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GRAVITATIONAL EFFECTS ON THE PHASE BEHAVIOUR OF DISPERSIONS[α]

P. BARTLETT and R.H. OTTEWILL[*]

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

ABSTRACT

   Gravity can influence the formation of highly ordered structures from monodisperse polymer colloid systems, i.e. crystallization. These effects are particularly significant in the formation of alloy type crystals from bimodal dispersions. In this situation the use of "time-average" gravity is beneficial for the formation of mixed crystals.

INTRODUCTION

   One of the major advances in the science of colloidal dispersions in the past few decades has been the development of chemical synthetic methods for the preparation of spherical particles, in the colloidal size range — nominally 1 nm to 1 μm, as dispersions with a very narrow spread of particle sizes. Those of particular interest have been polymer latices in both aqueous and nonaqueous environments [1–6] and organophilic silica dispersions for use in nonaqueous media [7]. Whereas in work prior to the 1970s much of it was dedicated to very dilute dispersions, it has been possible with the monodisperse systems to examine both strongly interacting systems [8] and very concentrated dispersions [9]. Simultaneous developments in experimental techniques such as photon correlation spectroscopy [8] and small angle neutron scattering [9] have provided methods for examining the behaviour of concentrated systems in some detail [10]. Furthermore, advances in computer technology have enhanced the possibilities of computer simulations.

   A fundamental property of a colloidal particle is that it moves in a dilute dispersion, in a fluid environment in a random fashion, a process of translational diffusion often termed Brownian motion. The theoretical

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[*]   Corresponding author.

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basis of diffusional motion was first treated by Einstein in 1906 [11]. Subsequently, a very systematic experimental study of this phenomenon was made by Jean Perrin [12]. He deduced from studies of the motion of colloidal particles viewed microscopically, that the random motion provided a proof of the existence of molecules and molecular motion. In fact, a fundamental property of colloid dispersions is that stabilised particles can frequently remain as single dispersed entities for very long periods of time as a consequence of the continued collisions with the solvent molecules of the dispersion medium. Under conditions where the particles are submicron in diameter and not too different in density from that of the medium of reasonable viscosity, then the effects of gravitational forces can be small, or even negligible, and are usually ignored in theories of the stability of lyophobic colloids. However, as particle size increases beyond 1 μm or the density becomes rather greater than that of the medium, then sedimentation or flotation (creaming) under gravitational forces becomes a significant effect and is well-known in the study of emulsions.

Since colloid science is rich in phenomenology, it is pertinent to enquire whether there are areas, other than those mentioned above and well-known in the literature, where the influence of gravitational effects is disadvantageous, and where experiments under zero gravity or micro-gravity conditions could lead to positive results unachievable in a normal gravity environment.

PROPERTIES OF MONODISPERSE PARTICLES

One of the first phenomena noted with spherical particles having a narrow size distribution, particularly with charged polystyrene particles in an aqueous environment with a low electrolyte content, was that when they were irradiated with white light a brilliant iridescence was observed [13–17]. This was explained as a consequence of electrostatic repulsion between the particles leading to the formation of an ordered structure with the centre-to-centre distance between the particles being of the order of the wavelength of light. Thus with white light essentially Bragg reflections were observed over a range of wavelengths and correspondingly the colours changed as the angle of viewing of the sample changed. This phenomenon was investigated by a number of authors [13–17] but can now be regarded as part of a general behaviour pattern of monodisperse systems. The rapid development of scattering techniques, particularly with light and neutron beams, has enabled very quantitative studies

to be made of these systems. In general terms, this can be defined as understanding the correlations between the particles as a function of the interactions between them and the influence of particle volume fraction on the type of structure produced. In physical terms this means determining the pair correlation function defined by,

$$g(r) = 1 + \frac{1}{2\,\pi^2\,rN_p} \int_0^\infty [S(Q) - 1]\, Q \sin Qr\, d\,Q \tag{1}$$

Essentially, $g(r)$ is the probability of finding another particle at a centre-to-centre distance r from a reference particle, where N_p is the average number of particles in the system per unit volume. The other terms in this equation include the scattering vector Q, which has dimensions of reciprocal length, and the structure factor $S(Q)$ defined by:

$$S(Q) = 1 + \frac{4\,\pi\,N_p}{Q} \int_0^\infty r[g(r) - 1] \sin Qr\, dr \tag{2}$$

namely, the Fourier transform of Eqn. (1). Both $g(r)$ and $S(Q)$ are important parameters which can be obtained from scattering experiments on colloidal dispersions [9,20].

   Some results obtained from small angle neutron scattering using polystyrene latex particles with a diameter of 31.2 nm are shown in Fig. 1. At a rather low average number concentration and an electrolyte concentration of 10^{-4} mol dm^{-3} the form of the $g(r)$ against r curve has the profile indicated in Fig. 1, namely that at distances which are long compared with the size of the particle, the probability of finding another particle is unity. However, as the particles approach more closely, strong repulsive interactions occur and the approaching particle becomes excluded from the region of the reference particle. This behaviour is reminiscent of molecules in a gas or vapour phase and suggests that under these conditions, the behaviour of a dilute colloidal dispersion has much in common with that of a gas; however, it should be remembered that the motion of molecules in a gas is ballistic and not Brownian. With an increase in volume fraction at the same electrolyte concentration peaks appear in the curve, as illustrated in Fig. 1, indicating a correlation between the particles and an increase in order in the system. The delay in amplitude of the peaks with increase in r suggests that the order is relatively short-ranged and at long range the system is much less
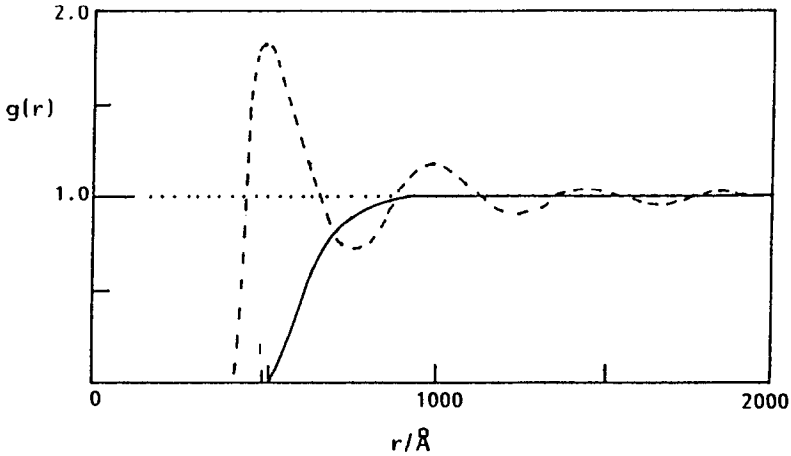
Fig. 1. g(r) against r for polystyrene latex particles (radius = 15.6 nm) in 10^{-4} mol dm^{-3} sodium chloride solution at two volume fractions: 0.01; 0.13.
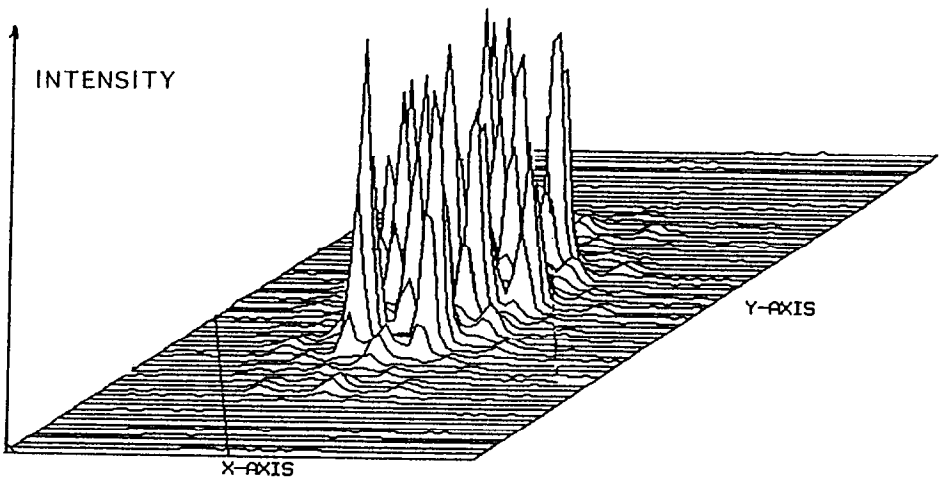

Fig. 2. 3-Dimensional plot of intensity against scattering vector on a 2-dimensional detector, for an ion-exchanged polystyrene latex, diameter 0.20 μm, at a volume fraction of 0.08.

ordered. This g(r) against r behaviour is typical of a "liquid-like" structure of the type seen in molecular liquids such as argon. At higher volume fractions a transition from a "liquid-like" to a crystalline structure can be observed and is illustrated by Fig. 2 which shows the strong diffraction peaks observed by the transmission of a neutron beam through a polystyrene latex sample containing particles of diameter 0.2 μm at a volume

fraction of 0.087 in a solution of low electrolyte concentration [19].

Similar phenomena have been observed with nonaqueous dispersions of poly(methylmethacrylate) stabilised by poly(hydroxy stearic acid) and with organosilica dispersions [7,19,20]. In several ways the nonaqueous environment has advantages over the aqueous environment. This includes the extensive variety of liquids available covering a wide range of polarities and consequently of refractive index. Hence, for both scattering and observational studies it is possible to match the refractive index of the dispersed particles to that of the medium by the use of liquid mixtures. Also, the potential energy of interaction of these particles, normally sterically stabilised, often closely resembles that of hard spheres. This provides an even closer link with molecular behaviour and again, with these systems, analogous states to gases, liquids, crystals and glasses have been observed [20,21].

An additional interesting feature of colloidal systems when compared with molecular systems is the fact that the motion in these various states is slowed down by many orders of magnitude (ca. 10^9) compared with molecules as a consequence of the mass of the particles. This suggests that many of the phenomena which occur very rapidly in the molecular state, e.g. nucleation and crystal growth, might with advantage be studied by using monodisperse spherical colloidal particles, since the time scale of the diffusional processes falls within the range of present-day instrumental techniques [22]. Thus the crystallization process is a particularly interesting one to explore in this context.

CRYSTALLISATION — MONODISPERSE SYSTEMS

The formation of essentially crystalline regions in monodisperse systems has been studied by a number of authors using bulk aqueous and nonaqueous dispersions. Many of these crystals show well-ordered arrangements of particles in the crystallites but stacking faults and dislocations are, as anticipated, frequently observed. Since the crystals are frequently formed at high particle volume fractions, the samples can often be dried and examined by scanning electron microscopy. A typical result is given in Fig. 3.

The rate of crystallisation and the size of the crystals formed appears, so far, to be variable. Often the formation of crystalline regions, as often observed by the brilliance of the iridescent colours, is a slow process. For example, bottles stored on a shelf in laboratory conditions (not necessarily temperature controlled) frequently take days, weeks or even months before colours appear. In a systematic study Pusey and van Megen [20]
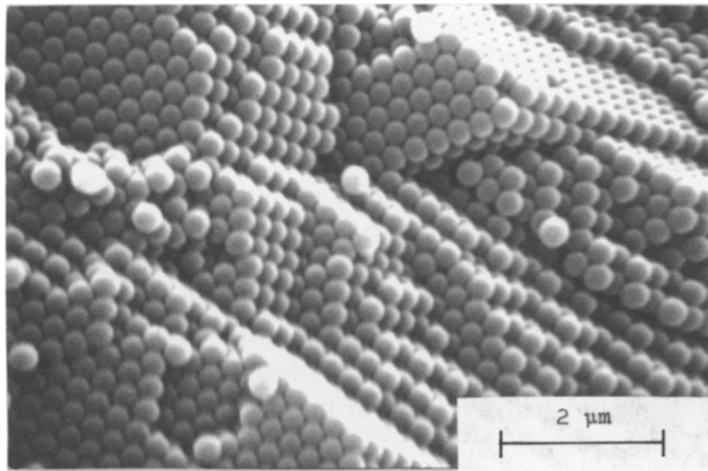
Fig. 3. Scanning electron micrograph of a crystal formed from polystyrene latex particles.

using poly(methylmethacrylate) latices stabilised by poly(12 hydroxy-stearic acid) in a refractive index matching fluid (decalin + carbon disulphide) and volume fractions of ca. 0.5 and greater, i.e. above the freezing volume fraction for hard spheres [23], found that crystallisation took periods of ca. 10 days. The maximum crystal size appeared at a volume fraction of about 0.55 and this seemed to coincide with the fastest rate of crystal growth. Above a volume fraction of ca. 0.6, a glassy state was formed. In this context measurements of self diffusion with a similar system showed that long-time self diffusion essentially ceased at a volume fraction of 0.5, whereas short-time self diffusion continued up to a volume fraction of ca. 0.64, i.e. random close-packing [24]. This is illustrated in Fig. 4.

In the case of aqueous polystyrene latex dispersions. crystallisation is very sensitive to electrolyte concentration. Early workers [16–18] found quite slow rates of crystallisation but from the recent work of Okubo it appears that with dilute dispersions and low electrolyte concentration, crystallites can form quite rapidly [25,26].

These experiments, however, all indicate that colloidal particles crystallise over time scales which are long compared with molecular processes, typically hours to days. Hence, with such slow crystallisation rates, sedimentation of the particles can often be significant over the time period of the experiment. The concentration gradients thus set up can complicate a quantitative examination of colloidal phase behaviour [27] and in extreme cases, gravitational settling can completely bypass the
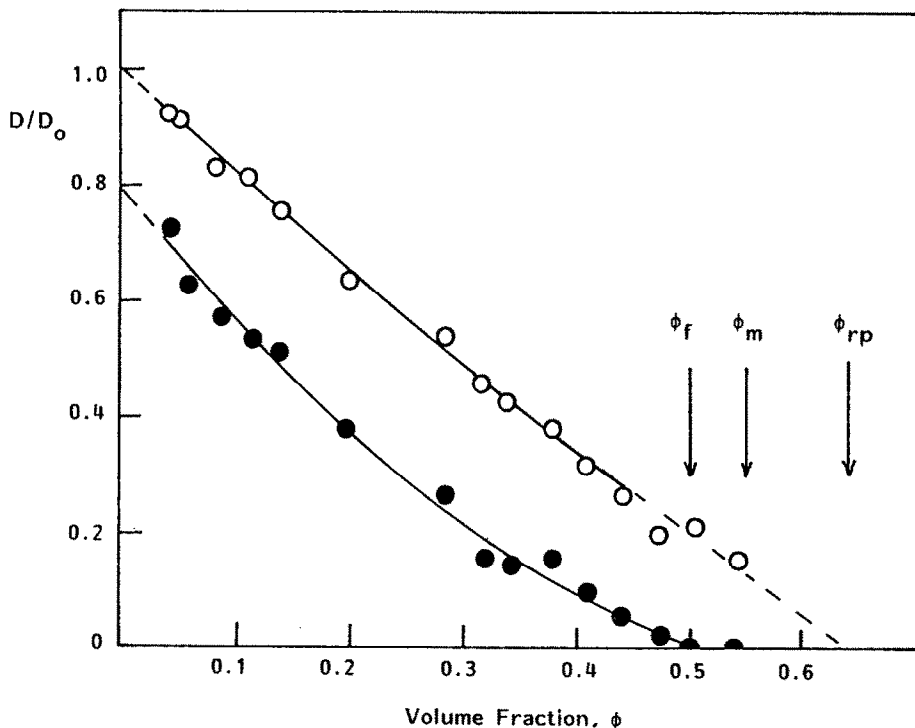
Fig. 4. Ratio of the self-diffusion coefficient, D, normalised by the single-particle diffusion coefficient, D_o, against volume fraction ϕ of a dispersion of polymethylmethacrylate particles stabilised by poly-12-hydroxy stearic acid, in decalin: —●—, long-time self-diffusion coefficient, D_I/D_o; —O— short-time self-diffusion coefficient, D^s/D_o. Volume fractions, ϕ_f, freezing; ϕ_m = melting; ϕ_{rp} = random packing.

freezing–melting transition. In order to obtain a reasonable estimate of equilibrium phase behaviour, the rate of gravitational sedimentation must be sufficiently slow compared with nucleation and growth rates to allow crystallites to form and separate from any co-existing fluid before significant overall sedimentation occurs, otherwise non-homogeneous amorphous sediments can result.

In many of the polymer colloid dispersions investigated containing essentially only one size of particle it appears that the crystallisation rate normally exceeds the rate of gravitational settling. However, in dispersions containing a multimodal distribution of particles, crystallisation can be sufficiently slow to allow sedimentation under gravity to dominate the phase behaviour and lead to dense inhomogeneous sediments. This is particularly the case with binary colloidal dispersions.

BINARY DISPERSIONS — TIME AVERAGE ZERO GRAVITY

As indicated above, crystallisation of colloidal particles depends upon the interplay between translational diffusion and gravitational processes. In the case of binary systems produced by the mixing of two monodisperse systems, where one system contains large particles and the other small, then in the mixture the larger particles will be more subjected to gravitational forces than the smaller ones. Ideally, therefore, in order to study these systems either microgravity conditions are required or the density of the particles and the medium must be matched. The latter condition is not easily attained with sterically stabilised particles, since the larger particles have a much larger core/layer ratio than the smaller ones. It was found, however, that a possible way of simulating time-average zero-gravity conditions was to rotate samples contained in cuvettes in the vertical plane at an angular velocity, ω, so that, averaged over one rotation, the mean sedimentation velocity of a particle (relative to the cell walls) was zero [27]. The optimum angular frequency is determined by a balance between the rate of sedimentation and the magnitude of the rotationally induced shear field within a sample. In fact, ω must be sufficiently large to ensure that composition gradients at any instant of time are not significant over the diameter of a crystallite. Furthermore, ω must also be small enough to ensure that the rotationally induced shear gradient does not significantly distort the equilibrium microstructure.

Experiments on binary systems composed of 670 nm diameter (A) spherical particles admixed with 407 nm diameter particles (B) indicated that an ω of ca. 7×10^{-5} rad s^{-1} (1 resolution per day) was adequate to ensure time-average zero gravity conditions. The dispersions remained homogeneous and crystallisation proceeded throughout the sample. It was also possible to stop the rotational procedure at any time to give normal conditions and thus to separate, if required, the co-existing fluid and highly concentrated phases. For these experiments the particles used were composed of a core of poly(methylmethacrylate) sterically stabilised by poly(12 hydroxy stearic acid); the dispersion medium was a mixture of cis-decalin and carbon disulphide in order to give a near refractive index match of the particles to the medium. The overall volume fraction of the particles, $\phi_A + \phi_B$, was 0.566 with a mixing ratio of AB$_{32}$. After slow rotation for 138 days the scattered intensity, shown in Fig. 5, was found to be the same at all positions in the dispersion, i.e. at all levels over approximately a 2.5 cm depth of the dispersion in a cuvette. The measured intensity as a function of scattering vector is consistent with a
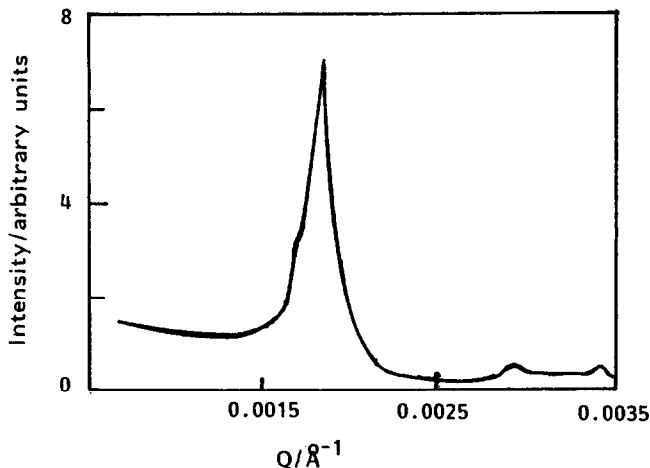
Fig. 5. Light powder diffraction pattern obtained from a binary particle dispersion after subjecting the sample to time-average zero gravity to give an identical pattern at all levels in the sample container.

crystalline phase of small spheres with the remaining, relatively small number of large spheres being in amorphous structures.

A further exploitation of the use of a time-average zero-gravity procedure was its use in the examination of binary alloy-type structures formed from mixtures of colloidal particles. This work followed an earlier illustration that a phase diagram could be used for illustrating phase equilibria in binary particulate mixtures by using the ordinate and the abscissa to specify the volume fractions of the two types of particles [28]. This suggested potential mixtures of particles A and B which could lead to the formation of AB_2 and AB_{13} alloy-type structures. Using particle radii, $R_A = 321$ nm and $R_B = 186$ nm and a number ratio of $n_B/n_A = 6$ and a total volume fraction of $\phi_A + \phi_B = 0.536$ followed by tumbling of the sample under time-average zero-gravity conditions a light intensity against scattering vector "powder diffraction" pattern was obtained which was consistent with an AB_2 structure (Fig. 6). An examination of the crystalline particulate phase by scanning electron microscopy gave the results illustrated in Fig. 7. This clearly illustrates the formation of long-range binary order with alternating hexagonal layers of large and small spheres. Under conditions with $n_B/n_A = 9$, 14, 20 and 30 and with $\phi_A + \phi_B$ in the range 0.512 to 0.553, a superlattice structure of composition AB_{13} was observed using both light "powder diffraction" and scanning electron microscopy [30].
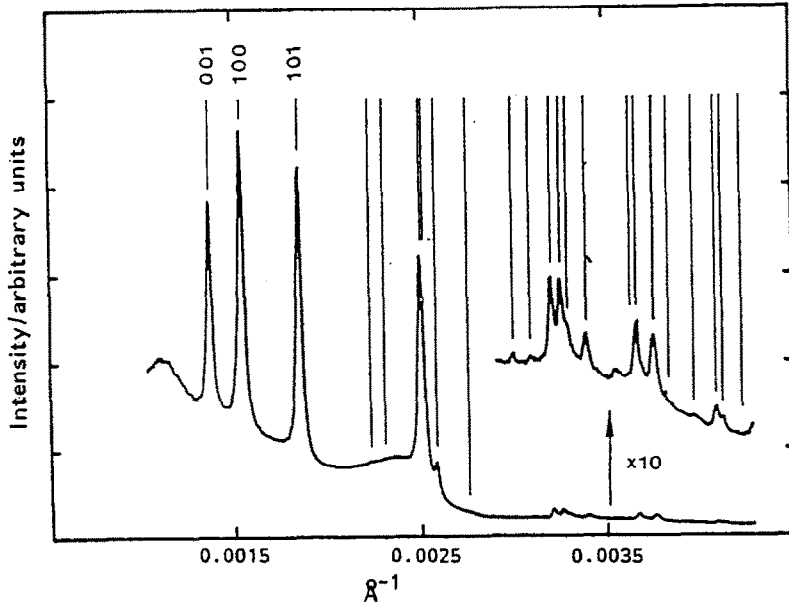
Fig. 6. Light powder diffraction pattern of an AB_2 crystalline sample for $n_B/n_A = 4$ and $\phi_A + \phi_B = 0.533$; the vertical lines indicate the expected Bragg reflections from an AB_2 lattice.
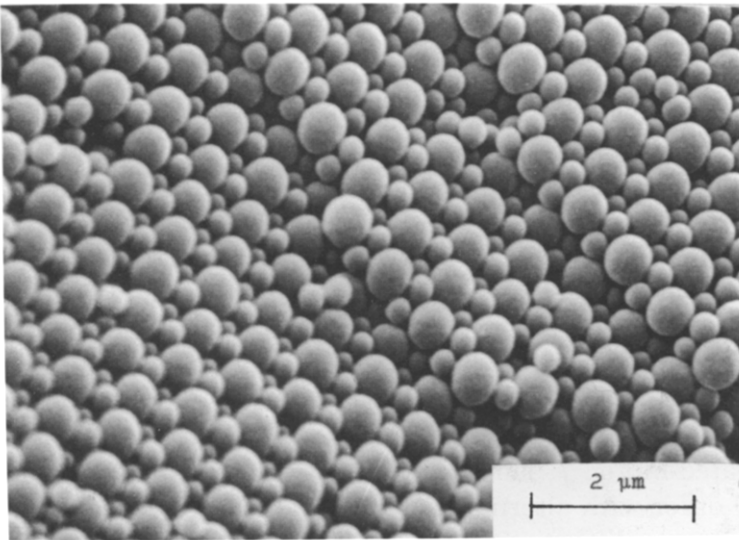

Fig. 7. Scanning electron micrograph of a section of an AB_2 crystal formed from a system with $n_A/n_B = 6$, $\phi_A + \phi_B = 0.536$ [30].

CONCLUSION

These experiments indicate that colloidal dispersions can simulate many phenomena usually associated with molecular systems, e.g. crystallisation. However, gravitational forces can play a role in determining the final state of a colloidal phase suggesting that in many experiments zero gravity conditions would be an advantage. A particular case would seem to be that of the formation of colloidal alloys, composed of particles of different size, where the use of time-average zero-gravity procedures has confirmed the formation of AB_2 and AB_{13} type mixed crystals.

ACKNOWLEDGEMENTS

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