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Modified weighted density approximation for binary hard-sphere solid mixtures

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The modified weighted density approximation is investigated in order to determine the thermodynamics of the ordered CsCl and NaCl structures. Our results indicate that one of the essential assumptions of the theory, namely, the uniform fluid limit, is not well defined for mixtures. [S1063-651X(98)11810-X]

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In recent years the modified weighted density approximation (MWDA) of Denton and Ashcroft [1] has been applied to the study of two apparently unrelated problems: the analysis of the uniqueness of its solutions [2,3] and the determination of the thermodynamic properties of high-density solids [4,5]. In the MWDA the excess free energy of a hard-sphere solid is mapped onto that of a hard-sphere fluid evaluated at an effective liquid density. This effective liquid density is obtained as the solution of a nonlinear equation, which in the original paper of Denton and Ashcroft was assumed to be unique. Although the multiplicity of solutions for the effective liquid density in the MWDA was pointed out by Kyrlidis and Brown [2], Likos and Ashcroft [3] showed that the correct application of the uniform fluid limit yields a unique solution for the effective liquid density for low-density solids. Very recently [6], however, it has been shown that the MWDA is unable to predict the existence of high-density solids in the case of a fcc hard-sphere crystal. In this paper we extend the latter investigation to two binary hard-sphere solid mixtures already studied within the MWDA in [7].

We consider a binary mixture of N_1 small hard spheres of diameter σ_1 and N_2 large hard spheres of diameter σ_2 in a volume V at temperature T. For average densities $\rho_1 = N_1/V$ and $\rho_2 = N_2/V$, the binary mixture can be characterized by three quantities: the concentration of the large spheres $x \equiv \rho_2/\rho$ $(\rho = \rho_1 + \rho_2)$, the hard-sphere diameter ratio $\alpha \equiv \sigma_1/\sigma_2 \leqslant 1$, and the packing fraction η (the fraction of volume occupied by the spheres) $\eta = \pi(\rho_1\sigma_1^3 + \rho_2\sigma_2^3)/6$.

The Helmholtz free energy of the binary hard-sphere solid mixture $F[\rho_1,\rho_2]$ is a functional (denoted by square brackets) of the local densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ $[\int d\mathbf{r}\rho_i(\mathbf{r}) = N_i,\ i=1,2]$ that may be split into ideal $F_{\rm id}[\rho_1,\rho_2]$ and excess $F_{\rm ex}[\rho_1,\rho_2]$ contributions. The functional dependence of the ideal part is exactly known, i.e.,

$$\beta F_{\rm id}[\rho_1,\rho_2] = \sum_{i=1}^{2} \int d\mathbf{r}\rho_i(\mathbf{r})\{\ln[\rho_i(\mathbf{r})\Lambda_i^3] - 1\}, \tag{1}$$

where $\beta = 1/k_BT$, k_B denoting Boltzmann's constant, and Λ_i is the thermal de Broglie wavelength of the component i, whereas the excess free energy can be formally written as

$$\beta F_{\rm ex}[\rho_1,\rho_2] = -\sum_{i=1}^{2}\sum_{j=1}^{2}\int d\mathbf{r}\rho_i(\mathbf{r})\int d\mathbf{r}'\rho_j(\mathbf{r}') \times \int_0^1 d\lambda(1-\lambda)c_{ij}(\mathbf{r},\mathbf{r}';[\lambda\rho_1,\lambda\rho_2]), \tag{2}$$

where

$$c_{ij}(\mathbf{r},\mathbf{r}';[\rho_1,\rho_2]) = -\frac{\delta^2\beta F_{\rm ex}[\rho_1,\rho_2]}{\delta\rho_i(\mathbf{r})\,\delta\rho_j(\mathbf{r}')} \tag{3}$$

are the direct correlation functions. The density functional theory of freezing states that $F[\rho_1,\rho_2]$ is minimized (at constant average density) by the equilibrium densities, but since the direct correlation functions are unknown for nonuniform fluids, some approximations are required for the evaluation of $\beta F_{\rm ex}[\rho_1,\rho_2]$.

The following recipes are considered in the MWDA of Denton and Ashcroft (see [7] for details). First, the excess free energy of the binary hard-sphere solid mixture is mapped onto that of some effective binary hard-sphere fluid mixture, i.e.,

$$\beta F_{\rm ex}^{\rm MWDA}[\rho_1,\rho_2] = N[(1-x)\psi(\hat{\rho}_1,x) + x\psi(\hat{\rho}_2,x)], \tag{4}$$

where $N = N_1 + N_2$ and $\psi(\rho,x) = \beta f_{\rm ex}(\rho,x)$, with $f_{\rm ex}(\rho,x)$ denoting the excess free energy per particle of the hard-sphere fluid mixture of density ρ and concentration x. This ''thermodynamic mapping'' defines the weighted densities $\hat{\rho}_1 \equiv \hat{\rho}_1[\rho_1,\rho_2]$ and $\hat{\rho}_2 \equiv \hat{\rho}_2[\rho_1,\rho_2]$, which are postulated to be bilinear weighted averages of the local densities, i.e.,

$$\hat{\rho}_i = \frac{1}{N_i}\sum_{j=1}^{2}\int d\mathbf{r}\rho_i(\mathbf{r})\int d\mathbf{r}'\rho_j(\mathbf{r}')w_{ij}(|\mathbf{r}-\mathbf{r}'|;\hat{\rho}_i,x), \tag{5}$$

where $w_{ij}(|\mathbf{r}-\mathbf{r}'|;\hat{\rho}_i,x)$ are weight functions normalized according to

$$\int d\mathbf{r}w_{ij}(r;\hat{\rho}_i,x) = 1. \tag{6}$$

These normalization conditions ensure that in the limit of a uniform mixture $[\rho_1(\mathbf{r}) \to \rho_1,\ \rho_2(\mathbf{r}) \to \rho_2]$, $\hat{\rho}_1 \to \rho$, $\hat{\rho}_2 \to \rho$, and therefore $f_{\mathrm{ex}}^{\mathrm{MWDA}}[\rho_1,\rho_2]\rightarrow f_{\mathrm{ex}}(\rho,x)$, i.e., the excess free energy per particle of the binary hard-sphere solid mixture $f_{\mathrm{ex}}^{\mathrm{MWDA}}[\rho_1,\rho_2]$ reduces to that of a uniform mixture of density ρ and concentration x.

In a second step, the MWDA establishes a unique specification of the weight functions by requiring that Eq. (4) exactly satisfies Eq. (3) in the uniform limit

$$\lim_{\rho_1(\mathbf{r})\rightarrow\rho_1}\ \lim_{\rho_2(\mathbf{r})\rightarrow\rho_2}\left[-\frac{\delta^2\beta F_{\mathrm{ex}}^{\mathrm{MWDA}}[\rho_1,\rho_2]}{\delta\rho_i(\mathbf{r})\,\delta\rho_j(\mathbf{r}')}\right]
=c_{ij}(|\mathbf{r}-\mathbf{r}'|;\rho_1,\rho_2), \tag{7}$$

where $c_{ij}(r,\rho_1,\rho_2)$ are the direct correlation functions of a binary hard-sphere fluid mixture, which are assumed to be known. These functional derivatives yield analytic expressions for the weight functions in terms of the direct correlation functions and the excess free energy of the binary hard-sphere fluid mixture, which have been approximated here using Lebowitz's solution of the Percus-Yevick equation [8]. Substitution of the weight functions obtained from Eq. (7) into Eq. (5) leads to two uncoupled equations for the determination of $\hat{\rho}_1$ and $\hat{\rho}_2$, which are functionals of the local densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$. The complicated functional dependence can be simplified by assuming that, in the case of ordered structures, the local densities can be parametrized as a sum of identical normalized Gaussians centered around the lattice sites of each sublattice with inverse Gaussian width parameters γ_i $(i=1,2)$. With the parametrizations the weighted densities become ordinary functions of γ_1 and γ_2. By fixing ρ, x, and α, the equilibrium solid is found by minimizing the variational solid free energy with respect to γ_1 and γ_2, once the crystal structure is specified. In this paper we have considered the cesium chloride (CsCl) and the sodium chloride (NaCl) structures.

It can be readily shown that the equations determining the weighted densities are quartic equations in $\hat{\eta}_1=\pi\hat{\rho}_1\sigma_1^3/6$ and $\hat{\eta}_2=\pi\hat{\rho}_2\sigma_2^3/6$ with real coefficients that are smooth functions of the Gaussian width parameters. Given a pair (γ_1,γ_2), each quartic equation has either two real roots $\hat{\eta}_i'$ and $\hat{\eta}_i''$ $(\hat{\eta}_i'<\hat{\eta}_i'',\ i=1,2)$ or no real roots, the number of real roots depending on the specific values of ρ, x, and α. In the former case only the lower branches $\hat{\eta}_1'$ and $\hat{\eta}_2'$ satisfy the uniform fluid limit

$$\hat{\eta}_1'\rightarrow\frac{2\alpha^3}{1+\alpha^3}\,\eta,\quad \hat{\eta}_2'\rightarrow\frac{2}{1+\alpha^3}\,\eta\quad(\gamma_1\rightarrow0,\quad\gamma_2\rightarrow0) \tag{8}$$

and these are the branches to be used for finding the minimum of the variational solid free energy. When this minimum exists, $(\gamma_1^{\mathrm{min}},\gamma_2^{\mathrm{min}})$, and it can be connected with the origin $(\gamma_1=\gamma_2=0)$ in the (γ_1,γ_2) plane by a continuous path of points for which both lower branches exist, then the MWDA predicts a mechanically stable solid. When that requirement is not fulfilled, the existence of a minimum of the variational solid free energy is not a sufficient condition for finding mechanically stable solids within the MWDA since the uniform fluid limit is not satisfied. Once a mechanically stable solid is found, the exchange of stability between the solid and the Percus-Yevick fluid [8] is obtained when both phases have the same Helmholtz free energy.

We first consider $\alpha=1$, in which case the CsCl and NaCl structures are simple bcc and sc crystals, respectively. For these symmetrical structures $\gamma_1=\gamma_2$ and $\hat{\eta}_1=\hat{\eta}_2$. In Figs. 1 and 2 we plot in the (γ_1^*,γ_2^*) plane $(\gamma_i^*=\gamma_i\sigma_2^2)$ the regions (denoted by dashed zones) where the lower branches $\hat{\eta}_1'$ and $\hat{\eta}_2'$ exist for a bcc crystal at packing fractions $\eta=0.638$ and $\eta=0.639$. The former case is the upper low-density solid for which the minimum of the variational solid free energy (at $\gamma_1^*=\gamma_2^*=1436$) can be connected with the origin through

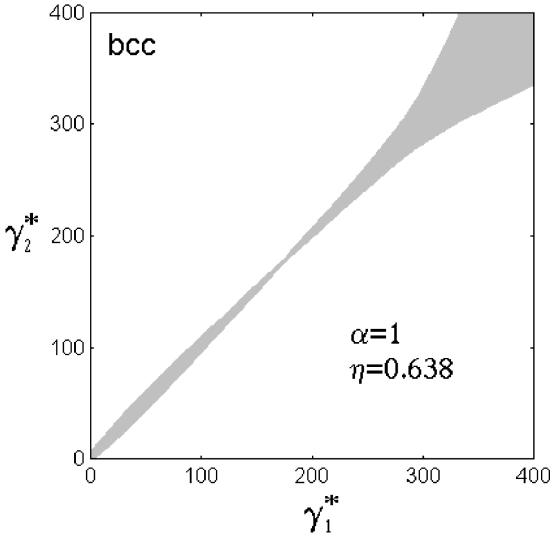

FIG. 1. Region of the (γ_1^*,γ_2^*) plane where the lower branches $\hat{\eta}_1'$ and $\hat{\eta}_2'$ exist (denoted by a dashed zone) for a bcc crystal at $\eta=0.638$. The minimum of the variational solid free energy is at $\gamma_1^*=\gamma_2^*=1436$ (not shown in the figure). Note that only the points on the diagonal represent a physical situation when $\alpha=1$.

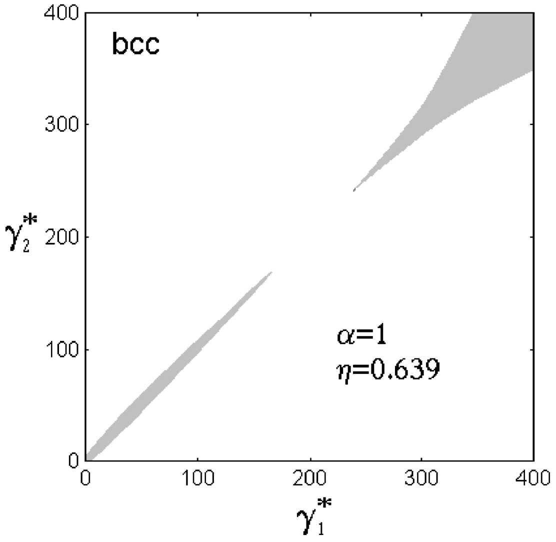

FIG. 2. Regions of the (γ_1^*,γ_2^*) plane where the lower branches $\hat{\eta}_1'$ and $\hat{\eta}_2'$ exist (denoted by dashed zones) for a bcc crystal at $\eta=0.639$. The minimum of the variational solid free energy is at $\gamma_1^*=\gamma_2^*=1513$ (not shown in the figure). Note that only the points on the diagonal represent a physical situation when $\alpha=1$.

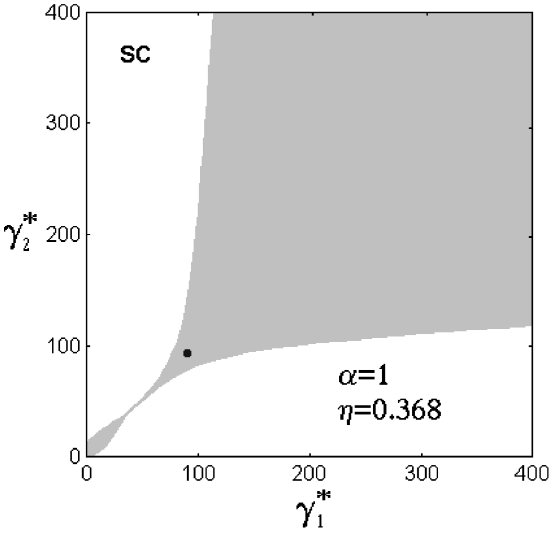

FIG. 3. Same as in Fig. 1 for a sc crystal at $\eta=0.368$. The minimum of the variational solid free energy, denoted by a full dot, is at $\gamma_1^*=\gamma_2^*=99.1$.

the dashed zone by a continuous path of points (the diagonal). This is an example of a mechanically stable solid satisfying the uniform fluid limit. In the latter case, however, the minimum (at $\gamma_1^*=\gamma_2^*=1513$) cannot be connected with the origin by the diagonal since there is a region with no solutions between $171.1\leqslant\gamma_1^*=\gamma_2^*\leqslant 241.4$. Figures 3 and 4 are the same as Figs. 1 and 2 for a sc crystal for packing fractions $\eta=0.368$ and $\eta=0.369$, the minimum of the variational free energy being located at $\gamma_1^*=\gamma_2^*=99.1$ and $\gamma_1^*=\gamma_2^*=102.0$, respectively. The region of nonexistence of solutions at $\eta=0.639$ is found in the range $48.9\leqslant\gamma_1^*=\gamma_2^*\leqslant 59.1$. These results indicate that for both crystals there is a density threshold above which the MWDA in unable to predict mechanically stable solids, a result similar to the one already found for the fcc crystal in [6].

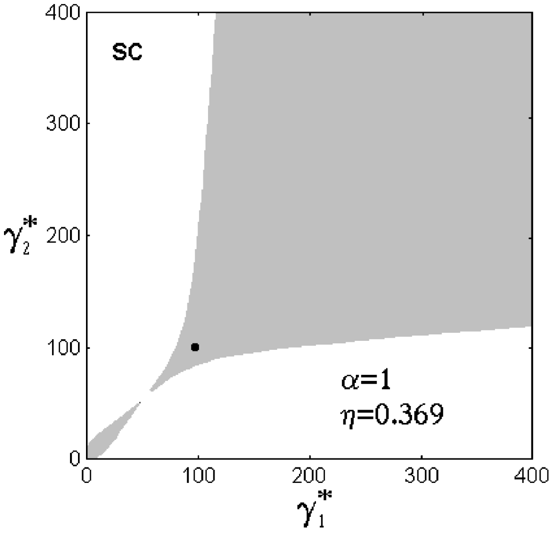

FIG. 4. Same as in Fig. 2 for a sc crystal at $\eta=0.369$. The minimum of the variational solid free energy, denoted by a full dot, is at $\gamma_1^*=\gamma_2^*=102.0$.

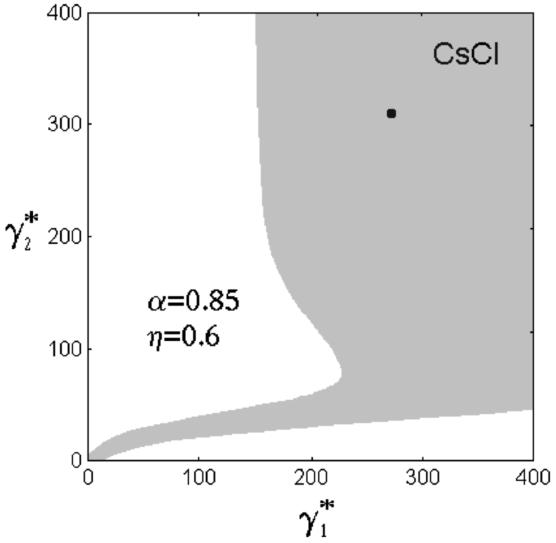

FIG. 5. Region of the (γ_1^*,γ_2^*) plane where the lower branches $\hat{\eta}_1'$ and $\hat{\eta}_2'$ exist (denoted by a dashed zone) for a CsCl structure at $\alpha=0.85$ and $\eta=0.6$. The minimum of the variational solid free energy, denoted by a full dot, is at $\gamma_1^*=276.5$, $\gamma_2^*=312.7$

Note that for the symmetrical structures (bcc and sc), starting from a point on the diagonal, $\gamma_1^{\min}=\gamma_2^{\min}$, the uniform fluid limit is uniquely defined because the only (physical) continuous path connecting that point with the origin is precisely the diagonal. In Fig. 5 we plot the region (denoted by a dashed zone) of solutions for the lower branches $\hat{\eta}_1'$ and $\hat{\eta}_2'$ for the CsCl structure at $\alpha=0.85$ and $\eta=0.6$. In this case the minimum of the variational solid free energy is at $\gamma_1^*=276.5$, $\gamma_2^*=312.7$. Clearly, this point can be connected with the origin by a continuous (somewhat artificial) path through the dashed zone, indicating in principle the existence of a mechanically stable solid within the MWDA. Lowering α, the dashed zone becomes increasingly deformed, as can be seen in Fig. 6 for the same structure at $\alpha=0.8$ and $\eta=0.6$, the minimum being now located at $\gamma_1^*=242.4$, $\gamma_2^*=359.7$ (compare the scales in Figs. 5 and 6). The main conclusion that can be inferred from these examples is that

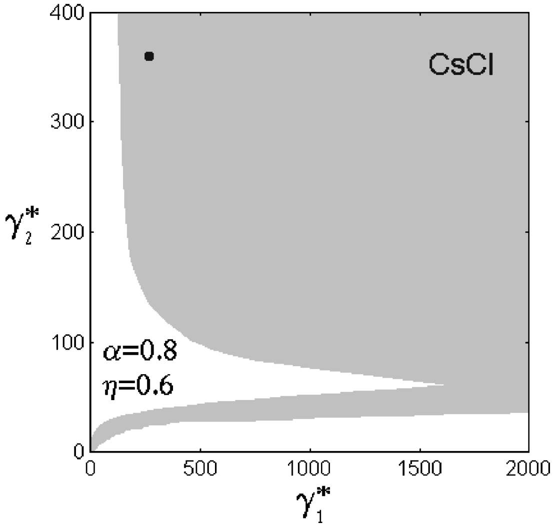

FIG. 6. Same as in Fig. 5 at $\alpha=0.8$ and $\eta=0.6$. The minimum of the variational solid free energy, denoted by a full dot, is at $\gamma_1^*=242.4$, $\gamma_2^*=359.7$. Note the different scales in Figs. 5 and 6.

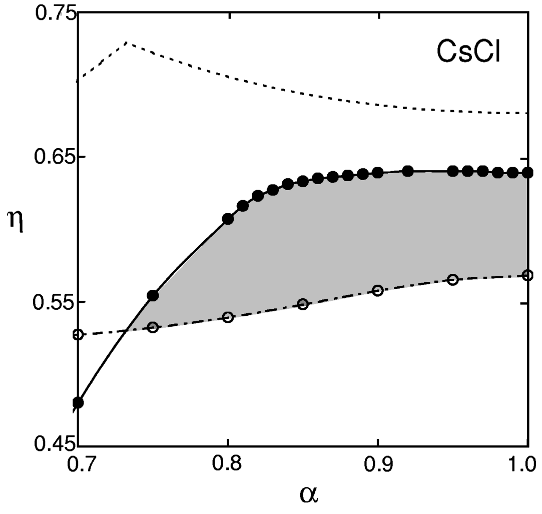

FIG. 7. Curves in the (α,η) plane of the breakdown of the existence of solutions for the lower branches $\hat{\eta}'_1$ and $\hat{\eta}'_2$ (full dots), exchange of stability with respect to the fluid (open dots), and close packing (dotted line) for the CsCl structure. The continuous and dashed curves are guides to the eye. The dashed zone satisfies the uniform fluid limit and the stability condition.

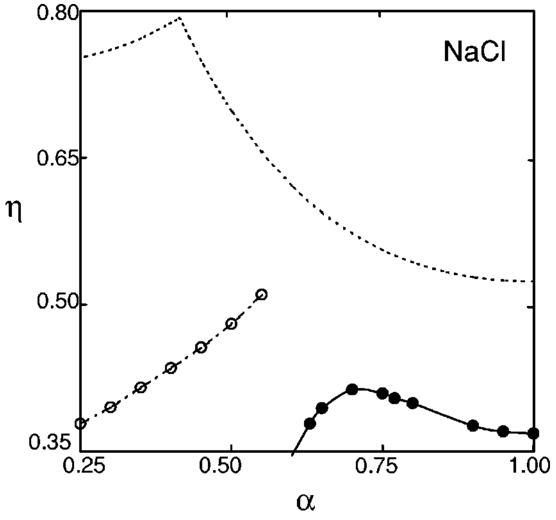

FIG. 8. Same as in Fig. 7 for the NaCl structure. Note that there is no region satisfying the uniform fluid limit and the stability condition.

the uniform fluid limit (7) is not well defined for mixtures since the way that has to be taken strongly depends on α. Nevertheless, by assuming that the uniform fluid limit exists whenever a continuous path connecting the minimum with the origin can be found, in Figs. 7 and 8 we plot in the (α,η) plane by a continuous line the breakdown curve of the existence of solutions for the lower branches $\hat{\eta}'_1$ and $\hat{\eta}'_2$, by a dashed line the curve of the exchange of the stability between the crystal structure and the fluid phase, and by a dotted line the close packing curve. It is seen that while for the CsCl structure there is a small region satisfying the uniform fluid limit (below the continuous line) and the stability condition (above the dashed line), this region does not exist for the NaCl structure.

In conclusion, we have shown that the uniform fluid limit is not well defined for binary hard-sphere mixtures within the MWDA. By assuming that this limit can be redefined in a very special way, which strongly depends on the hard-sphere diameter ratio, we have also found that the MWDA is unable to predict any stable NaCl structure with respect to the fluid phase.

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