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## Colloidal fluids, crystals and glasses

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**Abstract.** Various aspects of the behaviour of essentially hard spherical colloidal particles, suspended in a liquid, are outlined. We consider the phase behaviour and crystal structure of one- and two-component suspensions and the glass transition of a one-component system.

### 1. Introduction

Assemblies of hard spheres have played an important role in the development of theories for the liquid and solid states [1]. Hard-sphere atoms do not, of course, exist in reality and can only be studied by computer simulation. However one can prepare colloidal particles whose interaction, when they are suspended in a liquid, closely approximates that of hard spheres. The thermodynamic properties (phase behaviour, structure, etc) of such suspensions should be the same as those of the hypothetical hard-sphere atomic system [2]. The dynamic properties of colloids in suspension are fundamentally different from those of classical atoms, being described by Langevin equations rather than by Newton's second law. Nevertheless, at long times, where the particles or atoms have undergone many collisions, interesting similarities between the dynamics of the two systems have been found [2, 3].

Here we describe several recent studies of suspensions of hard-sphere colloids. The treatment is, perforce, sketchy and the literature cited can be consulted for more detail. We consider the phase behaviour and structure of both one-component (section 2) and two-component (section 3) suspensions. In section 4 the dynamics of particle diffusion in concentrated metastable fluid-like and glassy suspensions are described.

The particles used for these studies consisted of 'cores' of colloidal polymethylmethacrylate (PMMA), stabilized sterically by thin (10–15 nm) chemically grafted layers of poly-12-hydroxystearic acid. Their radii were in the range 170–330 nm. The suspension medium was a mixture of decalin and carbon disulphide in proportion chosen to have a refractive index which nearly matched that of the particles ( $\approx 1.50$ ). The resulting samples were nearly transparent and were thus suitable for direct observation and light scattering studies; they showed strong single scattering of light but only weak multiple scattering. Because of this refractive-index matching, van der Waals attractions between the particles are expected to be negligible; the interaction between two particles

appears to be steep and repulsive (i.e. approximately hard-sphere), arising from the compression of their polymer coatings on close approach. We do not believe that the relatively small polydispersity of the particles,  $\approx 4\%$ , seriously affected the measurements described below; thus the particles can be regarded as effectively monodisperse.

## 2. Phase behaviour and structure of one-component suspensions

The expected phase behaviour of assemblies of hard spheres has been established largely by computer simulation [4, 5]. For volume or packing fractions  $\phi$  below the freezing concentration,  $\phi_F = 0.494$ , the equilibrium state is fluid whereas at concentrations above that,  $\phi_M = 0.545$ , of melting it is crystalline [4]. If the system is compressed rapidly enough to avoid crystallization, long-lived metastable amorphous or glassy states are found above a 'glass transition' concentration,  $\phi_G = 0.58\text{--}0.60$  [5]. Several experimental studies (e.g. [6] and [7]) of the phase behaviour of the PMMA suspensions described above have found reasonable agreement with these predictions. Slow tumbling or shaking of samples, prepared over a range of concentrations which spanned both the freezing and glass transitions, drove them into metastable fluid states. Left undisturbed, samples at concentrations  $\phi_F < \phi < \phi_G$  showed homogeneous nucleation of the crystallization at random sites throughout their bulk. Polycrystalline phases containing many randomly-oriented crystallites were formed over periods of time ranging from minutes to hours. At  $\phi_F < \phi < \phi_M$  this (lower) polycrystalline phase, with  $\phi = \phi_M$ , coexisted with an (upper) colloidal fluid phase, with  $\phi = \phi_F$ . In samples with  $\phi > \phi_G$  only partial slow crystallization, nucleated heterogeneously at the sample surfaces, was observed.

Light scattering measurements of the static structure factors of fluid-like samples at  $\phi < \phi_F$  show reasonable agreement with those expected for hard spheres [8]. To study the crystal structure a laser beam was expanded to illuminate about  $1\text{ cm}^3$  of the sample; this volume contained at least  $10^6$  crystallites of typical dimension  $25\text{--}50\ \mu\text{m}$ . The structure factors obtained by this light-scattering analogue of powder crystallography had rather unusual forms for a crystal, comprising not only sharp Bragg reflections but also broad, but structured, bands of diffuse scattering [9]. We have established that these structure factors are consistent with a 'random-stacked close-packed' structure for the crystalline state of hard spheres [9]. Hexagonally arranged layers of particles are stacked in an essentially random sequence, e.g. . . . ABACBCBA . . . , of allowed lateral positions A, B, C; the faulted stacking is responsible for the diffuse scattering. This structure can be compared with the common close-packed structures of atomic systems, face-centred cubic, . . . ABCABC . . . , and hexagonal closed packed, . . . ABABAB . . . . Evidently the short range of the hard-sphere potential precludes significant 'communication' between next-nearest neighbours.

## 3. Phase behaviour and structure of two-component suspensions

In the experimental study of binary mixtures a large parameter space must be covered: as well as the total concentration, the number ratio of the two species can be varied as can, in principle, the size ratio. We have performed a fairly extensive study of a mixture of large, A, PMMA spheres, radius  $\approx 330\text{ nm}$ , and smaller, B, spheres, radius  $\approx 200\text{ nm}$ , corresponding to a size ratio of about 0.61 [10]. Samples were prepared having total volume fractions between about 0.50 and 0.62, where crystallization might be expected

to occur, at some 15 different number ratios. A variety of different phenomena was observed.

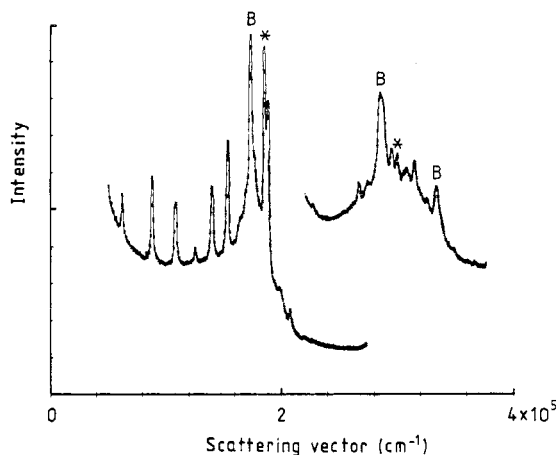
When B particles were added to a suspension containing predominantly A particles the behaviour resembled superficially that of the one-component system except that the rate of crystallization was increasingly slowed. At appropriate values of the total concentration, coexisting crystalline and fluid phases were found. However, analysis of the phases, by light scattering and by electron microscopy of the dried materials, revealed that the crystalline phase was composed almost entirely of the larger A particles whereas the fluid phase was enriched in B particles. This behaviour persisted up to number ratios,  $n_B/n_A$ , of about one. On the addition of A particles to a suspension of pure B particles, similar but reversed behaviour was found over a limited range of number ratio,  $n_B/n_A \geq 16$ : the crystalline phase was essentially pure B. Thus for  $n_B/n_A \leq 1$  and  $\geq 16$  there appears to be almost complete immiscibility of the particles in the crystalline phases but, it seems, complete miscibility in the fluid phases. Since reasonably accurate equations of state are known for one-component hard-sphere crystals and two-component hard-sphere fluids it is possible to calculate a theoretical phase diagram for this situation [11]. For the quite extended region  $n_B/n_A < 1$  good agreement was found between the experimentally measured and theoretically predicted values of such quantities as the concentration of the crystals and the amounts of crystalline phase [10].

For  $6 \geq n_B/n_A \geq 1.5$  no crystallization of the mixture was observed, over several weeks of observation, at any value of the total concentration. The samples remained either in equilibrium fluid or glassy states.

What is probably the most intriguing behaviour was found in a limited region of the phase diagram where  $10 \leq n_B/n_A \leq 16$  and the total volume fraction of both species ranged from 0.52 to 0.54. Here we concentrate on a sample for which  $n_B/n_A \approx 13$  and  $\phi \approx 0.54$ . After tumbling to randomize the particle positions, this sample separated into coexisting fluid and apparently crystalline phases within a day or two. Measurement of the structure of the latter by powder light crystallography revealed it to contain crystals of pure B particles; however a significant intensity of diffuse scattering at small angles suggested the presence of regions within the solid phase containing particles in amorphous arrangements. Subsequent measurements over a period of months showed the slow growth of a second, complex crystal structure. Figure 1 shows the powder diffraction pattern obtained after about four months. We believe this new structure to be the  $AB_{13}$  superlattice, which consists of a simple cubic array of the larger A particles, body-centred by icosahedrally arranged clusters of thirteen B particles. The icosahedra in adjacent cubic subcells are rotated relative to each other by  $90^\circ$ , so the unit cell consists of eight subcells. The interpretation of figure 1 is described briefly in the caption.  $AB_{13}$  has been observed previously in less well characterized colloidal systems [12, 13]. It seems remarkable that a mixture of hard spheres should spontaneously adopt such an exotic structure. The mechanisms of its nucleation and growth remain to be established as, indeed, does the equilibrium state of the sample; at the time of writing the structure was still changing slowly.

#### 4. The glass transition of one-component suspensions

As was mentioned in section 2, above a certain concentration a one-component suspension of hard-sphere colloids no longer shows homogeneously-nucleated crystallization; this observation suggests the intervention of a glass transition. To investigate



**Figure 1.** Powder light diffraction pattern of a binary mixture of hard-sphere colloids having size ratio 0.61 and containing crystals of both pure B (the smaller component) and the  $AB_{13}$  superlattice structure. The left-hand curve was measured with red light and the right-hand curve, magnified vertically, with blue light; therefore the latter extends to higher values of the scattering vector. The Bragg reflections marked B are from the B crystal and correspond to those common to both face-centred cubic and hexagonal close packed structures (indexed on a cubic lattice they are the 111, 220 and 311 lines). The remaining reflections are consistent with the  $AB_{13}$  structure. Those marked with asterisks indicate that the unit cell of the structure comprises eight cubic subcells.

this possibility further we have studied by dynamic light scattering, DLS, the dynamics of particle diffusion in the metastable fluid (and glassy) states of PMMA suspensions, achieved by tumbling the samples to 'shear-melt' any crystals present [14]. The non-ergodicity of the samples near the glass transition concentration requires special attention to be paid to the treatment of DLS data. Elsewhere we have described methods by which the measured time-averaged correlation function of the scattered light intensity can be analysed to provide the desired ensemble-averaged intermediate scattering function  $F(Q, t)$  (the time correlation function of one spatial Fourier component of the particle number density) [15].

At all concentrations the intermediate scattering functions, determined by these methods, showed initial rapid decays which varied only weakly with concentration and which could be associated with local motions of the particles within the instantaneous 'cages' formed by their nearest neighbours [14]. By contrast, the long-time decays of  $F(Q, t)$  slowed down strongly with increasing concentration, reflecting the restriction of long-distance diffusion by the increasingly tight neighbour cages. At a concentration which corresponds closely to that at which homogeneously-nucleated crystallization was observed to be suppressed  $F(Q, t)$  developed a component which did not decay in the duration, many minutes, of the experimental measurement. We interpret this observation as evidence of the partial 'freezing in' of density fluctuations at the glass transition.

These data have been compared with the predictions of mode-coupling theories applied to simple atomic systems [16], which, because of rapid crystallization, cannot be prepared in controllable metastable states suitable for experimental study. Good agreement is found for both the functional form and the concentration dependence of the intermediate scattering functions.

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