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A computer simulation investigation into the stability of the AB_2 superlattice in a binary hard sphere system

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The thermodynamic stability of the binary hard-sphere AB_2 superlattice structure has been confirmed by means of computer simulations. This is consistent with the results of experimental studies of suspensions of hard-sphere colloidal particles. A fit of the Helmholtz free energy surface for the region in phase space where AB_2 is found to be stable is presented, together with results for the c/a ratio of this hexagonal crystal.

1. Introduction

In the recent experiments of Bartlett *et al.* [1, 2] unusual superlattice structures were observed forming from binary mixtures of colloidal particles. These include AB_2, similar to the crystallographic aluminium boride (AlB_2) structure, and AB_{13}, isomorphous to the metallic alloy $NaZn_{13}$ with its complicated icosahedral arrangement of B atoms. The colloidal suspensions consisted of sterically stabilized polymethylmethacrylate (PMMA) spheres in a decalin/carbon disulphide medium. It has been shown that PMMA colloidal particles interact through a steep, repulsive potential closely approximating that of hard spheres [3–5]. This makes the very rich phase behaviour exhibited by these systems all the more extraordinary.

The first experiments were with spheres at a size ratio, $\alpha = \sigma_B/\sigma_A = 0{\cdot}62$ [1]. Crystalline AB_2 was not observed and AB_{13} (mixed with crystals of pure B) formed very slowly and subsequently disappeared after many months. The apparent metastability of AB_{13} at this size ratio prompted our previous computer simulation study of the thermodynamic stability of the hard-sphere AB_{13}-phase [6]. The results of the simulations showed hard-sphere AB_{13} to be stable, at least with respect to the simpler phases one would expect a binary system to adopt [7], for a range of diameter ratios, $\alpha = 0{\cdot}48$–$0{\cdot}62$. The calculated upper boundary to AB_{13} stability at $\alpha = 0{\cdot}62$ (for which the AB_{13} free energy is extremely similar to those of the competing phases) is consistent with the experimental metastability observed for AB_{13}. Later experiments for a size ratio, $\alpha = 0{\cdot}58$, saw the formation of a stable AB_{13} crystal phase at a faster rate and also the emergence of small crystallites of AB_2 [2]. The AB_{13} and AB_2 structures have also been observed in gem opals, consisting of colloidal silica spheres [8], in binary suspensions of charge-stabilized latex spheres [9, 10] and in high-pressure inert gas mixtures as van der Waals compounds [11].

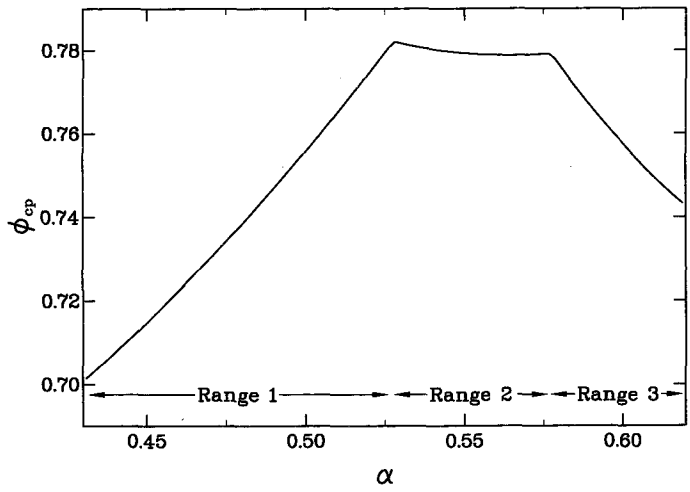

Figure 1. The space-filling curves, i.e. of maximum packing fraction, as a function of α for AB_2.

A density-functional hard-sphere study has recently provided further verification of the stability of AB_{13} and AB_2 in mixtures with compositions corresponding to the stoichiometry of these two phases [12]. Such calculations are free of system-size effects which may limit the reliability of simulation studies of phase equilibria. The Helmholtz free energies calculated for AB_{13} were in good agreement with our simulation values [6].

It is surprising that a 'real-life' binary hard-sphere system can arrange itself, at high density, into these complex structures. The transition is thought to be entropically driven with an increase in the free volume available to each of the spheres upon crystallization. In particular, if a crystal structure has a high close-packed density, then for lower densities its constituent particles will have a large free volume in which to move and thus a high translational entropy. On this basis, we would expect binary A_mB_n structures with close-packed densities greater than the close-packing fraction for monodisperse spheres, $\phi_{cp}^{(1)} = 0{\cdot}7405$, to be preferred, especially at high pressures, to phase separation into coexisting monodisperse face-centred-cubic (f.c.c.) crystals of A and B. Murray and Sanders have explored the stability of several binary structures by use of this *space-filling principle* [8]. The AB_2 structure is found to have close-packed packing fractions greater than $\phi_{cp}^{(1)}$ for size ratios in the range, $\alpha = 0{\cdot}482$–$0{\cdot}625$ (see figure 1).

Here, we report the results of an investigation into the stability of the AB_2-phase making use of the Frenkel–Ladd method for calculation of crystal-phase free energies [13] (the technique applied to a binary crystal is discussed in detail in [6]). The AB_2 structure consists of alternate hexagonal layers of large and small spheres. The large spheres (A) form close-packed layers which align directly above each other along the c-axis. The small spheres (B) ocupy the trigonal prismatic sites between these layers and form planar hexagonal rings resembling the carbon layers in graphite. In our simulations we employ a rhombic prismatic box consisting of $6 \times 6 \times 6$ unit cells (each of which is a rhombic prism containing one A and two B particles): the total number of particles used was $N = 648$. The stability of a binary crystal,

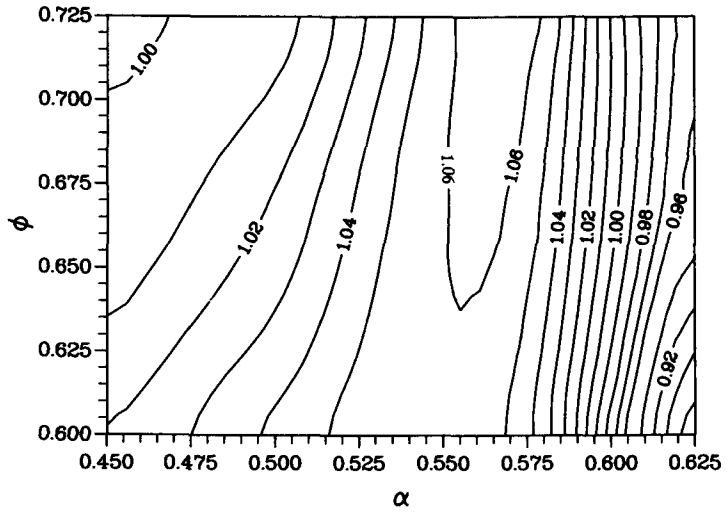

Figure 2. The c/a ratio as a function of ϕ and α for the strain-free AB_2 crystal phase.

A_mB_n, typically depends on two variables, namely the packing fraction, ϕ, and the diameter ratio, α. It is evident that the AB_2 crystal is complicated by an additional parameter, the layer-spacing or c/a ratio. To calculate the free energy of the AB_2-phase as a function of these variables, ϕ, α and c/a, would certainly be an exhausting task. However, since the experimentally observed AB_2 crystals form from a binary fluid suspension, it seems likely that they are free of strain. There is only one value of c/a for each point in ϕ, α-phase space for which AB_2 can be strain-free, so with this assumption the problem is reduced to one of two dimensions once again.

2. The c/a ratio and free energy calculations

We have calculated the c/a ratio for strain-free AB_2 as a function of ϕ and α within collision dynamics (MD) simulations using a simple scaling algorithm. We start the MD simulation with a reasonable guess for c/a then let the simulation proceed for a few thousand collisions monitoring the pressure components in the x-, y- and z-directions (the AB_2 crystal is set up such that its principal c-axis is aligned with the box z-axis; in this scenario the pressure components P_{xx}, P_{yy} and P_{zz} are equal to the diagonal stress tensor elements and the off-diagonal elements are zero on average). The xy-plane pressures, i.e. those acting within the AB_2 crystal planes are equal ($P_{xx} = P_{yy}$) and for a strain-free crystal are also equal to P_{zz}, the pressure normal to the planes. At various invervals throughout the simulation we scale the coordinates of the spheres and alter the shape of the enclosing simulation box in a manner which leads to making these pressures equal ($P_{xx} = P_{zz}$). For example, if $P_{zz} > P_{xx}$ it is obvious we need to increase the c/a ratio, i.e. elongate the rhombic box in the z-direction, while if $P_{zz} < P_{xx}$ we must decrease c/a. This scaling is accompanied by a rescaling of particle diameters to maintain a constant packing fraction, ϕ. Hence particle overlaps become a constraint on the degree of scaling one can perform in any one step. After a number of scaling steps the pressures P_{xx}, P_{yy} and P_{zz} become almost identical and c/a is well-established. The c/a ratio calculated in this way for strain-free AB_2 is plotted as a function of ϕ and α in figure 2.

The Frenkel–Ladd free energy calculations [13] have been supplemented by thermodynamic integration procedures to determine relative free energies within a crystal phase. Integrations have been made with respect to the packing fraction, ϕ (see [6]), and size ratio, α [14], to enable a more efficient 'mapping-out' of phase space, although the latter method does not appear to have the desired accuracy for the purposes of this study. The free energy of the binary fluid has been obtained by thermodynamic integration from the dilute gas phase. We make use of the well-known semi-empirical expression of Mansoori *et al.* [15] for the binary fluid equation-of-state.

We have fitted the AB_2 excess free energies in the ranges $\alpha = 0{\cdot}425$–$0{\cdot}625$, $\phi = 0{\cdot}60$–$0{\cdot}725$, to a function of the form

$$F^{\text{ex}} = \left(p_1 \ln y_1 + \sum_{i=2}^{m} p_i y_1^{i-2}\right)\left(1 + \sum_{j=1}^{n} q_j \alpha^j\right) + \left(r_1 \ln y_3 + \sum_{k=2}^{m} r_k y_3^{k-2}\right) \times \left(1 + \sum_{l=1}^{n} s_l \alpha^l\right) \tag{1}$$

where

$$y_1 = \left(\frac{\phi_{\text{cp},1}(\alpha)}{\phi} - 1\right), \tag{2a}$$

$$y_3 = \left(\frac{\phi_{\text{cp},3}(\alpha)}{\phi} - 1\right). \tag{2b}$$

The space-filling curves used here, $\phi_{\text{cp},1}$ and $\phi_{\text{cp},3}$, for ranges 1 and 3 shown in figure 1 have been extended beyond their applicable ranges. They are given by the following equations:

$$\text{Range 1: } \alpha < 0{\cdot}527, \qquad \phi_{\text{cp},1} = \frac{\pi}{3\sqrt{3}}(2\alpha^3 + 1), \tag{3a}$$

$$\text{Range 3: } 0{\cdot}577 < \alpha < 0{\cdot}667, \qquad \phi_{\text{cp},3} = \frac{\pi(2\alpha^3 + 1)}{9\sqrt{3}\alpha^2(1 + 2\alpha - 3\alpha^2)^{1/2}}. \tag{3b}$$

The function with $m = 4$ and $n = 2$, i.e.

$$\begin{aligned} F_{\text{fit}}^{\text{ex}} = {} & c_1 + c_2\alpha + c_3\alpha^2 + c_4 \ln y_1 + c_5 y_1 + c_6 y_1^2 + c_7\alpha \ln y_1 + c_8\alpha y_1 \\ & + c_9\alpha y_1^2 + c_{10}\alpha^2 \ln y_1 + c_{11}\alpha^2 y_1 + c_{12}\alpha^2 y_1^2 + c_{13} \ln y_3 + c_{14} y_3 \\ & + c_{15} y_3^2 + c_{16}\alpha \ln y_3 + c_{17}\alpha y_3 + c_{18}\alpha y_3^2 + c_{19}\alpha^2 \ln y_3 + c_{20}\alpha^2 y_3 + c_{21}\alpha^2 y_3^2, \end{aligned} \tag{4}$$

gives a reasonable fit (for a 269-point dataset the sum of square differences is 0·227) for a manageable number of coefficients. The 21 coefficients, c_i, are given in table 1.

3. The stability of AB_2

In addressing the question of the stability of the AB_2-phase we must first define the most probable competing phases for a particular point in phase space. At low densities this will certainly be the binary fluid, whereas at higher densities we would

Table 1. Coefficients for the polynomial fit of the AB_2 free energy surface.

	Coefficient	Basis function
c_1	107·52928	1
c_2	−78·16360	α
c_3	−214·63342	α^2
c_4	−36·13625	$\ln y_1$
c_5	−64·43814	y_1
c_6	−25·48693	y_1^2
c_7	−164·73168	$\alpha \ln y_1$
c_8	137·54093	αy_1
c_9	−30·01445	αy_1^2
c_{10}	−191·27993	$\alpha^2 \ln y_1$
c_{11}	177·26623	$\alpha^2 y_1$
c_{12}	−34·70501	$\alpha^2 y_1^2$
c_{13}	1·78932	$\ln y_3$
c_{14}	−80·95480	y_3
c_{15}	−28·91789	y_3^2
c_{16}	7·98936	$\alpha \ln y_3$
c_{17}	−13·83148	αy_3
c_{18}	183·23233	αy_3^2
c_{19}	−24·56534	$\alpha^2 \ln y_3$
c_{20}	112·27400	$\alpha^2 y_3$
c_{21}	−93·01429	$\alpha^2 y_3^2$

expect the phase-separation of two coexisting f.c.c. crystals (A and B). Bartlett has prescribed a simple approach to this problem [7], using approximations to the equation-of-state of the fluid (the Mansoori equation) and pure solid phases (the parametrization of Alder *et al.* [16]). These equations-of-state, when integrated with respect to volume, V, and then differentiated with respect to the number of particles of one of the species, N_i, yield the chemical potential of species i, μ_i, within that phase. Coexisting phases (α, β) in equilibrium obey the following relations:

$$P_\alpha = P_\beta, \tag{5a}$$

$$\mu_\alpha^A = \mu_\beta^A, \tag{5b}$$

$$\mu_\alpha^B = \mu_\beta^B. \tag{5c}$$

In Bartlett's picture, the fluid mixture at high density freezes into crystalline solid phases of pure A and pure B — impurities in the solid phases are not catered for. Following this approach for a given size ratio, α, we can compute a constant-volume phase diagram. An example for $\alpha = 0{\cdot}58$ is given in figure 3. Also indicated in this figure is the line of constant composition, $X = \frac{1}{3}$, corresponding to the AB_2 stoichiometry. If we prepare a system with this overall composition, we should therefore compare the free energy of AB_2 with the free energies of the following phases in order of increasing density: binary fluid (f), fluid coexisting with solid A($s_A + f$), the eutectic state where solid A and B coexist with the fluid ($s_A + s_B + f$) and the state in which the system has separated into pure solid A and pure solid B ($s_A + s_B$). The free energies of those phases are shown in figure 4 for $\alpha = 0{\cdot}58$. From this figure we can determine that AB_2 is stable (for $\alpha = 0{\cdot}58$) for packing fractions greater than $\phi = 0{\cdot}6164$. It should be pointed out that other phases or combinations of phases

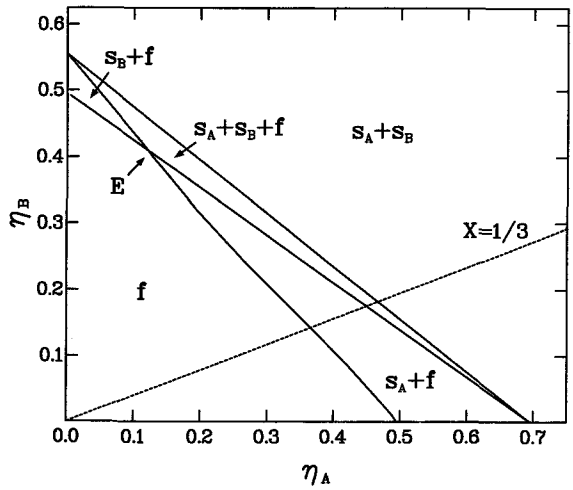

Figure 3. Constant-volume phase diagram for binary mixtures of hard spheres of diameter ratio, $\alpha = 0{\cdot}58$, arising from the description of Bartlett [7]. $\eta_{A(B)}$ is the partial packing fraction of the large (small) spheres. The labels s_A, S_B and f refer to the solid phase of large spheres (A), the solid phase of small spheres (B) and the fluid phase, respectively, E denotes the eutectic fluid. Also shown is the line of composition, $X + \frac{1}{3}$, corresponding to AB_2.

might be more stable here than AB_2, including a number of possible phases coexisting with the AB_{13} crystal phase. This issue will be discussed elsewhere where a more complete phase diagram with AB_2 and AB_{13} regions will be presented [17]. However, in the present work the analysis is restricted to a comparison of the AB_2 stability with respect to the phases listed above.

We have repeated comparisons of this nature over a wide range of diameter ratios. In figure 5 we present a 'phase diagram' showing the phase region (shaded) of thermodynamic stability of AB_2 over the competing phases arising from the model

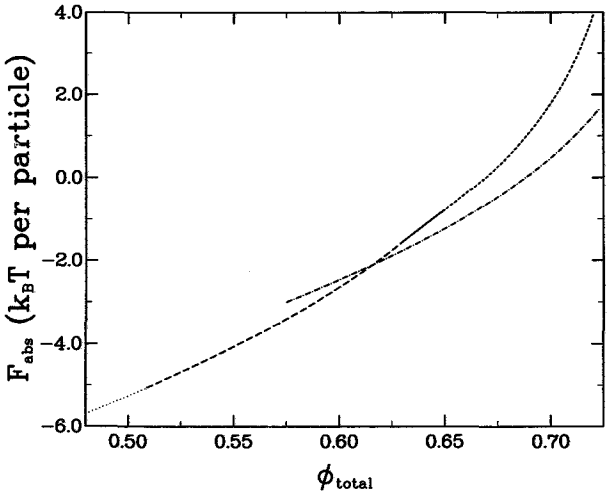

Figure 4. Absolute free energies of AB_2 (– · – ·) and the phases arising from the Bartlett approach [7] for a diameter ratio, $\alpha = 0{\cdot}58$. These phases are fluid (· · · · ·), solid A + fluid (— — —), solid A + solid B + fluid (———) and solid A + solid B (- - - - -).

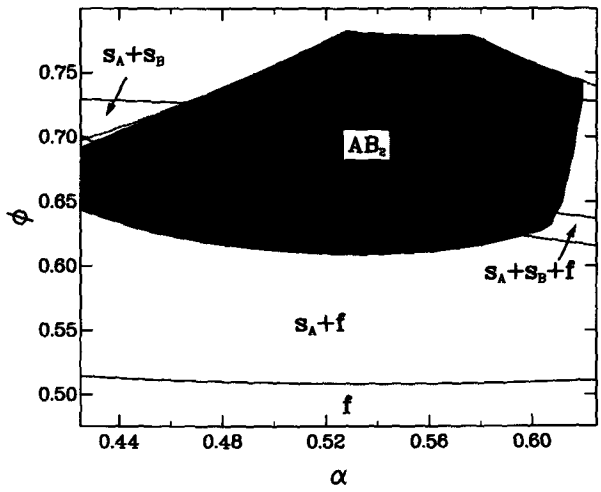

Figure 5. Phase diagram showing the region (shaded) of stability of AB_2 over the phases arising from the description of Bartlett [7]. The space-filling curve for AB_2 is shown as the dashed curve.

of Bartlett [7]. A measure of the stability of the AB_2 phase is given by the difference in absolute free energy of AB_2 and the underlying Bartlett phase (see figure 6),

$$\Delta F = F^{\text{abs}}_{\text{Bartlett}} - F^{\text{abs}}_{AB_2}. \tag{6}$$

The noteworthy feature of figure 6 is that it shows that over a large domain AB_2 is only just stable ($\Delta F < k_B T/2$, say). This suggests that the predicted stability of AB_2 in the true hard-sphere system could be easily affected by other factors in real colloidal suspensions such as polydispersity or the finite range (i.e. the not quite true hard-sphere nature) of the interparticle interaction.

The phase behaviour as seen in these diagrams is consistent with the observation

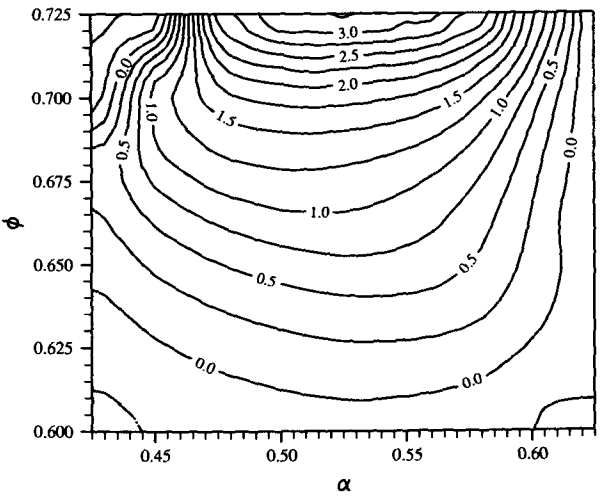

Figure 6. ΔF, the difference between the free energy of the AB_2-phase and the competing Bartlett phases, as a function of ϕ and α.

of AB_2 crystals in the colloidal suspensions for a size ratio, $\alpha = 0{\cdot}58$, with a packing fraction of about $\phi = 0{\cdot}64$. This density, and also the c/a ratio [18], were calculated from the line positions of the powder diffraction pattern. The calculated c/a ratio of 1·045 compares quite well with that computed in the equal stress-component MD simulation, a value of 1·049. Rather interestingly, the experimental suspensions prepared with an overall composition, $X = \frac{1}{3}$ (the AB_2 stoichiometry), remained amorphous, not crystallizing over several months (AB_2 did crystallize, though, for the compositions, $X = \frac{1}{5}$ and $X = \frac{1}{7}$). It is clear from our phase diagram that AB_2 would have been thermodynamically preferred for packing fractions in excess of $\phi = 0{\cdot}616$. However, the samples were prepared with lower overall volume fractions than this.

We find that the upper limit to AB_2 stability occurs for a size ratio, $\alpha \simeq 0{\cdot}62$, above which it becomes less stable with respect to phase separation of pure A and B crystals. This is consistent with the absence of any observation of AB_2 at $\alpha = 0{\cdot}62$ in the colloidal suspensions of Bartlett *et al.* [1, 2]. This is also in agreement with the study of Murray and Sanders [8], based on packing considerations. They showed that the AB_2 structure exhibits close-packed packing fractions greater than that of a monodisperse f.c.c. phase for size ratios in the range, $\alpha = 0{\cdot}482$–$0{\cdot}625$ (the space-filling curve for AB_2 is shown in figure 1). They expect the system to form a state in which crystals of A and B have phase separated for $\alpha < 0{\cdot}482$ at high density. Our results show AB_2 to be thermodynamically stable for diameter ratios as low as $\alpha = 0{\cdot}425$. The $s_A + s_B$ phase is reentrant though, for very high packing fractions at diameter ratios, $\alpha < 0{\cdot}468$, with AB_2 stable at lower ϕ. AB_2 is seen (in figure 6) to be most stable, i.e. ΔF greatest, for diameter ratios in the range, $\alpha = 0{\cdot}48$–$0{\cdot}575$, at high densities. Here, the particles have a larger free volume as a result of the AB_2 structure than they would have had if phase-separated into f.c.c. crystals, and so a higher entropy.

We should note that the reliability of the Mansoori equation-of-state for the fluid becomes questionable for the lower diameter ratios used. The lower packing fraction boundary on the AB_2 phase diagram is particularly affected. This is because the estimated coexistence density of the binary fluid in the $s_A + f / s_A + s_B + f$ phases is very high, and the Mansoori equation leads to an overestimate of the fluid free energy. Hence we would expect these phases to be slightly more favourable with respect to AB_2 than depicted. The effect is not thought to be large since a plot of their free energies as a function of ϕ shows curves which run smoothly into each other with no great differences (or 'jumps') on going from stable $s_A + f$ to $s_A + s_B + f$ to the $s_A + s_B$ phase. Such 'jumps' were only evident for $\alpha = 0{\cdot}425$.

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