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1990 J. Phys.: Condens. Matter 2 4979

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A model for the freezing of binary colloidal hard spheres

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Received 29 January 1990

Abstract. Phase boundaries are calculated for the freezing of a binary mixture of colloidal hard spheres which are assumed to be immiscible in a single solid phase. Results are reported for mixtures of diameter ratio $\gamma = 0.85$ and 0.65 . It is shown that the fluid phase is stable to a higher density in the binary mixture than the monodisperse system. The maximum fluid freezing density occurs at the binary eutectic in suspensions rich in small spheres. The proportion of small spheres in the eutectic fluid increases sharply with decreasing diameter ratio. At phase coexistence the hard sphere crystal is compressed relative to the monodisperse system. The increase in density is most pronounced for the crystal of large spheres. The hard sphere phase behaviour is described at constant volume which enables a direct comparison with experimental measurements on colloidal systems to be made.

1. Introduction

In recent years it has become widely recognised that colloidal suspensions demonstrate a range of equilibrium phase behaviour which is reminiscent of simpler one phase atomic and molecular liquids [1]. With a careful control of the interparticle potential, colloidal systems can, for example, show both gas–liquid and liquid–solid phase transitions [2]. In suspensions of (uncharged) sterically stabilised colloids the interparticle potential is steeply repulsive and has been approximated by a hard sphere interaction [3, 4]. By analogy with the phase behaviour expected for hard spheres of uniform size, and determined largely by numerical simulation [5], suspensions of volume fraction $\xi > \xi_f = 0.494$, the freezing density, are observed to freeze into a translationally ordered crystalline phase. For suspensions of volume fraction $\xi \geq \xi_m = 0.545$, the melting concentration, the equilibrium colloid phase is crystalline. The crystal structure, revealed by light scattering, may be physically realised by the irregular stacking of hexagonally packed layers of particles [6]. The degree of randomness in this structure has been correlated with the rate of crystal nucleation and growth. Colloidal crystals grown slowly, while still containing many stacking faults, show a tendency towards a face centred cubic sequence of layers. At volume fractions intermediate between the freezing and melting concentrations, $\xi_f < \xi < \xi_m$, experiments demonstrate that colloidal fluid (of density ξ_f) coexists with a crystalline phase (of density ξ_m). In concentrated suspensions, $\xi > \xi_g \approx 0.58$, a glass transition occurs [7] and suspensions prepared at or above this density remain amorphous.

If colloidal spheres of two different diameters are mixed, the situation becomes much more complicated. Although colloidal hard spheres are expected to be completely miscible in a single fluid phase [8], a binary mixture of spheres can, in principle, exist in

Table 1. The maximum diameter ratio of the sphere that can fit into various interstitial sites in a FCC or HCP lattice occupied by larger spheres at a volume fraction ξ . At $\xi = 0.7405$ the larger spheres are close packed. The maximum diameters at $\xi = 0.545$, the single component hard sphere melting density [5], illustrate the extent of the expansion of the interstitial sites at melting.

Volume fraction ξ	Octahedral	Tetrahedral	Triangular
0.7405	0.414	0.225	0.155
0.545	0.566	0.356	0.279

any one of a wide variety of solid phases. We shall distinguish between three distinct classes of crystalline solids: (i) a substitutionally disordered binary crystal in which each colloidal component is distributed largely at random on a common lattice, (ii) an ordered binary crystal in which each component lies on a crystalline sublattice, and finally (iii) a pure component crystal. The relative stability of these phases depends both upon the thermodynamic variables, which for colloidal systems are most conveniently chosen as the overall volume fraction ξ and the number fraction x_1 of species 1, as well as the relative hard sphere diameter ratio $\gamma = \sigma_2/\sigma_1$ (with the larger sphere labelled as species 1 so $\gamma \leq 1$). The stability of the face centred cubic substitutionally disordered phase has been explored in the recent work of Barrat *et al* [9] using approximate density functional methods. In particular these calculations predict that mixtures of hard spheres of diameter ratio $\gamma < 0.92$ are no longer miscible in all proportions in a single solid phase. Freezing occurs with segregation into a crystal containing predominantly small spheres and a second crystalline phase rich in large spheres. As the size ratio is lowered still further, towards $\gamma = 0.85$, the solubility of large spheres in the crystal of smaller spheres shrinks to zero. The calculation however predicts that, at $\gamma = 0.85$, the crystal rich in large spheres still contains an appreciable fraction (up to 25% by number) of small spheres. For $\gamma < 0.85$, the substitutional crystal was reported to be mechanically unstable over a wide range of intermediate compositions and nearly complete solid state immiscibility was predicted.

For spheres of very dissimilar diameters (γ say less than 0.85) the possible formation of ordered solid phases must also be considered. Unfortunately, even for a specific solid composition, there is a very wide variety of possible crystal symmetries. On purely geometric grounds however, we expect crystals geometrically related to interstitial close packed structures to be particularly important. With large spheres in a close packed FCC or HCP structure at a volume fraction $\xi_{cp} \approx 0.7405$ (so that the particles are necessarily touching) there are octahedral holes which can accommodate spheres of diameter ratio 0.414 and smaller tetrahedral holes that can only accommodate spheres of diameter ratio 0.225. Occupying all of the octahedral holes, for example, gives structures geometrically related to either the NaCl structure, if the close packed layers are FCC, or NiAs if the sequence of layers is HCP. A variety of other important crystallographic structures (for example, wurtzite and zinc blende, see [10]) may be derived from either complete or partial occupancy of the octahedral and tetrahedral interstitial sites. At melting, $\xi = 0.545$ and the lattice of the larger spheres is expanded with an increase in the size of the interstitial holes. The largest size of the smaller particle that can be introduced into these interstitial holes at $\xi = 0.545$ is estimated in table 1 as $\gamma \approx 0.57$. Although a perturbation

calculation [11] has demonstrated that the interatomic distance in the large sphere crystal coexisting with a fluid phase will increase upon addition of a smaller component, the effect is small with approximately a 1% reduction in density for $\gamma = 0.1$. Molecular dynamics calculations [11] for larger diameter ratios, similarly conclude that the large sphere crystal cannot be stabilised to an appreciably lower density than the pure system by introducing a second interstitial component. Consequently hard sphere mixtures of diameter ratio $\gamma > 0.57$ seem unlikely to form stable interstitial compounds.

Murray and Saunders [12] have explored the stability of several non-interstitial binary structures which are geometrically related to ordered crystalline phases observed in metallic alloys. The authors argue that a space filling principle alone determines the relative stability of binary crystals with a mixture of hard spheres preferentially freezing into a binary structure which maximises the total packing fraction. Apart from a series of interstitial structures at $\gamma < 0.46$, only two arrangements related to the AIB_2 and $NaZn_{13}$ structures have maximum volume fractions greater than the volume fraction ξ_{cp} of the separate close packed phases. For $\gamma > 0.62$ both binary crystal structures are expected to be unstable with respect to a solid state phase separation. Parthé [13] has also calculated the space filling characteristics of the $NaCl$, ZnS , $CsCl$, $NaTi$, $NiAs$, WC , CaF_2 and the Laves (e.g. $MgCu_2$) structures. For $\gamma > 0.62$ none of the phases examined by Parthé have maximum volume fractions which exceed the monodisperse close packed density ξ_{cp} . Consequently Murray and Saunders conclude that for $\gamma > 0.62$ mixtures of hard spheres segregate into two pure crystalline phases.

The prediction of large regions of solid immiscibility has been confirmed in a recent experimental study [14] of the crystallisation of mixtures of colloidal poly(methyl methacrylate) spheres of diameter ratio $\gamma = 0.61$. Colloidal suspensions prepared at either end of the composition range ($x_1 \sim 0$ or $x_1 \sim 1$) froze with almost complete segregation into crystals of each pure component. The solubility of small spheres in the crystal of large spheres was estimated at less than 1%. In metallic alloys this degree of solid immiscibility is often accompanied by the formation of a deep eutectic at which point the fluid freezing temperature is a minimum. The depth of this eutectic has been correlated with the enhanced glass forming tendency observed in metallic alloys at the eutectic composition [15]. Consistent with these observations, mixtures of intermediate composition formed homogeneous disordered solids with dynamic structure factors characteristic of colloidal glasses. In a narrow range of compositions the binary compound AB_{13} (where A refers to the larger colloidal species) was found although later experiments [16] have demonstrated this crystal is metastable and might be associated with the proximity of the experimental diameter ratio ($\gamma = 0.61$) to the crystal phase boundary at $\gamma = 0.58$ where Murray and Saunders [12] predict a stable $NaZn_{13}$ structure.

Qualitatively similar phase behaviour has also been observed in binary suspensions of charged colloids although the softness of the screened Coulombic potential appropriate to these systems precludes a direct comparison with hard spheres colloids. Hachisu *et al* [17], for example, has directly observed with light microscopy the segregation of 1 μm poly(styrene) spheres during the crystallisation of spheres of 300 or 600 nm in diameter. Values for the relative number fraction were not given in this work but it is apparent from their photographs that the small spheres were in excess (i.e. $x_1 \approx 0$). Lindsay and Chaikin [18] observed glass formation in suspensions of equal numbers of poly(styrene) spheres of diameters 220 and 109 nm. For the same colloidal mixture calculations [19] found no stable substitutional alloys apart from small regions of composition near $x_1 = 0$ and $x_1 = 1$. At intermediate compositions the liquid phase remained stable up to a higher number density in the mixture than in the individual pure suspensions consistent with the experimental observation of glass formation.

The purpose of this paper is to describe an approximate model for the phase behaviour of hard sphere suspensions containing two different sizes of spheres. The exact form of the phase diagram in binary mixtures of hard spheres must await detailed numerical simulation studies. However since this study is principally concerned with the qualitative form of the phase diagram it is convenient (and as the discussion above indicates realistic in mixtures of diameter ratio $0.62 < \gamma < 0.85$) to assume total immiscibility of each species in a single solid phase. Section 2 describes in detail the methods used in the present calculations. Section 3 presents phase diagrams for hard sphere mixtures of diameter ratio $\gamma = 0.85$ and 0.65 . For ease of comparison with experiments on colloidal systems, which are normally conducted at constant volume, the phase diagrams are given in terms of component densities. The constant volume phase diagram contains a eutectic region in which the binary fluid is stable to a particularly high density. By correlating the enhanced fluid stability found in the eutectic region with ease of glass formation we predict the composition of binary suspensions which will most readily form colloidal glasses. Finally in section 4 we make a few concluding remarks.

2. The model system

We model the colloidal system by a binary mixture of hard spheres of diameters σ_1 and σ_2 where we adopt the convention $\sigma_1 > \sigma_2$. In the following we shall assume freezing of a binary suspension occurs, at all compositions, with complete segregation to give stable FCC crystals of each pure component. In fact, recent measurements [6] have indicated that the actual structure of crystals of hard colloidal spheres is a strongly faulted sequence of hexagonal planes of particles. However it seems likely that the difference in free energies between this structure and FCC are very small. Indeed, several calculations [20] have suggested that for hard spheres the difference in free energy per particle between the two simplest periodic close packed structures, FCC and HCP, is of the order of 2×10^{-3} kT or less. Consequently we shall confine ourselves to considering only freezing into FCC crystals. The phase diagrams for freezing into the other close packed structures are expected to be very similar.

At thermodynamic equilibrium, under conditions of constant temperature T and external pressure P , the chemical potential of each component is constant throughout all phases. A binary colloidal suspension consists of three components: the suspension medium (labelled as component 0) and two colloidal species (labelled as 1 and 2). To a good approximation the total volume of a colloidal suspension is a constant independent of the specific arrangement of the colloidal species. Correspondingly the partial molar volume of the suspension medium (\bar{V}_0) will be approximately identical in all colloidal phases. This assumption is justified by the low compressibility of the suspension medium compared with the corresponding ease of compression of an assembly of colloidal particles. The chemical potential of the suspension medium (μ_0) is given by the expression

$$\mu_0 = \mu_0^{\circ} - \Pi \bar{V}_0 \quad (1)$$

where μ_0° is the chemical potential of the suspension medium in the absence of colloidal particles and Π is the osmotic pressure. Equation (1) demonstrates that equality of the chemical potential of the suspension medium in coexisting phases is assured by conditions of constant osmotic pressure.

The osmotic pressure of a binary fluid of colloidal hard spheres may be accurately, but not exactly, represented by the expression of Mansoori *et al* [21]. For a fluid of N_1 particles of component 1 and N_2 particle of component 2 in a volume V_f the osmotic pressure (in dimensionless units) is given by

$$\frac{\Pi_f V_f}{(N_1 + N_2)kT} = \frac{1 + \xi + \xi^2 - 3\xi(y_1 + \xi y_2) - \xi^3 y_3}{(1 - \xi)^3}$$

$$y_1(x_1\sigma_1^3 + x_2\sigma_2^3) = x_1x_2(\sigma_1 - \sigma_2)^2(\sigma_1 + \sigma_2)$$

$$y_2(x_1\sigma_1^3 + x_2\sigma_2^3)^2 = x_1x_2\sigma_1\sigma_2(\sigma_1 - \sigma_2)^2(x_1\sigma_1^2 + x_2\sigma_2^2)$$

$$y_3(x_1\sigma_1^3 + x_2\sigma_2^3)^2 = (x_1\sigma_1^2 + x_2\sigma_2^2)^3$$
(2)

where ξ is the total volume fraction

$$\xi = \eta_1 + \eta_2$$

$$\eta_i = \frac{\pi}{6} \sigma_i^3 \left(\frac{N_i}{V_f} \right) \quad \text{with } i = 1 \text{ or } 2$$

and x_1, x_2 are the number fractions of big and small spheres respectively

$$x_1 = \frac{N_1}{N_1 + N_2}; \quad x_2 = \frac{N_2}{N_1 + N_2}.$$

This is a generalisation to mixtures of the average of the compressibility and virial solutions of the Percus–Yevick integral equation which for a system of uniform hard spheres leads to the well tested Carnahan and Starling [22] equation of state. For a diameter ratio of $\gamma = 0.6$ the equation of state of Mansoori *et al* has been tested against Monte Carlo and molecular dynamics simulations by Smith and Lea [23] at low densities and Jackson *et al* [24] at high densities. Both are in good agreement with the equation of state of Mansoori *et al* although small deviations were found at very high fluid densities $\xi > 0.52$.

The Helmholtz free energy A_f of a binary fluid of hard spheres is obtained by integrating the equation of state, (2). Differentiation of A_f gives the chemical potential $\mu_i(f)$ of component i in the hard sphere fluid as

$$\frac{\mu_i(f)}{kT} = \frac{\mu_i^{\circ}}{kT} + \frac{3}{2}(\theta_1 - \theta_2 - \theta_3 - 1) + (\theta_3 - 1) \ln(1 - \xi) + \frac{2\theta_3 + 3\theta_2}{1 - \xi}$$

$$+ \frac{3(1 - \theta_1 - \theta_2) - \theta_3}{2(1 - \xi)^2} + \left(\frac{\eta_i}{x_i} \right)$$

$$\times \left[\frac{1 - y_3}{1 - \xi} + \frac{2y_3 + 3y_2}{(1 - \xi)^2} + \frac{3(1 - y_1 - y_2) - y_3}{(1 - \xi)^3} \right]$$
(3)

where $\theta_j = y_j + N(\partial y_j / \partial N_j)$ for $j = 1, \dots, 3$ and $\mu_i^{\circ}/kT = \ln[(N_i/V)(2\pi\hbar^2/m_i kT)^{3/2}]$ is the ideal gas (kinetic) part of $\mu_i(f)$.

Molecular dynamics calculations of the (osmotic) pressure Π_s of a FCC crystal of volume V_s containing N_i uniformly sized hard spheres of diameter σ_i has been parametrised by Alder *et al* [25] in the form

$$\Pi_s V_s / N_i kT = 3/(V^* - 1) + 2.566 + 0.55(V^* - 1) - 1.19(V^* - 1)^2$$

$$+ 5.95(V^* - 1)^3$$
(4)

where the reduced volume $V^* = V_s/V_0$ and V_0 is the close packed volume $N_i\sigma_i^3/\sqrt{2}$. Although this expression lacks a theoretical basis, agreement between the fitted results and calculations is accurate to better than 0.5%. The corresponding chemical potential $\mu_i(s)$ of component i in the high density solid phase is given by the expression

$$\mu_i(s)/kT = \mu_i^*/kT - 3 \ln(V^* - 1) + 9.124 \ln V^* - 9.52V^{*2} + 3.966V^{*3} + 3V^*/(V^* - 1) + C_0. \quad (5)$$

The dimensionless integration constant C_0 is determined from the molecular dynamics calculation of the fluid–solid phase transition in a one-component system [5]. With $C_0 = 6.5794$, freezing occurs for volume fractions $0.4954 \leq \eta_i \leq 0.5478$ at a reduced (osmotic) pressure $\Pi^* = 8.431$, where $\Pi^* = \Pi V_0/(N_i kT)$, in close agreement with computer predictions [5].

With the assumption of complete immiscibility, the constant volume phase diagram contains a three-phase eutectic region which separates the two regions of fluid–solid equilibrium in which a binary fluid coexists with a single crystalline phase of either component 1 or 2. In the three-phase region, a fluid of eutectic composition is in equilibrium with both a crystalline phase of component 1 and a second crystalline phase of component 2. Within this region the osmotic pressure is fixed.

In the two-phase coexistence region a binary fluid is in equilibrium with a crystal of, for example, component 1. The phase behaviour, at a fixed temperature, is determined by two equilibrium conditions between the fluid phase (characterised by the partial volume fractions $\eta_1(f)$ and $\eta_2(f)$) and the crystalline phase (characterised by $\eta_1(s)$), namely:

$$\Delta\mu_1 = \mu_1(s) - \mu_1(f) = 0 \quad \Delta\Pi = \Pi_s - \Pi_f = 0. \quad (6)$$

Further relations needed arise from the conservation of the volumes of the individual colloid species. If R_1 is the ratio of the volume of the crystalline phase of component 1 to the volume of the system then it is easily seen that

$$R_1 = \frac{V_s}{V_s + V_f} = \frac{\eta_1 - \eta_1(f)}{\eta_1(s) - \eta_1(f)} = \frac{\eta_2(f) - \eta_2}{\eta_2(f)} \quad (7)$$

where η_1 and η_2 are the initial partial volume fractions (before crystallisation and phase separation has occurred). The four equalities in (6) and (7) can now, in principle, be solved for the unknown variables $\eta_1(f)$, $\eta_2(f)$, $\eta_1(s)$ and R_1 given the diameter ratio γ and the initial volume fractions η_1 and η_2 . Rearranging (7) into the expression

$$\eta_2 = \eta_2(f)\eta_1(s)/(\eta_1(s) - \eta_1(f)) - \eta_1[\eta_2(f)/(\eta_1(s) - \eta_1(f))] \quad (8)$$

demonstrates that the set of initial states $\{\eta_1, \eta_2\}$ which at equilibrium phase separate into a fluid phase of partial densities $\{\eta_1(f), \eta_2(f)\}$ and a crystalline phase of volume fraction $\eta_1(s)$ lie on a straight line connecting the points $(\eta_1(f), \eta_2(f))$ and $(\eta_1(s), 0)$. Equation (7) shows that by representing the phase behaviour in the (η_1, η_2) plane the equilibrium volume of each phase is given by the conventional inverse lever rule construction.

The phase behaviour within the three phase eutectic region may be calculated by similar procedures. Equation (6) is now supplemented by the two equivalent conditions of equilibrium for a second crystalline phase consisting solely of component 2. The four equilibrium conditions together with the two additional relations expressing the conservation of volume (similar to (7)) may be solved for the six unknown variables

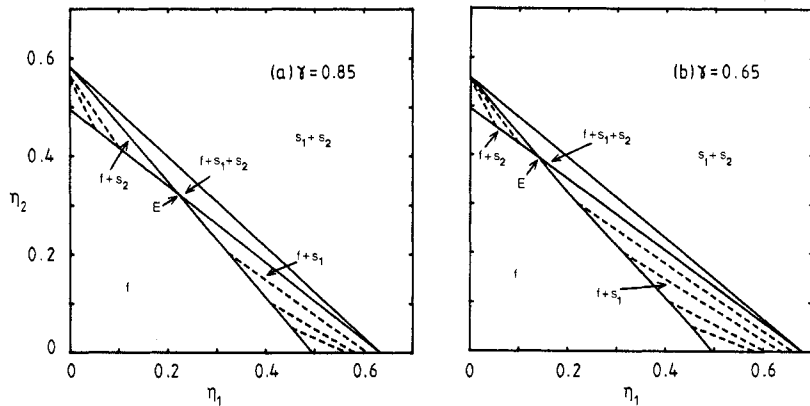


Figure 1. Phase diagrams for binary mixtures of hard spheres of diameter ratio (a) 0.85, and (b) 0.65. η_1 and η_2 are the volume fractions of species 1 (larger spheres) and species 2 respectively. The full lines give the phase boundaries. The dashed lines represent the compositions of coexisting fluid and crystal phases. The eutectic fluid is marked by E . The labels f , s_1 and s_2 refer to fluid, solid phase of species 1 and the solid phase of species 2 respectively.

which characterise the coexisting fluid ($\eta_1(f)$, $\eta_2(f)$), the density of the crystalline phase of component 1 ($\eta_1(s)$) and that of component 2 ($\eta_2(s)$) and the fractional volumes of the crystalline phases of component 1 (R_1) and of component 2 (R_2). In a representation of the constant volume phase diagram in the (η_1, η_2) plane the phase volumes R_1 and R_2 have a simple geometric interpretation. The three phase eutectic region is represented by the interior of a triangle formed by linking together the three points corresponding to the compositions of the three coexisting phases. The volume of, for example the fluid phase, is proportional to the area of the internal triangle formed by joining the point representing the initial composition to the two vertices corresponding to the two remaining phases (crystal 1 and crystal 2).

3. Results

Figure 1 shows the projection on the (η_1, η_2) plane of the phase diagrams for a binary mixture of hard spheres of diameter ratio $\gamma = 0.85$ and 0.65 . In these figures suspensions of a constant composition x_1 correspond to points along a straight line radiating from the origin while lines which intersect both the η_1 and η_2 axes at 45 degrees describe suspensions of constant total volume fraction $\xi = \eta_1 + \eta_2$. Within the regions of fluid–solid coexistence fractionation takes place, the extent of which depends on the initial densities (η_1, η_2) of the suspension (before phase separation has occurred). The composition of the phase separated binary fluid and crystal phases are depicted in figure 1 by the set of dashed tie lines. To illustrate the sequence of phase behaviour consider a suspension of fixed composition x_1 which lies within the region of fluid–solid 1 coexistence shown in figure 1. With increasing total volume fraction ξ the suspension separates into a fluid which becomes progressively depleted in component 1 together with an increasing volume of crystal 1. The densities of the coexisting fluid and crystal phases depend both on the initial volume fraction ξ and the initial composition x_1 . At a sufficiently high total

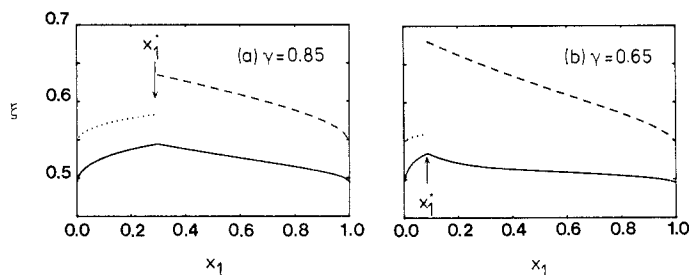


Figure 2. The total volume fraction ξ of the fluid phase (solid line), crystals of species 1 (dashed line) and the crystals of species 2 (dotted line) at phase coexistence for a hard sphere mixture of diameter ratio (a) 0.85, and (b) 0.65. The total volume fraction ξ of the initial suspension (before phase separation occurred) was fixed at the equilibrium eutectic fluid volume fraction of (a) $\xi = 0.544$, and (b) $\xi = 0.533$. x_1 is the molar number fraction of species 1 (larger sphere) in the initial suspension. x_1^* labels the eutectic composition.

volume fraction the composition of the equilibrium fluid phase becomes equal to the eutectic fluid composition (point E in figure 1) and a second crystalline phase of component 2 appears. With further increase in the initial volume fraction the compositions and densities of the three coexisting phases remain unchanged but the relative volume of the fluid phase shrinks. Finally suspensions of still higher total volume fraction fully crystallise into two solid phases.

The calculations show that the fluid freezing volume fraction ξ_f depends on the initial composition x_1 and is a maximum at the eutectic fluid composition (point E in figure 1). To illustrate this point more clearly figure 2 shows the densities of equilibrium phases formed from an initial suspension with the same total volume fraction ξ as the eutectic fluid as a function of initial suspension composition x_1 . The maximum in the freezing density versus x_1 curve indicates that the fluid phase remains stable to a higher density in the mixture than in the pure case. We shall show below that this maximum in the freezing density is equivalent to a minimum in the freezing temperature. The maximum freezing density occurs in small particle rich mixtures at a composition x_1^* which decreases sharply with decreasing particle diameter ratio. For example at $\gamma = 0.85$ the present calculation predicts a eutectic fluid composition of $x_1^* \approx 0.29$ while for $\gamma = 0.65$ this has reduced to $x_1^* \approx 0.09$.

From figure 2 it is apparent that crystals formed from a binary suspension are compressed relative to the pure component case. The increase in density is most marked for the crystal of larger spheres (component 1) and is strongly dependent on the initial suspension composition x_1 . Note that there is a maximum in the melting density ξ_m versus x_1 curve at the eutectic region demonstrating that the crystal phase becomes unstable at a higher density in the mixture than in the pure case. In addition the increase in density of the crystal of component 1 becomes more pronounced as the diameter ratio is progressively decreased. For example, for crystals of component 1 in the eutectic region, the density increases from $\xi \approx 0.63$ at a diameter ratio $\gamma = 0.85$ to $\xi \approx 0.68$ in mixtures of $\gamma = 0.65$. The crystals of smaller spheres (component 2) however show the opposite trend. The density at the eutectic point reduces as the diameter ratio decreases and the composition of the eutectic fluid shifts towards $x_1 \approx 0$.

Finally we note that for hard spheres the phase behaviour is a unique function of the ratio of temperature to osmotic pressure. At a constant osmotic pressure Π this ratio

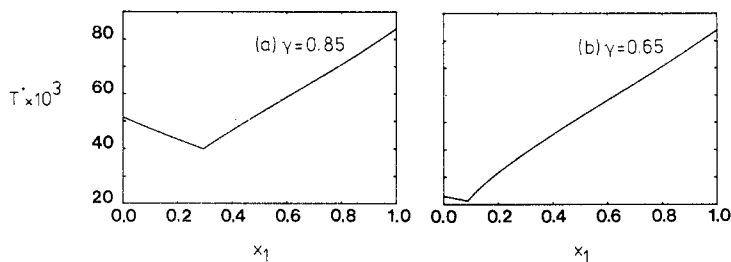


Figure 3. Reduced temperature (T^*)-composition phase diagram for binary hard sphere mixtures of diameter ratio (a) 0.85, and (b) 0.65. The reduced temperature is expressed in units of $\Pi\sigma_1^3/k$ where σ_1 is the diameter of the larger sphere. x_1 is the number fraction of larger spheres in the initial suspension.

defines an effective temperature $T^* = kT/\Pi\sigma_1^3$ where σ_1 is the diameter of the larger sphere. In figure 3 the effective freezing temperature is plotted as a function of suspension composition for mixtures of diameter ratio $\gamma = 0.85$ and 0.65 . This representation of the hard sphere phase behaviour is akin to the conventional temperature-composition phase diagrams commonly used in metallurgy for example. Figure 1 shows the equivalent constant volume representation which as the discussion above illustrates is much more relevant to colloidal systems. Comparison between figures 2 and 3 illustrates the correspondence between the maximum fluid freezing density found at the eutectic and the minimum in the equilibrium freezing temperature.

4. Concluding remarks

The aim of this work is to describe an approximate model for the freezing of a binary mixture of colloidal hard spheres. The different sized colloidal species are assumed to be immiscible, in all proportions, in a single crystalline phase. Freezing proceeds with complete segregation to give two distinct crystalline phases. The boundaries between the fluid and crystalline phases have been calculated from accurate statistical equations of state for both the binary hard sphere fluid [21] and the single component hard sphere crystal [25]. Calculations are reported for mixtures of diameter ratio $\gamma = 0.85$ and 0.65 . This model, although simple, contains the basic physics of the problem. All expressions for the chemical potentials are analytic and allow the phase behaviour to be readily represented either in a constant pressure or constant volume phase diagram. For colloidal systems, experiment [14] demonstrates that the constant volume phase diagram is most relevant.

The calculations indicate that the fluid phase remains stable to a higher density or equivalently a lower effective temperature in the mixture than in the pure case. The maximum freezing density occurs in a fluid of eutectic composition in which the number of smaller spheres exceeds the number of larger spheres. With decreasing diameter ratio the eutectic composition shifts towards increasingly small particle rich mixtures. The enhanced stability of the fluid at the eutectic suggests that a binary glass will be most readily formed in suspensions with the eutectic composition. The preferential formation of a high density glass has important practical consequences, for example, in colloidal ceramic processing where a high 'green' compact density is desired. Sintering experiments [26] on binary mixtures of spheres have demonstrated that the microstructure of

the 'green' compact is crucial to producing ceramics containing small sized defects. Samples with large crystalline domain boundaries developed cracks during sintering. In contrast disordered glassy structures sintered homogeneously to give a ceramic free of large flaws.

Finally we point out that the predictions of the present model are in qualitative (and for several aspects quantitative) agreement with recent experiments [14] on the phase behaviour of mixtures of colloidal hard spheres. Suspensions prepared with compositions either rich in component 1 ($0.66 \leq x_1 \leq 1.00$) or rich in component 2 ($0 \leq x_1 \leq 0.057$) separated, at volume fractions $\xi_f < \xi < \xi_m$, into a pure crystalline phase and a coexisting colloidal fluid. Experimental values of the coexisting crystal density and phase volume were in very close accord with the predictions of the present model for hard spheres mixtures of diameter ratio $\gamma = 0.61$. In suspensions of intermediate composition, close to the predicted eutectic point at $x_1 = 0.067$, crystallisation was totally suppressed at all volume fractions. Although binary glasses may be formed at any composition (at a sufficiently high density) glass formation is expected from thermodynamic considerations to be easiest in the vicinity of a eutectic. The absence of crystallisation at intermediate compositions is therefore in qualitative agreement with the present prediction of the eutectic position. However, clearly to test the present model in greater detail will require a very careful study of a colloidal binary phase diagram.

Acknowledgments

I am particularly indebted to P N Pusey and R H Ottewill for a number of very useful discussions and comments on various aspects of this work.

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