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LETTER TO THE EDITOR

A density functional study of superlattice formation in binary hard-sphere mixtures

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Abstract. A theoretical investigation of a binary mixture of hard spheres confirms that stable superlattice structures, with a complex long-range order of the AB_{13} type, can form in these simple systems for intermediate values of the diameter ratio, in agreement with recent computer simulations and experimental studies of colloidal suspensions. It is shown that the larger entropy of mixing of the AB_{13} structure relative to that of the competing structures is responsible for its thermodynamic stability.

In recent years, colloidal suspensions with a well defined small degree of polydispersity and a well characterized interaction potential have become currently available [1]. Because the periodicities of the ordered structures which can appear in such suspensions are comparable to the wavelength of visible light, these structures are iridescent and can be analysed by means of standard light scattering techniques [2]. The detailed analysis of these structures has revealed an astonishingly rich phase behaviour [3] which provides a challenge to the current theories of freezing [4]. In the present investigation we will be concerned with a particular type of suspension, namely, a binary mixture of ‘hard-sphere’ colloids, i.e. colloids for which the short-ranged repulsion between the colloidal particles has been arranged so as to mimic a hard-sphere (HS) interaction by means of a suitable coating of the colloidal particles [5]. Experimental studies of such binary mixtures have revealed the formation of complex superlattice structures [6] similar to those of some inter-metallic alloys and of some unusual gem opals [7]. Because the underlying HS potential can only drive phase transitions where the configurational entropy is balanced by geometric packing effects [8], the appearance of such complex phases is quite unexpected. In view of the possible presence in the experimental systems of a small amount of polydispersity and a weak departure from perfect HS behaviour, as well as the very long nucleation times involved, any alternative confirmation of these findings should be considered welcome. It is therefore comforting that recent Monte Carlo (MC) computer simulations of binary mixtures of A and B hard spheres have confirmed the stability of the AB_{13} structure [9]. The efficient exploration of the phase space of HS mixtures by MC simulations is however not a simple problem either [10], while the finite-size effects in mixtures containing only 64 spheres of type A are equally difficult to assess leaving some doubt as to whether the true (infinite system) equilibrium conditions have

been met. For these reasons we report here a theoretical study, based on a density functional approach which has proven [11] to provide a very accurate description of one-component HS solids, which adds further evidence for the existence of the superlattice structures found in the above experiments [6] and simulations [9].

We consider a system composed of N_A large spheres of diameter σ_A and N_B smaller spheres of diameter σ_B with the $N = N_A + N_B$ spheres enclosed at temperature T in a volume V and interacting only through the HS potential which is infinite when two spheres overlap and zero otherwise. The appropriate thermodynamic potential is the (Helmholtz) free energy, $F = F(T, V; N_A, N_B)$, which for spatially ordered phases described by the partial local densities at \mathbf{r} , $\rho_i(\mathbf{r})$ with $N_i = \int d\mathbf{r} \rho_i(\mathbf{r})$ for $i = A, B$, becomes a functional (indicated by square brackets) of the $\rho_i(\mathbf{r})$ given by

$$F(T, V; [\rho_A, \rho_B]) = k_B T \sum_{i=A,B} \int d\mathbf{r} \rho_i(\mathbf{r}) (\ln(\Lambda_i^3 \rho_i(\mathbf{r})) - 1) + F_{\text{ex}} \quad (1)$$

where k_B denotes Boltzmann's constant, Λ_i the thermal de Broglie wavelength of species i , while for notational convenience the implicit dependence on T and V has not been indicated explicitly in the RHS of (1). The excess free energy, F_{ex} of (1), can in turn be expressed in terms of the Ornstein-Zernike direct correlation functions (DCF), $c_{ij}(\mathbf{r}, \mathbf{r}')$ as

$$\beta F_{\text{ex}}(T, V; [\rho_A, \rho_B]) = - \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda (1 - \lambda) \times \sum_{i,j}^{A,B} c_{ij}(\mathbf{r}, \mathbf{r}'; [\lambda \rho_A, \lambda \rho_B]) \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') \quad (2)$$

where λ is a 'charging' parameter and $\beta = 1/k_B T$. For a spatially uniform fluid phase (superscript zero) of densities $\rho_i = N_i/V$, equation (2) reduces to

$$\beta F_{\text{ex}}^0(T, V; \bar{\rho}_A, \bar{\rho}_B) = -V \int d\mathbf{r} \int_0^1 d\lambda (1 - \lambda) \sum_{i,j}^{A,B} \bar{\rho}_i \bar{\rho}_j c_{ij}^0(|\mathbf{r}|; \lambda \bar{\rho}_A, \lambda \bar{\rho}_B) \quad (3)$$

as discussed in more detail in [11,12]. Following the prescription of [11] we now turn the exact relation (2) into a manageable one by replacing the exact DCF c_{ij} of (2) by their approximate analytic Percus-Yevick (PY) expression for a binary HS fluid mixture (see [12]), $c_{ij}(\mathbf{r}, \mathbf{r}'; [\lambda \rho_A, \lambda \rho_B]) \rightarrow c_{ij}^{\text{PY}}(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}_A(\lambda), \bar{\rho}_B(\lambda))$, where $\{\bar{\rho}_A(\lambda), \bar{\rho}_B(\lambda)\}$ are the effective uniform densities describing the non-uniform phase of densities $\{\lambda \rho_A(\mathbf{r}), \lambda \rho_B(\mathbf{r})\}$. Taking the effective liquid to be of the same composition, $N_A/N \equiv x_A = 1 - x_B$, as the original system we write $\bar{\rho}_A(\lambda) = x_A \bar{\rho}(\lambda)$ and $\bar{\rho}_B(\lambda) = x_B \bar{\rho}(\lambda)$, and determine the (total) effective density $\bar{\rho}(\lambda)$ by equating the excess free energy per particle of the non-uniform phase as determined by (2) to the excess free energy per particle of the effective liquid as obtained from (3). This yields an integral equation for $\bar{\rho}(\lambda)$ which has to be solved for $\bar{\rho}(\lambda = 1)$ knowing that $\bar{\rho}(\lambda = 0) = 0$. The result is a straightforward generalization to mixtures of the 'generalized effective liquid approximation' (GELA) originally formulated for a one-component system [11]. As usual, the explicit evaluations will be performed by

parametrizing the HS density profiles in terms of Gaussians centred at the lattice sites $\{R^{(i)}\}$ occupied by species i :

$$\rho_i(\mathbf{r}) = \sum_{R^{(i)}} \left(\frac{\pi}{\alpha_i} \right)^{3/2} \exp\{-\alpha_i(\mathbf{r} - R^{(i)})^2\} \quad i = A, B \quad (4)$$

where the width parameters $\{\alpha_A, \alpha_B\}$ are determined so as to minimize the total free energy of (1). These calculations can now be routinely performed and yield, for instance, a very accurate description of the one-component HS system [11].

The general phase diagram of a mixture can then be found by computing F for various phases as explained in [12]. The phase behaviour of binary HS mixtures is known to be a very sensitive function of the diameter ratio $\gamma = \sigma_B/\sigma_A (< 1)$. For nearly similar spheres ($1 > \gamma > 0.8$) the HS fluid was predicted [12] (using a primitive version of the above theory, see [11]) to freeze into a substitutionally disordered or mixed crystal where both species occupy the sites of a compact lattice structure with a fluid–solid phase diagram which transforms rapidly, when decreasing γ , from a spindle shape into an azeotropic and finally into an eutectic phase diagram. This theoretical scenario was later confirmed by MC simulations on HS mixtures [10] and also found to be consistent with the experiments on colloids [3]. For very dissimilar spheres ($0.5 > \gamma > 0$) one expects the HS fluid to freeze into an AB structure of the NaCl type where the small spheres occupy the interstitial holes of a compact lattice structure formed by the large spheres but this situation has not yet been investigated for colloids. The region of interest here concerns instead the intermediate γ -values, $0.8 > \gamma > 0.5$, for which the experiments, on both opals [7] and colloids [6], have found superlattice structures of the AB_n type with n as large as 13 leading to an unexpectedly complex long-range order with a unit cell of 112 spheres [7]. Both AB_2 and AB_{13} structures have been found. The presence of the AB_2 structure, an alternate stacking of hexagonal A planes and honeycomb B planes [7], can be understood as due to an optimization of the excluded volume effects resulting in a better packing (higher close-packing fraction) compared to that of a phase-separated solid A + solid B, system where both A and B form a compact structure. This geometric packing argument does not hold, however, for the AB_{13} structure, a simple cubic lattice of A spheres with the cubes filled by a centred icosahedra of B spheres rotating by $\pi/2$ when going from one sub-cell to the next [7], whose close-packing fraction is lower than that of the solid A + solid B phase. A tentative explanation for the stability of the AB_{13} structure in terms of the entropy of mixing will be given below.

The dimensionless free energy per particle, $\beta F/N$, depends (apart from a trivial constant) on the composition $x_B = 1 - x_A$, the overall packing fraction $\eta = \sum_{i=A,B} (\pi/6)(N_i \sigma_i^3/V)$ and the diameter ratio γ . In order to explore the two-dimensional parameter space (η, x_B) in search of stable AB_n structures we will increase η along a line of constant composition equal to that of the AB_n structure ($x_B = n/(n+1)$) at the experimentally studied γ -value ($\gamma = 0.58$). The phase diagram at constant total volume (so as to mimic the incompressibility of the host fluid of the colloidal particles [6]) can be obtained by computing the values of $\beta F/N$, obtained as described above, for various phases. Although the experimentally determined structures are slightly non-ideal we have fixed the ratio c/a of the interplane to in-plane distances at their ideal value (see [7]). For example, we used $c/a = \sqrt{(1 + 2\gamma - 3\gamma^2)}/3 / \gamma$ for the AB_2 structure, yielding that $c/a = 1.068$ for $\gamma = 0.58$, a value close to the experimental [6] and simulation ones [9]; for the

AB_{13} structure, we used $a_A/a_B = \sqrt{4(d/a_B)^2 - 1} + \frac{1}{2}\sqrt{4(d/a_B)^2 - 2}$, where a_A is the lattice constant of the A spheres, a_B the edge length of the icosahedra formed by the B spheres and d the distance between a vertex and the centre of the icosahedra ($d/a_B = 0.951$). For the phase behaviour of the $n = 2$ mixture we find the scenario illustrated in figure 1.

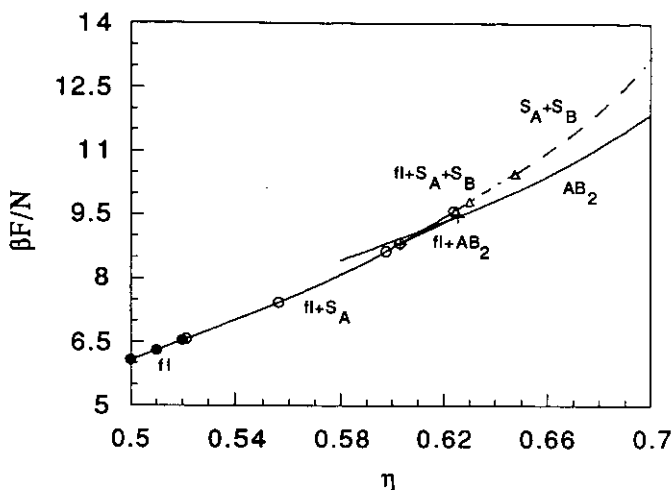


Figure 1. The dimensionless free energy per particle, $\beta F/N$ (shifted by the constant term $-1 + \ln(\Lambda_A^3/\sigma_A^3)$), as a function of the total packing fraction η for a fixed overall composition $x_B = \frac{2}{3}$ and a diameter ratio $\gamma = 0.58$. It is assumed that $m_A/m_B = (\sigma_A/\sigma_B)^3$. The phases represented are: fluid (filled circles), fluid + solid A (empty circles), fluid + solid A + solid B (triangles), solid A + solid B (dashed line), fluid + AB_2 (the line connecting the two crosses) and the AB_2 phase (solid line).

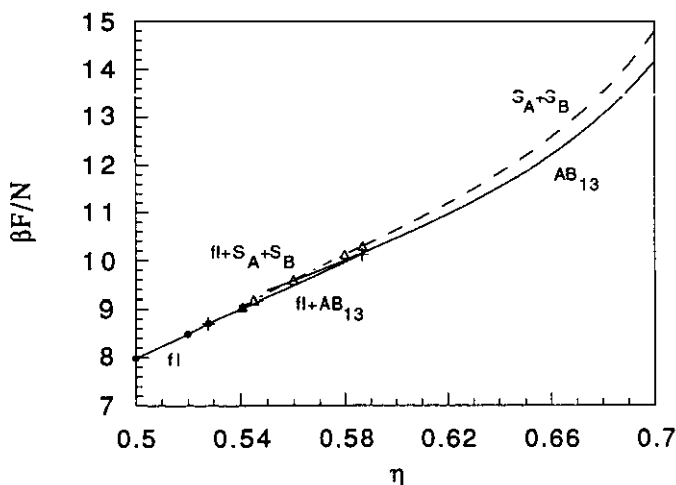


Figure 2. The same as figure 1 but for $x_B = \frac{13}{14}$. The same sequence of phases are represented, but the superlattice phase is now AB_{13} . The fluid + solid A phase is not visible on this scale since its range of stability is very small ($0.528 < \eta < 0.541$), and its free energy is very close to that of the fluid + AB_{13} phase.

At low density ($\eta < 0.52$) the fluid mixture is the only stable phase (its free energy has been represented here by the equation of Mansoori *et al* [13]). Increasing the density there appears a stable phase fluid + solid A consisting of a fluid mixture in coexistence with a solid of A spheres arranged in a compact lattice for which we have considered the face-centred cubic structure. The composition and density of the coexisting fluid phase, as well as the fraction of the total volume occupied by it, are fixed by the given overall composition ($x_B = \frac{2}{3}$), total density (η) and the total volume (V) [14]. This implies for instance that $x_B > \frac{2}{3}$ in the coexisting fluid phase (since $x_B = 0$ in the solid A phase). At $\eta > 0.52$ this fluid + solid A phase becomes stable WRT the pure fluid mixture and, hence, the large spheres crystallize first. At higher densities ($\eta > 0.54$) an AB_2 structure is formed leading for $\eta > 0.603$ to a stable fluid + solid AB_2 phase with this time $x_B = \frac{2}{3}$ both in the coexisting solid and fluid phases. Finally for $\eta > 0.625$ only the pure solid AB_2 phase survives as a stable phase while other phases, like solid A + solid B, are found to be metastable (higher free energy) in the range of densities considered ($\eta < 0.70$). We notice that our transition densities agree very well with recent simulation results on the same mixture [9], where the fluid + solid A phase becomes stable at $\eta = 0.51$, and the AB_2 structure is stable for $\eta > 0.615$. When n is increased, this scenario is slightly modified (see figure 2). For $n = 13$, and hence $x_B = \frac{13}{14}$, we find that at $\eta = 0.528$ the fluid mixture is transformed directly into a fluid + solid AB_{13} phase with $\eta_l = 0.528$ and $\eta_s = 0.586$; at $\eta = 0.586$ the mixture transforms into a pure solid AB_{13} phase which remains stable WRT the phase-separated solid A + solid B phase up to the highest density considered, i.e. $\eta = 0.70$. Notice [7] that the close-packing fraction for the AB_{13} structure at our γ is $\eta_{ep} = 0.713$. We also observe that the free-energy difference between the AB_{13} and the solid A + solid B phases is quite small. In the simulation of [9], the fluid + solid AB_{13} phase was not considered. Instead, the authors found that at $\eta = 0.523$ the fluid + solid A phase becomes stable and transforms into a pure AB_{13} phase at $\eta = 0.545$, which is found to be stable with respect to the solid A + solid B phases up to $\eta \approx 0.71$. In figure 3, we show a comparison between the theoretical and simulation free energies for the AB_{13} structure, in the density range $0.55 \leq \eta \leq 0.70$. The agreement is very good (notice that the simulation results have not been corrected for possible finite-size effects). Comparing the two situations ($n = 2$ and $n = 13$) we also observe that although AB_{13} has a higher free energy than AB_2 it is stable at lower packing fractions than AB_2 . This finding and the above scenarios are in good agreement with the experimental observations on colloids [6]. The stability of the AB_{13} structure can be understood here on the basis of the observation [8] that while the excess free energy F_{ex} of (2) favours compact lattice structures, the configurational or 'ideal' free energy $F - F_{ex}$ of (1) favours structures with a high configurational entropy. As a result, the less compact AB_{13} structure has a higher excess free energy than the competing solid A + solid B structure but this difference is compensated by its lower configurational free energy resulting from its higher entropy of mixing (see figure 4).

From the above we conclude that the experimental studies on binary mixtures of colloidal particles [6], the MC simulations of [9] and the present theoretical density functional study of binary HS mixtures reveal that, for intermediate diameter ratios, a thermodynamically stable superlattice structure of the AB_{13} type can be formed on the basis of pure excluded volume interactions. An entropy-of-mixing effect can be invoked to explain the stability of the AB_{13} structure while pure space-filling arguments [7] would disfavour it.

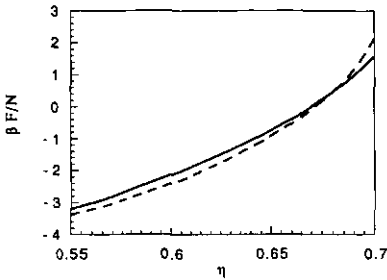


Figure 3. The dimensionless free energy per particle, $\beta F/N$ (shifted by a constant), versus the packing fraction, η , for the ideal AB_{13} structure ($x_B = \frac{13}{14}$, $\gamma = 0.58$) as obtained from the present theory (solid line) compared to the MC simulation results (dashed line) of [9]. Notice that the simulation results are for a finite system of 64 A spheres and 832 B spheres.

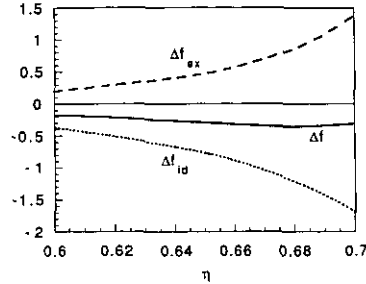


Figure 4. Difference of the dimensionless excess and 'ideal' (or configurational) free energies per particle ($f = \beta F/N$), as obtained from (1) and (2), between the AB_{13} and solid A + solid B phases at $x_B = \frac{13}{14}$ and $\gamma = 0.58$. In the density range shown, $\Delta f_{ex} \equiv f_{ex}[AB_{13}] - f_{ex}[S_A + S_B]$ (dashed line) is positive, favouring the solid A + solid B phase as expected on the basis of packing arguments while Δf_{id} (dotted line) is negative, favouring the AB_{13} structure. The difference of the total free energies $\Delta f = \Delta f_{id} + \Delta f_{ex}$ (solid line) is negative, indicating an AB_{13} phase which is thermodynamically stable relative to the phase-separated solid A + solid B phase.

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