phase and parametrizing the local density of the solid as a sum of identical normalized Gaussians centered around the lattice sites, the effective liquid density $\hat{\eta}$ in the real space version of the MWDA [6] is given, by inserting Eq. (3) in Eq. (1), by one of the solutions of the equation

$$\frac{2\hat{\eta}\{(1-\hat{\eta})^2+3\}}{(1-\hat{\eta})^3}=\frac{1}{(1-\hat{\eta})^4}\left[(1+2\hat{\eta})^2S_0-\frac{3}{2}\hat{\eta}(2+\hat{\eta})^2S_1+\frac{1}{2}\hat{\eta}(1+2\hat{\eta})^2S_3-\eta\hat{\eta}\{(1-\hat{\eta})^2+9\}\right], \tag{4}$$

where $\eta=\pi\rho\sigma^3/6$, with ρ the average density of the solid, and $(n=0,1,3)$

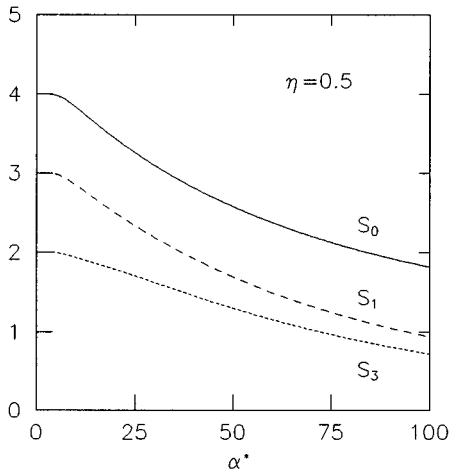

FIG. 1. S_0 (continuous line), S_1 (dashed line), and S_3 (dotted line) [see Eq. (5)] vs the localization parameter α^* for a fcc hard-sphere solid of packing fraction $\eta=0.5$.

$$S_n \equiv S_n(\alpha^*,\eta)=\left(\frac{\alpha^*}{2\pi}\right)^{1/2}\sum_j \frac{1}{x_j}\int_0^1 dx\; x^{n+1} \times[e^{-\alpha^*(x-x_j)^2/2}-e^{-\alpha^*(x+x_j)^2/2}]. \tag{5}$$

In Eq. (5) $\alpha^*=\alpha\sigma^2$ is the localization or order parameter, α being the inverse width of the Gaussians, the sum runs over the Bravais lattice vectors $\{\mathbf{r}_j\}$, and $x_j \equiv x_j(\eta)=|\mathbf{r}_j|/\sigma$ [7]. As the integrals in Eq. (5) can be performed analytically, the determination of S_0, S_1, and S_3, for fixed η and α^*, reduces to the evaluation of three lattice sums. We have found that, for a fcc crystal, converged sums with a relative error smaller than 10^{-8} are obtained for $\alpha^*\geqslant 0.1$ and $0.1\leqslant\eta\leqslant 0.73$ with 300 lattice shells.

Note moreover that, when $\hat{\eta}\neq 1$, Eq. (4) can be further reduced to a quartic equation $\hat{\eta}^4+a_3\hat{\eta}^3+a_2\hat{\eta}^2+a_1\hat{\eta}+a_0=0$ with real coefficients $a_0=S_0/2$, $a_1=-4-5\eta+2S_0-3S_1+S_3/4$, $a_2=6+\eta+2S_0-3S_1+S_3$, and $a_3=-3-\eta/2-3S_1/4+S_3$. Here we consider the real roots of this quartic equation for two representative cases: $\eta=0.5$, corresponding to the low density region already discussed in [2], and $\eta=0.7$, i.e., to an average solid density near close packing [6,8]. The former case corresponds to a metastable solid near the first-order fluid-solid transition whereas the latter is a representative example of a high density solid.

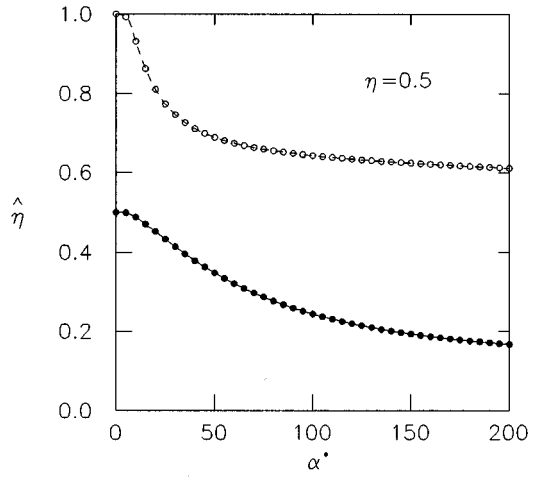

FIG. 2. Upper and lower branches of Eq. (4) vs the localization parameter α^* for a fcc hard-sphere solid of packing fraction $\eta=0.5$.

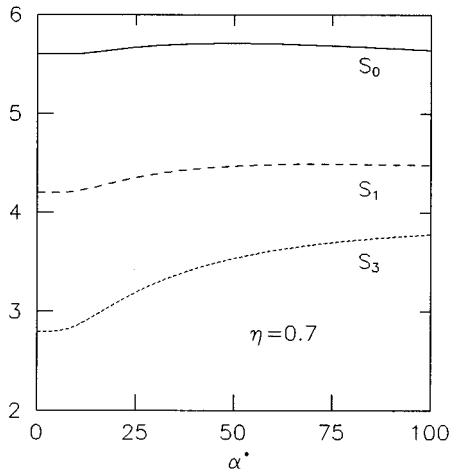

FIG. 3. S_0 (continuous line), S_1 (dashed line), and S_3 (dotted line) [see Eq. (5)] for localization parameters $0.1\leqslant\alpha^*\leqslant 100$ for a fcc hard-sphere solid of packing fraction $\eta=0.7$.

In Fig. 1 we represent S_0, S_1, and S_3 for a fcc hard-sphere solid of packing fraction $\eta=0.5$ for $0.1\leqslant\alpha^*\leqslant 100$. It is seen that the curves are smooth functions of α^* which increase when decreasing the localization parameter and reach in the uniform fluid limit, $\alpha^*\to 0$, plateaus given by

$$S_0\to 8\eta, \quad S_1\to 6\eta, \quad S_3\to 4\eta \quad (\alpha^*\to 0). \tag{6}$$

Within this range of localization parameters the quartic equation has two real roots which are plotted in Fig. 2. Both the upper and lower branches are decreasing functions of α^* approaching, as $\alpha^*\to 0$, to $\hat{\eta}\to 1$ and $\hat{\eta}\to\eta$, respectively. The overall picture encountered in this case is therefore the same as in Fig. 1 in the paper by Kyrlidis and Brown. Note,

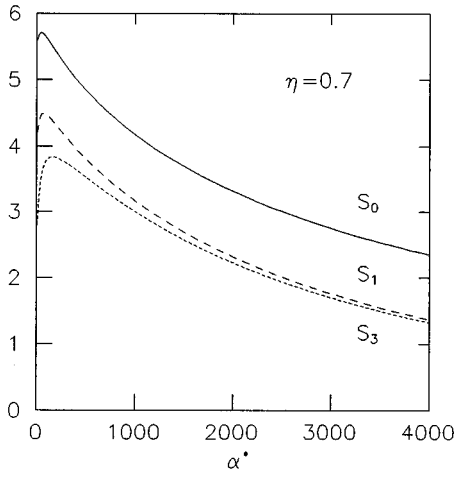

FIG. 4. S_0 (continuous line), S_1 (dashed line), and S_3 (dotted line) [see (5)] for localization parameters $0.1\leqslant\alpha^*\leqslant 4000$ for a fcc hard-sphere solid of packing fraction $\eta=0.7$.

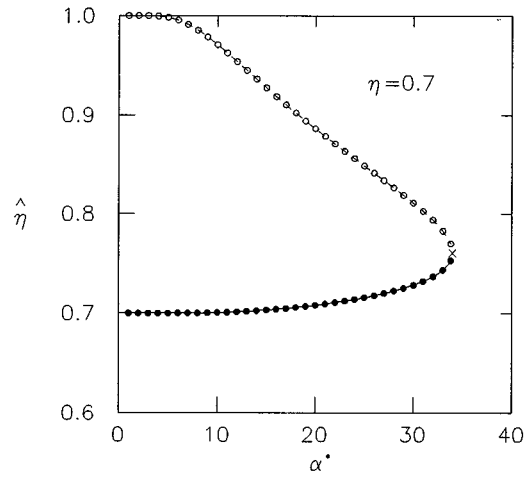

FIG. 5. Small-α^* branches of Eq. (4) vs the localization parameter α^* for a fcc hard-sphere solid of packing fraction $\eta=0.7$. The cross denotes the location of the double real root: $\alpha^*=33.985$ $\hat{\eta}=0.761$.

however, that, as $\hat{\eta}\to 1$, we have to be careful with the singularity of the PY approximation and take instead the uniform fluid limit (6) in Eq. (4) to find

$$\frac{2\hat{\eta}\{(1-\hat{\eta})^2+3\}}{(1-\hat{\eta})^3}=\frac{1}{(1-\hat{\eta})^4}[2\eta\{(1-\hat{\eta})^2+3\}(1-\hat{\eta})] \qquad (\alpha^*\to 0), \quad (7)$$

with a unique real root $\hat{\eta}=\eta$. This condition is an essential constraint of the MWDA [2], required by the normalization of the weight function and pointed out by Likos and Ashcroft [5], which leads to a unique identification of the two branches of solutions of the MWDA. With this identification, the lower branch yields a minimum of the solid free energy at $\alpha^*_{\min}=72.5$ corresponding to an effective liquid packing fraction $\hat{\eta}=0.291$ [6].

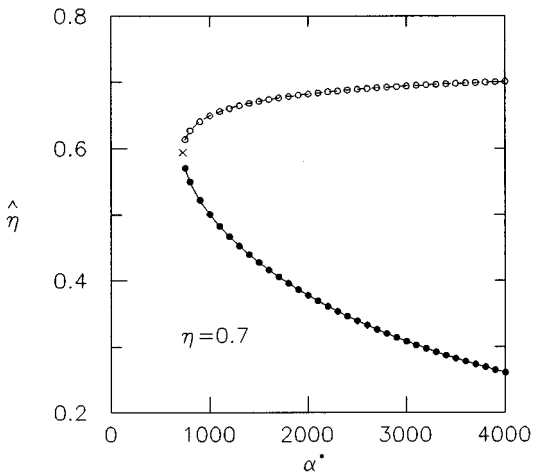

FIG. 6. Large-α^* branches of Eq. (4) vs the localization parameter α^* for a fcc hard-sphere solid of packing fraction $\eta=0.7$. The cross denotes the location of the double real root: $\alpha^*=727.69$, $\hat{\eta}=0.594$.

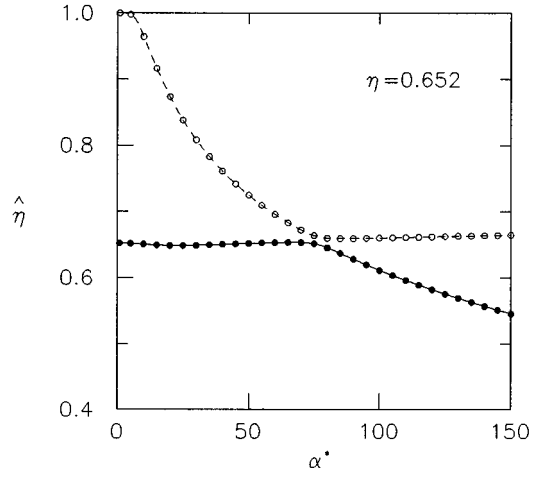

FIG. 7. Upper and lower branches of Eq. (4) vs the localization parameter α^* for a fcc hard-sphere solid of packing fraction $\eta=0.652$.

In Figs. 3 and 4 we represent S_0, S_1, and S_3 for a fcc hard-sphere solid of packing fraction $\eta=0.7$ for $0.1\leqslant\alpha^*\leqslant 4000$. Note that the curves are again smooth functions of the order parameter approaching the limit (6) for small-α^* values (Fig. 3). By increasing α^* the curves first increase, then reach a maximum to finally decrease at very large localizations (Fig. 4). The real roots of the quartic equation are shown in Figs. 5 and 6. For small-α^* values there are two branches which converge, as $\alpha^*\to 0$, to $\hat{\eta}\to 1$ and $\hat{\eta}\to 0.7$, respectively (Fig. 5). As explained above, the upper branch must be discarded by taking proper account of the uniform fluid limit (7). An important difference with respect to the low density case is that now the lower branch increases with α^*, the upper and lower branches approaching each other when increasing localization. At $\alpha^*=33.985$ the quartic equation has a double real root $\hat{\eta}=0.761$ and for larger localizations the roots are all imaginary.

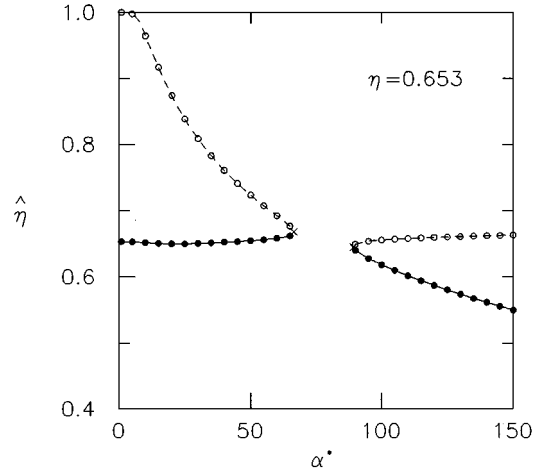

FIG. 8. Small-α^* and large-α^* branches of Eq. (4) vs the localization parameter α^* for a fcc hard-sphere solid of packing fraction $\eta=0.653$. The crosses denote the double real roots located at $\alpha^*=66.451$, $\hat{\eta}=0.668$ and $\alpha^*=89.131$, $\hat{\eta}=0.645$.

This scenario changes at $\alpha^*=727.69$ where the quartic equation has a new double real root $\hat{\eta}=0.594$ (Fig. 6). Two large-α^* branches develop from this point: the upper branch is an increasing function of α^* while the lower branch decreases with localization of the hard spheres. This large-α^* lower branch has been considered in the literature [6,8] to represent the solution of the MWDA for high density hard-sphere solids, probably because in these studies this branch was assumed to verify all the requirements of the MWDA. From Fig. 6 it is readily seen that the uniform fluid limit does not exist for this branch and therefore it cannot be considered as a solution of the MWDA. Note that the nonexistence of solutions for $\hat{\eta}$ in the MWDA cannot be ascribed to the PY approximation. For instance, adopting the same approximation for the fluid phase in the GELA, the unique branch of solutions is a continuous function of α^* satisfying the uniform fluid limit for low and high density solids.

We expect the gap between the double real roots of the small-α^* and large-α^* branches to be narrowed as the average density of the solid decreases, indicating the existence of a density threshold above which the MWDA is unable to predict hard-sphere solids. This density threshold is located in the range $0.652<\eta<0.653$ as it can be inferred from Figs. 7 and 8.

In summary, we have determined the branches of solutions for the effective liquid density of a fcc hard-sphere solid in the real space version of the MWDA. These branches are the real roots of a quartic equation with real coefficients which are smooth functions of the order parameter. For low density solids we have shown that there is a unique branch of solutions satisfying the uniform fluid limit, as required by the MWDA. Since the original paper of Denton and Ashcroft this branch has been known to produce stable or metastable hard-sphere solids with respect to the hard-sphere fluid and to provide an accurate description of the hard-sphere fluid-solid transition. For high density solids the existence of a range of order parameters with no real roots of the quartic equation indicates that, above a threshold average density of the solid, there is no decreasing branch of solutions satisfying the uniform fluid limit. Our conclusion is therefore that the MWDA is unable to predict high density hard-sphere crystals.

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[7] The great advantage of the Gaussian parametrization is that the ideal and excess free energies per particle become ordinary functions of the order parameter α^*, i.e., $f[\rho]\equiv f(\alpha^*,\eta)=f_{\rm id}(\alpha^*,\eta)+f_{\rm ex}(\hat{\eta}(\eta,\alpha^*))$. The value of α^* describing the equilibrium solid is then obtained by minimizing, for fixed η, $f(\alpha^*,\eta)$ with respect to the localization parameter. Note that, in order to stabilize the solid (i.e., to find a minimum of the free energy) $f_{\rm ex}(\hat{\eta}(\alpha^*,\eta))$ has to be a decreasing function of the order parameter, since $f_{\rm id}(\alpha^*,\eta)$ increases monotonically with α^*; that is, stable solids can only be found whenever the effective liquid density $\hat{\eta}$ decreases with α^*.

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