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LETTER TO THE EDITOR

Freezing of very asymmetric binary hard-sphere mixtures

Hong Xu† and Catherine Barentin‡

† Département de Physique des Matériaux (URA 172 du CNRS), Université Claude Bernard-Lyon 1, 69622 Villeurbanne Cedex, France

‡ Ecole Normale Supérieure de Lyon, 69364 Lyon Cedex 07, France

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Abstract. The freezing behaviour of a binary hard-sphere mixture with diameter ratio 0.1 is studied within the formalism of the density functional theory (DFT). The stability of a ‘sublattice-melt’ (SLM) phase, wherein the large spheres are localized on crystal lattice sites and the small ones are fluid-like, is examined. The non-uniform one-particle densities of the small and large spheres in the SLM phase have been calculated. The fluid–solid phase diagram has been drawn.

The purpose of the present work is to study the freezing behaviour of very asymmetric binary hard-sphere mixtures. By ‘very asymmetric’ we mean that one species of hard spheres has a diameter much larger than the other species. Despite active investigations of binary hard-sphere mixtures in recent years [1–3], the phase diagrams of very asymmetric mixtures are not yet well understood. Those mixtures are nonetheless interesting since they can in a first approximation modelize dense colloidal systems. Furthermore, it has recently been predicted [4] that when such mixtures are very rich in small spheres, they will phase separate into two coexisting pure fluids. We propose here to study the crystallization of an asymmetric mixture over the whole range of concentration of the small spheres in order first to draw the phase diagram and second to locate the freezing transition with respect to the fluid phase separation. Another interesting aspect is the solid phase itself which is formed by such a mixture. Because of the large size difference among the two species one expects it to be a ‘sublattice-melt’ (SLM) phase in which the large spheres are localized on lattice sites and the small ones can move freely through the space left by the larger ones. This phase is reminiscent of the superionic conductors. It has also been found in asymmetric binary hard-sphere mixtures by a simulation study [5] and some previous DFT work [6, 7]. But in [5] and [6] the question of its possible metastability with respect to the pure crystal formed by the large-sphere (denoted here S_2) phase was not examined, whereas in [7], for a fluid of concentration 0.5, the coexisting SLM phase has been found to be metastable compared with the S_2 phase. However, in [6] and [7] the one-particle density of the smaller species in SLM was assumed to be uniform in the whole space. This was somewhat unphysical because the localization of the large spheres excludes some regions to the smaller ones. In the present work we shall remove such an assumption and thus expect to give a better description of the SLM phase. First we shall examine the stability of the SLM phase by calculating its free energy. Then we study the fluid–solid coexistence as a function of the reduced pressure P/T , by considering both of the solid phases i.e. the SLM and S_2 .

The theoretical framework here is the modified weighted density approximation (MWDA) proposed by Denton and Ashcroft [7], which is easy to implement and has been shown

to give good results for the freezing of one-component hard spheres [8] and for binary mixtures with various diameter ratios [7]. We therefore refer readers to [7] for technical details. We consider a binary mixture formed of N_1 small spheres and N_2 large spheres in a volume V . The diameter ratio is $\alpha = \sigma_1/\sigma_2 (< 1)$. The concentration of large spheres $x = N_2/(N_1 + N_2)$. At given T , the free energy F is a functional of the spatial densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$. Whereas the ideal-gas part of the free energy functional can be exactly expressed in terms of the densities, the excess part has to be approximated. In MWDA, for a binary mixture, F_{ex} per particle is assumed to be given by that of two homogeneous systems having the same concentration but different uniform densities [7]:

$$F_{\text{ex}}^{\text{MWDA}} = N_1 f_0(\hat{\rho}_{(1)}, x) + N_2 f_0(\hat{\rho}_{(2)}, x) \quad (1)$$

where f_0 is the excess free energy per particle of the uniform phase, and the uniform densities $\hat{\rho}_{(1)}$ and $\hat{\rho}_{(2)}$ are related to the actual non-uniform densities through some weighting functions:

$$\hat{\rho}_{(i)} = \frac{1}{N_i} \sum_{j=1,2} \int d\mathbf{r} \int d\mathbf{r}' \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') \omega_{ij}(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}_{(i)}, x) \quad i = 1, 2. \quad (2)$$

The normalized weighting functions w_{ij} ($ij = 11, 22$ and 12) are determined by the following self-consistency criterion:

$$\lim_{\rho_i(\mathbf{r}) \rightarrow \rho_i} \beta \frac{\delta^2 F_{\text{ex}}^{\text{MWDA}}[\rho_1, \rho_2]}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}')} = -c_{ij}^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_1, \rho_2) \quad (3)$$

where on the right hand side $c_{ij}^{(2)}$ are the direct correlation functions of the uniform fluid (supposed to be known). Here they shall be the analytic ones given by the Percus-Yevich theory [9], which are expected to predict correctly the liquid structure for moderate concentrations of small spheres ($x > 0.2$) [10].

We fix $\alpha \equiv \sigma_1/\sigma_2 = 0.1$. The main solid phase we are interested in is the ‘sublattice-melt’ (SLM) structure, in which the large spheres form a faced-centred cubic (FCC) lattice and the small ones remain fluid-like in the lattice. We assume a Gaussian-sum representation of the density of large particles:

$$\rho_2^{(\text{SLM})}(\mathbf{r}) = \left(\frac{\gamma}{\pi}\right)^{3/2} \sum_{\mathbf{r}_i} \exp(-\gamma(\mathbf{r} - \mathbf{r}_i)^2) \quad (4)$$

where $\{\mathbf{r}_i\}$ are the FCC lattice sites. Since the smaller ones are fluid-like, we could in a first approximation assume $\rho_1(\mathbf{r})$ to be uniform, as in previous DFT studies of the SLM phase [6, 7]. But a more realistic assumption is to allow it to be modulated by $\rho_2(\mathbf{r})$. We thus expand $\rho_1(\mathbf{r})$ in the reciprocal lattice of the FCC lattice:

$$\rho_1^{(\text{SLM})}(\mathbf{r}) = \rho_1 \left(1 + \sum_{\mathbf{G} \neq 0} \nu_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}\right) \quad (5)$$

where $\{\mathbf{G}\}$ are the reciprocal lattice sites and $\{\nu_{\mathbf{G}}\}$ are the Fourier coefficients. From the fundamental theorem of the DFT [11], the parameters γ and $\{\nu_{\mathbf{G}}\}$ should minimize $F[\rho_1, \rho_2]$ at given T , x and $\rho = N/V$. If we assume $|\nu_{\mathbf{G}}| \ll 1$, we can make a Taylor expansion of $F[\rho_1, \rho_2]$ around $\{\nu_{\mathbf{G}} = 0\}$. The minimization of $F[\rho_1, \rho_2]$ with respect to $\{\nu_{\mathbf{G}}\}$ gives, to the first order of $\{\nu_{\mathbf{G}}\}$ and within the MWDA, the following relation between $\{\nu_{\mathbf{G}}\}$ to γ :

$$\nu_{\mathbf{G}} = \frac{1}{2} \exp\left(-\frac{G^2}{4\gamma}\right) \rho_2 \{c_{12}(\mathbf{G}; \rho, x) + c_{12}(\mathbf{G}; \hat{\rho}, x) A(\gamma, \hat{\rho}, x)\} \quad (6)$$

where

$$A(\gamma, \hat{\rho}, x) = \left\{ 1 - \frac{1}{N_2} \int dr \int dr' \rho_2(r) \rho_2(r') \frac{\partial w_{22}(|r-r'|; \hat{\rho}, x)}{\partial \hat{\rho}} \right\}^{-1}. \quad (7)$$

The function $c_{12}(G)$ in (7) is the Fourier transform of $c_{12}(r)$ and $\hat{\rho}(\gamma)$ is the weighted uniform density for an SLM phase with the 'zeroth order approximation', i.e. $\rho_1(r) = \rho_1$ and $\rho_2(r)$ given by (4).

Another solid phase we studied was an FCC lattice formed solely by the large spheres (the S_2 phase). In this phase, we have $\rho_1^{(S_2)}(r) = 0$ and $\rho_2^{(S_2)}(r) = \sum_{r_i} \exp(-\gamma(r-r_i)^2)$. Such a one-component solid can coexist with a fluid mixture since we are studying phase coexistence at fixed pressure and temperature. The fluid–solid coexistence is determined by the conditions $P_s = P_l$, $\mu_1^s = \mu_1^l$ (for fluid–SLM coexistence only) and $\mu_2^s = \mu_2^l$. Here the symbol (s) refers to the solid phase and (l) to the fluid one. The pressure of the solid phase is related to its free energy through the thermodynamic relation $P = -\frac{\partial F}{\partial V}|_{T,x,N}$ and the chemical potentials $\mu_i = \frac{\partial F}{\partial N_i}|_{T,V,N_{j \neq i}}$. For the coexisting fluid, we used the equation of state proposed by Mansoori *et al* [12], which gives better agreement with the simulation results than that obtained from the Percus–Yevick compressibility equation [12].

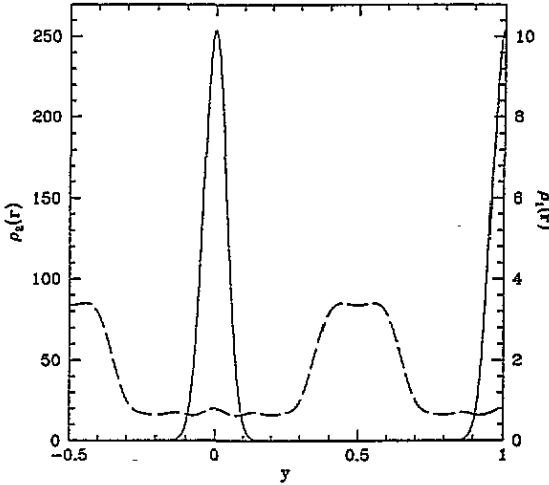


Figure 1. The density profiles $\rho_2(r)$ (solid line) and $\rho_1(r)$ (dashed line) at the SLM phase, for $\eta = 0.56$, $x = 0.90$. The densities are drawn in the (1,0,0) direction and the abscissa y is measured in units of the cubic lattice constant a .

We first examined the effect of concentration on the stability of the SLM phase. We find that for a given packing fraction of the large spheres (the packing fraction for the species i ($i = 1, 2$) is $\eta_i = \rho_i \frac{\pi}{6} \sigma_i^3$), when we decrease x (i.e. putting in more small spheres), the free energy of the SLM phase is increased. This can be explained by the fact that the disordered small spheres in the SLM phase increase the excess free energy by increasing the excluded volume to the large spheres. Another observation is on the structure of $\rho_1(r)$ resulted from (6). Figure 1 shows the density profiles of large and small spheres in the SLM phase. One notices that $\rho_2(r)$ is strongly peaked around the lattice sites whereas $\rho_1(r)$ is much flatter, reflecting its fluid-like nature. In detail, $\rho_1(r)$ displays some prominence around the interstices of the FCC sites, which are the expected favourable places for the small spheres in the SLM phase, and it shows some hollowness in the proximity of the FCC lattice sites because of the exclusion by the large spheres. Still, $\rho_1(r)$ is not close enough to zero in that area. We think this is due to the fact that (6) is only a first-order approximation of $\{\nu_G\}$.

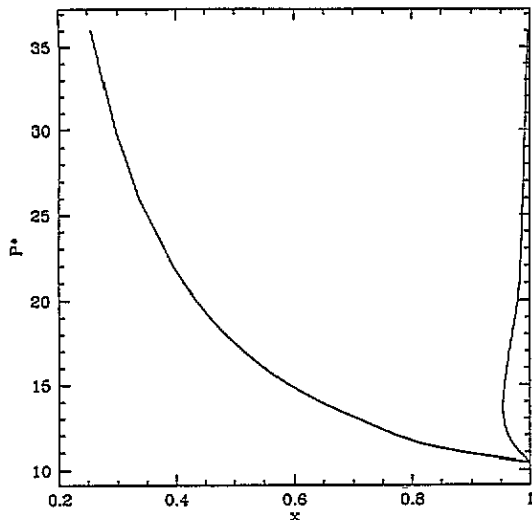


Figure 2. The fluid-SLM coexistence concentrations versus the reduced pressure $P^* \equiv \beta P \sigma_2^3$. For each P^* , x_l is on the left curve and x_s on the right one.

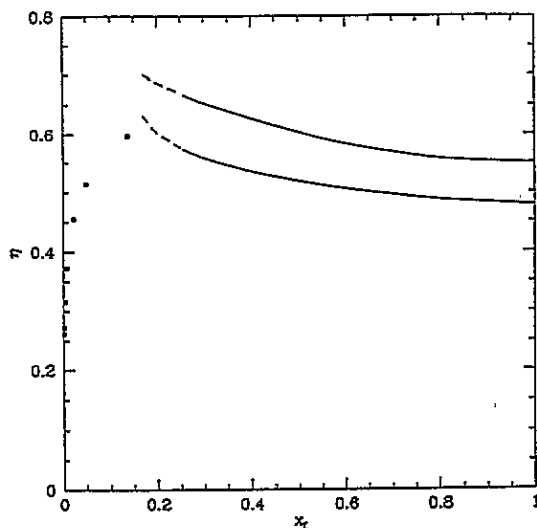


Figure 3. Coexistence packing fractions ($\eta = \rho_1 \frac{\pi}{6} \sigma_1^3 + \rho_2 \frac{\pi}{6} \sigma_2^3$) versus the concentration of large spheres in the coexisting fluid. For each x_l where there is fluid-solid coexistence, η_l is on the lower curve, η_s on the upper one. The solid lines correspond to the fluid-SLM coexistence; the dashed ones to the fluid-S₂ coexistence. Data for the fluid phase separation (filled squares) are from [10].

Secondly, we have studied the phase behaviour of the system as a function of the reduced pressure $P^* = \beta P \sigma_2^3$. At given P^* , there is a pair of coexisting concentrations (x_l, x_s) to which also corresponds a pair of total packing fractions (η_l, η_s) . Figure 2 shows (x_l, x_s) as a function of P^* . One notices that when P^* is increased from its one-component fluid-solid coexistence value, x_l decreases rapidly whereas x_s is much less sensitive to P^* . Furthermore, for all P^* in the figure ($10.4 \leq P^* \leq 36$), x_s remains close to 1 (typically, $x_s \geq 0.95$), meaning that in the SLM phase coexisting with a fluid at a given P^* , the amount of small spheres is quite limited. In figure 3 we show the fluid-solid coexisting packing fractions (η_l, η_s) as a function of the fluid concentration x_l . Both η_l and η_s increase when x_l decreases. The phase behaviour is also represented in the figure: fluids with high and moderate concentrations of large spheres, i.e. $0.256 \leq x_l < 1$, corresponding to the pressure range $10.4 < P^* \leq 36$, coexist with the SLM phase; fluids with rather low concentrations ($0.17 \leq x_l < 0.256$), corresponding to the pressure range $36 < P^* \leq 72$ coexist with the S₂ solid phase; for very low concentrations, i.e. $x_l < 0.17$ ($P^* > 72$), no fluid-solid

coexistence has been found. We should also point out that for $x_1 = 0.17$, $\eta_s = 0.701$, which is quite close to its close packing value ($\eta_{\text{close packing}} = 0.74$). We think that this is the limit of applicability of MWDA.

In conclusion, using MWDA, we have studied the fluid–SLM transition of an asymmetric hard-sphere mixtures. We have characterized the non-uniform densities $\rho_1(r)$ and $\rho_2(r)$ in such a phase. We have also carried out the fluid–solid phase diagram calculation. It has been found that above a certain value of the concentration of small spheres in the fluid phase ($x_1 < 0.17$), no more fluid–solid coexistence could be found. This last point is consistent with the fluid-phase separation phenomenon found by Biben *et al* [4] in mixtures which are very rich in small spheres ($x_1 \leq 0.14$). But we have to bear in mind that the Percus–Yevich direct correlation functions we used in the present work are not suitable for describing very asymmetric mixtures with $x \ll 0.5$ [4]. So our results cannot exclude there being, in that region of concentrations, phase equilibrium between a solid phase and a fluid phase of very low density, as found by a free volume theory [13]. Therefore it would be interesting to use, in further DFT work, direct correlation functions obtained by a more self-consistent theory (e.g. [4]).

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