COLLOIDAL FLUIDS, CRYSTALS AND GLASSES

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Various aspects of the behaviour of essentially hard spherical colloidal particles, suspended in a liquid, are outlined. We consider the phase behavior 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 (for a more detailed discussion of colloid/atom analogies, see ref. [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, as 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].

In this somewhat expanded version of an earlier paper [4] we describe briefly several recent studies of suspensions of hard-sphere colloids; 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.

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The particles used for these studies consisted of "cores" of colloidal poly-methylmethacrylate (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 (~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, ~4%, seriously affected the measurements described below; thus here we regard the particles as effectively monodisperse.

2. Phase behaviour and structure of one-component suspensions

The expected phase behaviour of assemblies of identical hard spheres has been established largely by computer simulation [5, 6]. For volume or packing fractions ϕ below the freezing concentration, $\phi_F = 0.494$, the equilibrium state is fluid whereas at concentrations above that of melting, $\phi_M = 0.545$, it is crystalline [5]. If the system is compressed rapidly enough to avoid crystallization, long-lived metastable amorphous or glassy states are found above a "glass transition" concentration, $\phi_G = 0.58$–0.60 [6]. Several experimental studies (e.g. refs. [7, 8]) 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 homogeneously nucleated crystallization at random sites throughout their bulk. For $\phi_F < \phi < \phi_M$ the crystallites so formed settled under gravity, creating polycrystalline phases (with $\phi = \phi_M$) separated from upper colloidal fluid phases (with $\phi = \phi_F$) by clearly defined boundaries. The time taken for crystallization and phase separation depended on concentration and ranged from minutes to hours. In samples with $\phi > \phi_G$ only partial slow crystallization, nucleated heterogeneously at the sample surfaces, was observed.

Accurate measurement of the relative volumes of the coexisting fluid and crystalline phases in these systems is complicated by the variation with time of the position of their mutual boundary, caused initially by the settling of the

crystallites and ultimately by the slow sedimentation of the particles in both phases. Paulin and Ackerson [8] have described a method of circumventing this difficulty by measuring the position of the boundary over many days. They plot this position against time, measured from the initial mixing of the sample, and obtain accurate estimates of the relative phase volumes by extrapolating to zero time the long-time linear portion of the curve. Fig. 1 shows the phase diagram of PMMA spheres of radius 210 nm obtained recently [9] by this method. Extrapolation of the fractional volume of the crystalline phase in the coexistence region to zero and one yields respectively the freezing and melting concentrations. Because the density of the composite core/shell PMMA particles is not known precisely, the volume fractions of the samples cannot be calculated reliably from their (accurately measured) weight fractions. Thus, as in previous work [7, 8], the weight fraction corresponding to freezing is identified with the hard-sphere volume fraction $\phi_F = 0.494$. Scaling the weight fractions of other samples by the same factor yields the effective hard-sphere volume fractions ϕ shown in fig. 1. It is apparent that the melting concentration, $\phi_M = 0.540 \pm 0.002$, observed in fig. 1 is only slightly smaller than the hard-sphere value of 0.545.

The intensity $I(Q)$ of light scattered by an assembly of identical rigid spheres can be written

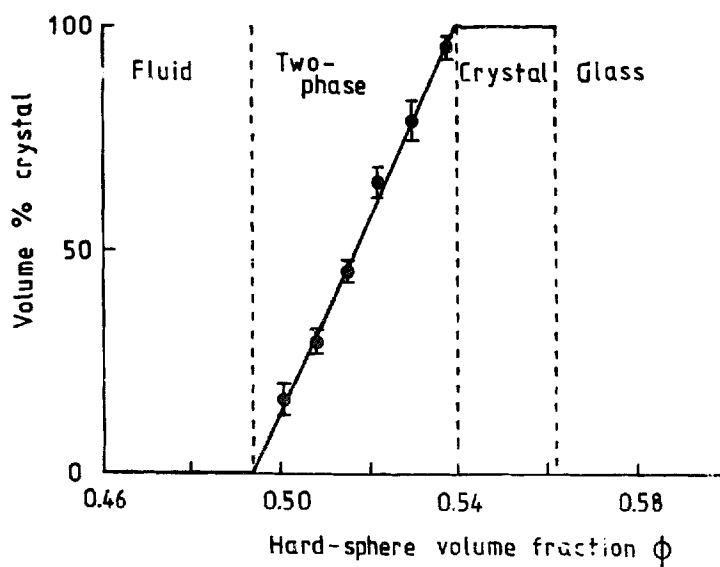$$I(Q) \propto P(Q)\, S(Q) \,. \tag{1}$$

Fig. 1. Phase behaviour of "hard-sphere" PMMA particles of radius 210 nm suspended in a decalin/carbon disulphide mixture. The data points in the two-phase coexistence region represent the fraction of the volume of the sample which is occupied by the crystalline phase. As discussed in the text, the measured weight fractions of the samples are scaled so that freezing occurs at an effective hard-sphere volume fraction ϕ of 0.494. From ref. [9].

Here $Q = (4\pi/\lambda) \sin(\frac{1}{2}\theta)$ is the usual scattering vector, λ being the wavelength of light and θ the scattering angle, $P(Q)$ is the single-particle form factor and $S(Q)$ is the structure factor,

$$S(Q) = N^{-1} \sum_{j=1}^{N} \sum_{k=1}^{N} \langle \exp\{i\boldsymbol{Q} \cdot [r_j(t) - r_k(t)]\} \rangle_E , \qquad (2)$$

where $r_j(t)$ is the position of particle j at time t and the $\langle \cdots \rangle_E$ indicates an ensemble average. The form factor for a particular system can be obtained from a measurement of $I(Q)$ on a dilute sample for which $S(Q) = 1$. Then use of eq. (1) with this form factor and a measurement of $I(Q)$ yields the structure factor of a concentrated sample. Such measurements of the static structure factors of fluid-like samples at $\phi < \phi_F$ show reasonable agreement with those expected for hard spheres [10]. To study the crystal structures a laser beam was expanded to illuminate about $1 \, \text{cm}^3$ of the sample [11]; this volume contained at least 10^6 crystallites of typical dimension 25–$50 \, \mu\text{m}$. Fig. 2 shows the structure factor obtained by this light-scattering analogue of powder crystallography for a suspension of PMMA spheres of radius $170 \, \text{nm}$ at a concentration close to that of melting. This structure factor has a rather unusual form for a crystal, comprising not only a sharp Bragg reflection but also a broad, but structured, band of diffuse scattering. We have established that this structure factor is consistent with a "random-stacked close-packed" structure for the crystalline state of hard spheres [11]. 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-centered cubic, ...ABCABC...,
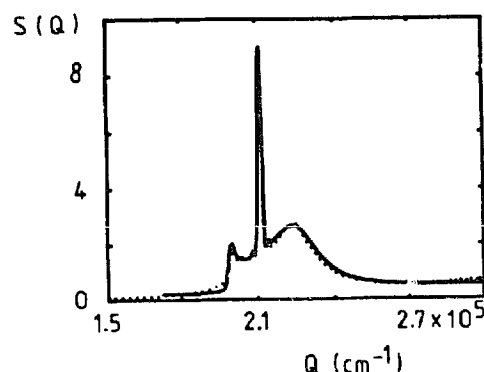

Fig. 2. Static structure factor $S(Q)$ of a polycrystal of PMMA particles of radius $170 \, \text{nm}$ at concentration close to melting, measured by "powder light crystallography"; Q is the scattering vector. The points are the experimental measurements and the curve is the theoretical prediction for the "random-stacked close-packed" structure described in the text. From ref. [11].

and hexagonal close-packed, ...ABABAB. ... The solid line in fig. 2 is the theoretical prediction for such a random-stacked close-packed structure in which there is no correlation between the lateral positions of next-nearest-neighbouring layers, i.e. following an ...AB stacking, the sequences ...ABA... and ...ABC... are equally likely. Agreement between experiment and theory is seen, in fig. 2, to be quite good. Evidently the short range of the hard-sphere potential precludes significant "communication" between next-nearest neighbours.

Finally we mention that the existence of a freezing transition of hard spheres, which lack any attraction, is at first sight somewhat counter-intuitive and was the subject of much discussion in the early days of liquid state physics [12]. As discussed by Lekkerkerker [12], the free energy of an assembly of hard spheres contains only entropic contributions, that associated with the configuration of the particles (in particular the absence or presence of long-ranged order), and that associated with the local free volume available to the particles. Freezing occurs at concentrations at which the entropy lost by long-ranged ordering of the particles is more than offset by the entropy gained from the larger free volume available to them in an ordered structure. We note that the concentration $\phi_M = 0.545$ of the most dilute crystal is significantly smaller than that, 0.74, of touching close packing so that the particles have considerable freedom for local motions about their lattice sites.

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 ~330 nm, and smaller, B, spheres, radius ~200 nm, corresponding to a size ratio of about 0.61 [13]. 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 down. 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, $n_B/n_A \gtrsim 16$: the crystalline phase was essentially pure B. Thus for $n_B/n_A \lesssim 1$ and $\gtrsim 16$ 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 [14]. For the quite extended region $n_B/n_A \lesssim 1$ 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 [13].

For $6 \gtrsim n_B/n_A \gtrsim 1.5$ 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 $10 \lesssim n_B/n_A \lesssim 16$ and the total volume fraction of both species ranged from ~ 0.52 to ~ 0.54. Here we concentrate on a sar 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 amorph ous arrangements. Subsequent measurements over a period of months showed the slow growth of a second, complex crystal structure. Fig. 3 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°, so that the unit cell consists of eight subcells. The interpretation of fig. 3 is described briefly in the caption.

AB_{13} has been observed previously in gem opals [15], dried crystals of colloidal silica spheres, and in mixtures of charged polystyrene spheres [16]. Murray and Sanders [15] have pointed out that spheres of size ratio of 0.558 show the most efficient packing in the AB_{13} structure; then the concentration of a fully compressed crystal is $\phi = 0.738$. By contrast, at size ratio 0.61, the value applying to the mixture described above, the maximum concentration of AB_{13} is about 0.687. Murray and Sanders argued that systems which have high concentrations when fully compressed are the most likely to form stable crystalline structures at lower concentrations (because, as discussed at the end
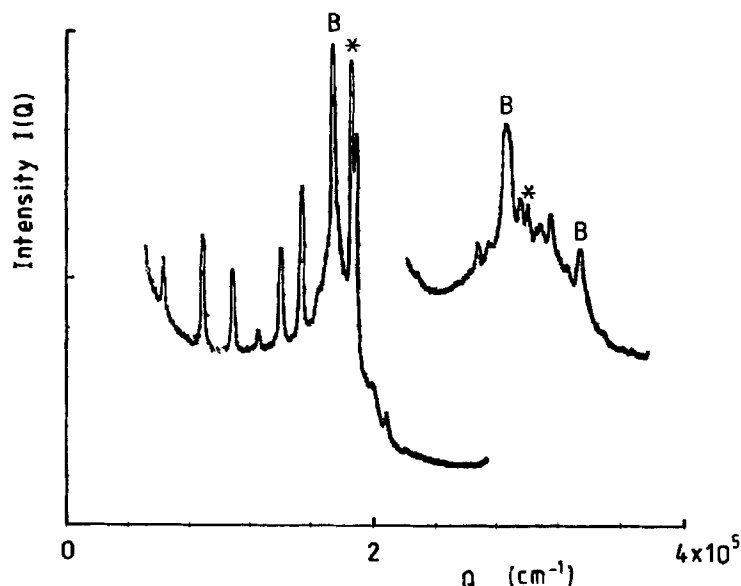
Fig. 3. Intensity $I(Q)$ of light scattered by a binary mixture of PMMA colloids having size ratio 0.61 at number ratio $n_B/n_A \approx 13$ (where B is the smaller component) and total volume fraction $\phi \approx 0.54$. The sample contains crystals of both pure B and the AB_{13} superlattice structure. 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 random-stacked close-packed 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. From ref. [4].

of section 2, of the large free-volume contribution to the entropy). This may explain the above-mentioned reluctance of AB_{13} to form at size ratio 0.61. Indeed, in recent work [17] we have found that a mixture of PMMA particles at size ratio 0.58 (closer to the optimum value 0.558), number ratio $n_B/n_A \approx 13$ and concentration $0.50 \lesssim \phi \lesssim 0.54$ crystallizes within a few days into an apparently pure and stable AB_{13} phase.

It seems remarkable that a mixture of hard spheres should spontaneously adopt such an exotic structure as AB_{13}. The mechanisms of its nucleation and growth remain to be established. No calculations of the free energy of the AB_{13} phase of hard spheres have been reported and, to date, only the qualitative arguments, outlined above, based on packing considerations have been used to estimate its stability [15].

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 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 [18]. The non-ergodicity of the samples near the glass transition concentration requires special attention to be paid to the treatment of DLS data. Elsewhere [19] we have described methods by which the measured time-averaged correlation function of the scattered light intensity can be analyzed to provide the normalized ensemble-averaged intermediate scattering function

$$f(Q, t) = F(Q, t)/F(Q, 0) . \tag{3}$$

The intermediate scattering function

$$F(Q, t) = N^{-1} \sum_{j=1}^{N} \sum_{k=1}^{N} \langle \exp\{iQ \cdot [r_j(0) - r_k(t)]\} \rangle_E \tag{4}$$

can be identified as the time correlation function of one spatial Fourier component of the particle number density; note that $F(Q, 0) = S(Q)$, where $S(Q)$ is the static structure factor, eq. (2).

The data points in fig. 4 show normalized intermediate scattering functions $f(Q, t)$, measured at scattering vectors corresponding to the main peaks in the
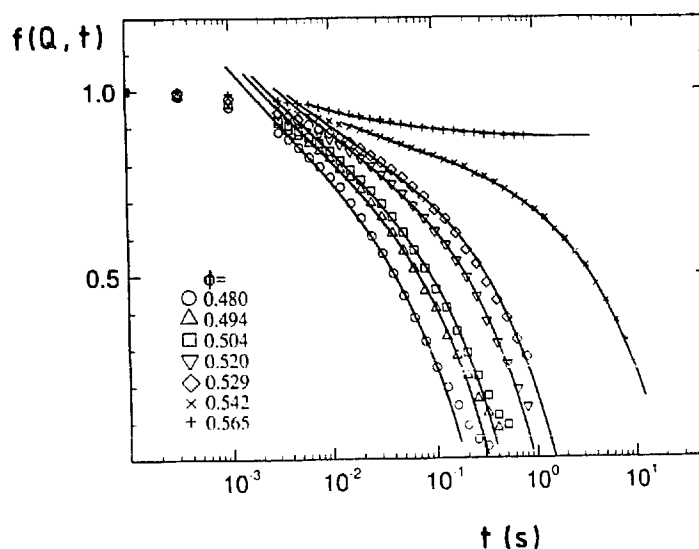

Fig. 4. Data points are normalized intermediate scattering functions $f(Q, t)$ of equilibrium fluid ($\phi = 0.480, 0.494$), metastable fluid ($\phi = 0.504, 0.520, 0.529, 0.542$) and glassy ($\phi = 0.565$) suspensions of PMMA particles of radius 170 nm, measured by DLS at the main peaks of the static structure factors. Solid lines are the predictions of mode-coupling theory for the β-relaxation, eq. (5), of hard-sphere atoms. From ref. [20].

static structure factors, for suspensions of PMMA spheres of radius 170 nm [18, 20]. The data span a range of (indicated) concentrations extending from the equilibrium colloidal fluid, $\phi = 0.480$, 0.494, through the metastable fluid (studied immediately after shear-melting the crystals), to the glass, $\phi = 0.565$. At all concentrations the intermediate scattering functions exhibit initial rapid decays, which vary only weakly with concentration and which can be associated with local motions of the particles within instantaneous "cages" formed by their nearest neighbours. By contrast, the long-time decays of $f(Q, t)$ slow down strongly with increasing concentration, reflecting the restriction of long-distance diffusion by the increasingly tight neighbour cages. At concentration $\phi = 0.565, f(Q, t)$ 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. This concentration corresponds quite closely to that at which homogeneously nucleated crystallization was observed to be suppressed. Thus, from a combination of macroscopic and microscopic observations (the suppression of crystallization and the persistence of density fluctuations) we identify the glass transition concentration for this system as $\phi_G = 0.56 \pm 0.005$.

Over the last few years significant progress has been made towards understanding the glass transition, a subject of longstanding interest, through the application of mode-coupling theories (developed originally to describe the dynamics of critical liquids and applied subsequently to equilibrium liquids away from their critical points) (for a review of mode-coupling theories of the glass transition, see ref. [21]). Mode-coupling theories make detailed predictions for both the functional forms and the concentration dependence of the intermediate scattering functions $f(Q, t)$. Of particular interest is the β-relaxation regime which applies to times scales intermediate between the initial decays of $f(Q, t)$, describing local motions, and the final decays, associated with the long-distance diffusion. To date, mode-coupling theories have been applied mainly to simple atomic systems [21], which, because of rapid crystallization, cannot be prepared in controllable metastable states suitable for experimental study.

In the time range of the β-relaxation the mode-coupling prediction for the intermediate scattering function is

$$f(Q, t) = f^c(Q) + h(Q) c(\sigma)g_\pm (t/t_\sigma) ,\tag{5}$$

where the "separation parameter" σ is defined as

$$\sigma = (\phi - \phi_G)/\phi_G .\tag{6}$$

Here $f^c(Q)$ is a critical amplitude, $h(Q)$ and $c(\sigma)$ are prefactors and $g_\pm$ are

universal functions with t_σ a concentration-dependent time constant; g_+ applies in the glass, $\sigma > 0$ ($\phi > \phi_G$), g_- in the (metastable) fluid, $\sigma < 0$. Götze and Sjögren [20] have recently compared the colloid data of fig. 4 with the predictions of eq. (5), evaluated for hard-sphere atoms. The universal functions $g_\pm$ were calculated for hard spheres; the prefactor $c(\sigma)$ and the time constant t_σ were adjusted at each sample concentration to give the best fit of eq. (5) to the experimental data. The results of this analysis are shown as the solid lines in fig. 4. Remarkably good agreement between theory and experiment is seen for the relaxation of $f(Q, t)$ in the intermediate (β-relaxation) time range. Furthermore, the dependence on concentration of the values of $c(\sigma)$ and t_σ required to fit the data are also in good agreement with the specific predictions of mode-coupling theory [20].

The validity of comparing the theory for atoms with data obtained on a colloidal system can be questioned. On time scales short compared to the time between collisions, the dynamics of atoms and colloids are fundamentally different: atoms undergo free flight whereas colloidal particles perform (hydrodynamically hindered) diffusion. However it has been suggested [2, 3, 18] that, at the longer times associated with the β-relaxation, over which many collisions have occurred, the motions in each case are similar and can be called "interactive diffusion". Nevertheless an evaluation of mode-coupling theory using Langevin, rather than Newtonian, dynamics is still required to check the validity of this suggestion.

Another quantity of interest is $f(Q, \infty)$, the non-decaying part of $f(Q, t)$ in the glass state, variously called the non-ergodicity parameter, the glass form factor, the Edwards–Anderson order parameter and the Debye–Waller factor [21]. This is essentially a structural property, which describes the component of density fluctuations of wavevector Q which is frozen-in in the glass, and, as such, should be the same for hard-sphere atoms and colloids. Fig. 5 shows recent measurements [22] by DLS of $f(Q, \infty)$ for the glass state of a colloidal system, similar to that discussed above (fig. 4), at three concentrations. The solid lines are the predictions of mode-coupling theory [23] for hard-sphere atoms at almost the same values of the separation parameter, eq. (6), as those corresponding to the lower concentration colloidal samples. In view of the fact that there are no adjustable parameters in this comparison, agreement between experiment and theory is quite good. One would expect that at random close packing, $\phi \approx 0.64$, there should be no motion of the particles so that $f(Q, \infty) = 1$; the sample at $\phi = 0.626$, for which $f(Q, \infty) \geq 0.85$ at all values of the scattering vector, is clearly approaching this limit.

Currently more detailed experimental and theoretical work is being undertaken to investigate further the apparent success of the mode-coupling approach in describing the glass transition of hard-sphere colloids.
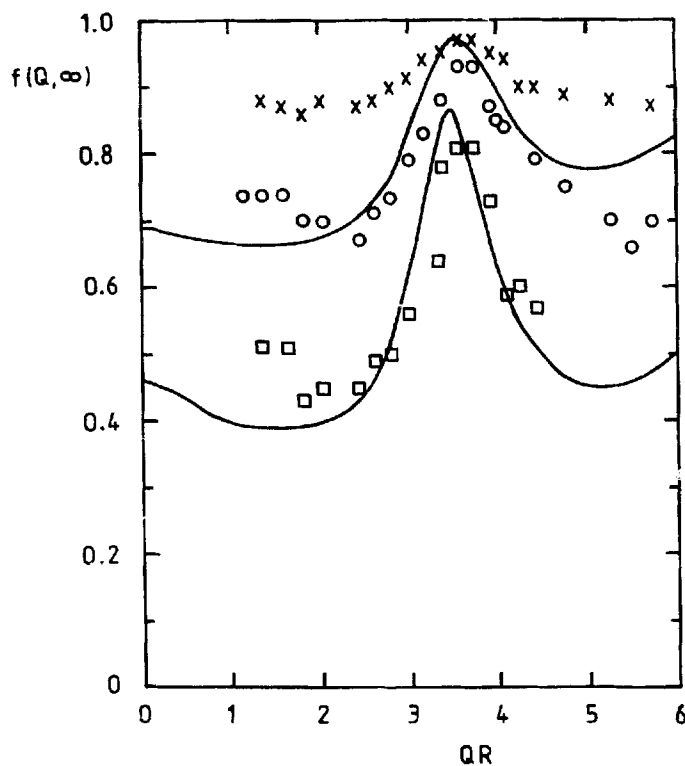
Fig. 5. Non-decaying components $f(Q, \infty)$ of the intermediate scattering functions of glassy states of suspensions of PMMA particles, radius $R = 210$ nm, as functions of scattering vector Q (see e.g. the long-time asymptote of the top curve, $\phi = 0.565$, of fig. 4). Squares: $\phi = 0.561$, separation parameter $\sigma \approx 0$; circles: $\phi = 0.597$, $\sigma = 0.064$; crosses: $\phi = 0.626$, $\sigma = 0.116$. Solid curves are predictions of mode-coupling theory for $\sigma = 0$ (lower curve) and $\sigma = 0.066$. From ref. [22].

References

[1] J-P. Hansen and I.R. McDonald, Theory of Simple Liquids (Academic Press, London, 1986).

[2] P.N. Pusey, in: Liquids, Freezing and the Glass Transition, Les Houches Session LI, D. Levesque, J-P. Hansen and J. Zinn-Justin, eds. (Elsevier, Amsterdam, 1991).

[3] P.N. Pusey, H.N.W. Lekkerkerker, E.G.D. Cohen and I.M. de Schepper, Physica A 164 (1990) 12.

[4] P.N. Pusey, W. van Megen, S.M. Underwood, P. Bartlett and R.H. Ottewill, J. Phys.: Condens. Matter 2 (1990) SA373.

[5] W.G. Hoover and F.H. Ree, J. Chem. Phys. 49 (1968) 3609.

[6] L.V. Woodcock, Ann. N.Y. Acad. Sci. 37 (1981) 274.

[7] P.N. Pusey and W. van Megen, Nature 320 (1986) 340.

[8] S.E. Paulin and B.J. Ackerson, Phys. Rev. Lett. 64 (1990) 2663.

[9] W. van Megen and S.M. Underwood, to be published.

[10] I. Livsey and R.H. Ottewill, Colloid Polym. Sci. 267 (1989) 421; C.G. de Kruif, W.J. Briels, R.P. May and A. Vrij, Langmuir 4 (1988) 688.

[11] P.N. Pusey, W. van Megen, P. Bartlett, B.J. Ackerson, J.G. Rarity and S.M. Underwood, Phys. Rev. Lett. 63 (1989) 2753.

[12] H.N.W. Lekkerkerker, Introductory Lecture. Physica A 176 (1991) 1. this workshop.

[13] P. Bartlett, R H. Ottewill and P.N. Pusey, J. Chem. Phys. 93 (1990) 1299.

[14] P. Bartlett, J. Phys.: Condens. Matter 2 (1990) 4979.

[15] J.V. Sanders, Philos. Mag. 42 (1980) 705; M.J. Murray and J.V. Sanders, Philos. Mag. 42 (1980) 721.

[16] S. Yoshimura and S. Hachisu, Prog. Colloid Polym. Sci. 68 (1983) 59.

[17] P. Bartlett, R.H. Ottewill and P.N. Pusey, to be published.

[18] P.N. Pusey and W. van Megen, Phys. Rev. Lett. 59 (1987) 2083; Ber. Bunsenges. Phys. Chem. 94 (1990) 225; and to be published.

[19] P.N. Pusey and W. van Megen, Physica A 157 (1989) 705.

[20] W. Götze and L. Sjögren, to be published.

[21] W. Götze, in: Liquids, Freezing and the Glass Transition, Les Houches Session LI, D. Levesque, J-P. Hansen and J. Zinn-Justin, eds. (Elsevier, Amsterdam, 1991).

[22] W. van Megen, S.M. Underwood and P.N. Pusey, to be published.

[23] U. Bengtzelius, W. Götze and A. Sjölander, J. Phys. C 17 (1984) 5915.