Observation of a Glass Transition in Suspensions of Spherical Colloidal Particles

P. N. Pusey and W. van Megen[(a)]
Royal Signals and Radar Establishment, Malvern, Worcestershire, WR14 3PS, United Kingdom

(Received 17 August 1987)

Concentrated suspensions of submicron colloidal spheres were studied both by dynamic light scattering and by direct observation of their phase behavior. In agreement with recent theory and computer simulation, the measured dynamic structure factor developed an essentially nondecaying component, implying "structural arrest," at almost the same concentration as that at which a long-lived amorphous or glass phase was first observed.

PACS numbers: 64.70.Pf, 78.20.Dj, 82.70.Kj

The idea that sufficiently rapid compression should transform a liquid composed of spherical particles into a long-lived metastable amorphous solid or glass dates back at least to the sphere-packing experiments of Bernal[1] and Scott[2] and to the free-volume model of Cohen and Turnbull.[3] More recently this simple "glass transition" has been studied in a number of computer experiments.[4] Since 1984 the subject has gained impetus with the prediction of such a glass transition by kinetic[5,6] and hydrodynamic[7,8] theories of liquids which incorporate a nonlinear feedback mechanism.[9] The transition from the ergodic liquid state to the nonergodic glass is signaled by divergence of the shear viscosity, by vanishing of the self-diffusion coefficient, and by "structural arrest," the partial freezing-in of density fluctuations.

To date these ideas have not been tested on real systems composed of spherical molecules because compression and/or temperature-quench rates high enough to bypass crystallization in a controllable fashion are not attainable.[10] In this Letter we report the observation of a glass transition in concentrated suspensions in a liquid of solid submicron colloidal spheres having a narrow distribution of size. The static[11] and dynamic[12] properties of suspensions of identical spheres have many features in common with those of simple liquids. In particular, the full range of phase behavior, fluid → crystal → glass, is observed.[13] However, the relaxation times of the diffusive motions of particles in suspension are at least 10^9 times larger than those of atoms in a liquid. Thus the lifetimes of the metastable fluid phases of suspensions, observed before significant crystallization takes place, can be long enough, minutes to hours (see below), to allow detailed study of their properties. Here we compare measurements by dynamic light scattering (DLS) of $F(Q,\tau)$ [Eq. (3)], the temporal correlation function of particle-density fluctuations, in the metastable fluid and glass phases with both theoretical predictions[5,6,14] and a recent computer simulation.[15] Good qualitative agreement is observed. Our main finding is that $F(Q,\tau)$ develops an essentially nondecaying component, associated with structural arrest, at almost exactly the same suspension concentration as that at which long-lived colloidal glasses are first observed.[16]

A useful, if oversimplified, picture of this archetypal glass transition can be given in terms of a neighbor cage in which the motion of individual particles is partially or completely constrained. At normal liquid densities, a particle is able to achieve long-distance diffusion although its motion is continually hindered by temporary entrapments in cages formed by its current nearest neighbors. As the density of the liquid is increased towards the glass transition, it appears that the probability that a hole opens up in the cage, large enough to admit the passage of a particle, becomes extremely small. Consequently, although the particles retain some freedom for local motions, they are then essentially localized or trapped (structural arrest).

The particles used in these experiments consisted of poly-(methylmethacrylate), PMMA, cores stabilized by a thin layer, $\simeq 10$ nm, of poly-(12-hydroxystearic acid).[17] They were dispersed in a mixture of decalin and carbon disulphide in proportion (2.52:1 by weight) chosen to nearly match the refractive index ($\simeq 1.51$) of the particles thus providing nearly transparent samples with adequate single scattering but negligible multiple scattering. Measurements by DLS on dilute suspensions gave a particle diameter of 340 nm and a polydispersity[18] (standard deviation of the particle-size distribution divided by the mean) of about 0.05.

Ten samples were prepared from a stock suspension in $1 \times 1 \times 3\text{-cm}^3$ scattering cells. They were brought to the desired concentration by centrifugation, to provide a dense sediment, removal of a weighted amount of clear supernatant, and subsequent redispersal of the particles by slow tumbling of the samples for about 24 h. This procedure seemed to randomize the particle positions effectively so that, at this point, all the samples were amorphous; i.e., they showed no sign of crystallization.[16] The samples were then left undisturbed and were observed over several days. With increasing particle concentration, we observed phase behavior, summarized in Table I, ranging from colloidal fluid (sample A) to colloidal fluid coexisting with a polycrystalline phase (B,C,D) to fully crystalline (E,F) and finally, at the

TABLE I. Sample designations, volume fractions ϕ_E, phases and relaxation times T_L.

Sample	Our designation	ϕ_E	Phase	$T_L(s)$
A	11(2)	0.480	Fluid	0.10
C*	1*	0.494	Coexisting Fluid	0.15
B	11(3)	0.504	Fluid+Crystal	0.2
C	1	0.520	Fluid+Crystal	0.5
D	2	0.529	Fluid+Crystal	1
E	7	0.542	Crystal	6
F	3	0.554	Crystal	$>10^3$
G	8	0.565	Glass	$>10^3$
H	4	0.582	Glass	$>10^3$
I	5	0.594	Glass	...
J	6	0.614	Glass	...

highest concentrations, an amorphous or glass phase (G,H,I,J) which did not crystallize over several weeks. Photographs of samples showing similar behavior have been published elsewhere.[13] In this previous work[13] we argued that the interaction between these particles is steep and repulsive (slightly soft) and can therefore be represented reasonably well by an effective hard-sphere model. Thus, as before,[13] we identify the effective volume or packing fraction ϕ_E where crystallization is first observed with the freezing density $\phi_E = 0.494$ found in computer simulations of hard spheres.[19] Values of ϕ_E for the other samples, listed in Table I, are then obtained by appropriate scaling of their measured weight fractions.[13]

The nonergodicity of the metastable-glass phase requires careful consideration to be given to the operation of the DLS technique. In the usual case of a fluidlike assembly of particles, in which diffusion over long distances occurs, the scattered-light field consists of a speckle pattern which at any point in space undergoes many complete fluctuations in the typical duration of an experimental measurement. Thus the time averaging inherent in DLS is equivalent to ensemble averaging: The system is ergodic. However, for glassy samples, the speckle pattern will contain both a fluctuating component, associated with local motions of the particles, and a nonfluctuating component, associated with the frozen-in density fluctuations, which will show strong spatial variation. In order to perform a full ensemble average, it is then necessary to sample many different scattering volumes while accumulating data. Rather than following this tedious procedure literally for the nonergodic phases (samples F to H, see below) we adopted a more economical approach. A large scattering volume ($\simeq 1$ mm^3) was obtained by use of an unfocused laser beam and a $\simeq$1-mm detection slit so that the detector accepted about ten coherence areas (or speckles) in the scattered-light field, corresponding to ten independent spatial Fourier components of the particle-density fluctuations. Then measurements, each of 10^3 s duration, were made for $M = 10$ spatially separated scattering volumes, achieved by moving the sample between measurements. The mean intensities and (unnormalized) intensity correlation functions for the ten measurements were then summed. In the limit $M \to \infty$, this procedure would provide the full ensemble average so that our actual measurements, which sample roughly 100 Fourier components (10 coherence areas in each of 10 scattering volumes), should give a reasonable estimate of it.

The normalized time correlation function of $I(Q,t)$, the intensity seen by the detector at time t, is given by

$$g^{(2)}(Q,\tau) = \langle I(Q,t) I(Q,t+\tau)\rangle / \langle I(Q,t)\rangle^2, \tag{1}$$

where angular brackets indicate averaging, Q is the scattering vector, and τ is the correlation delay time. Provided the average is a full ensemble average (as discussed above) and the particles in suspension have a range of spatial correlation small compared to the dimensions of the scattering volume, we have[20]

$$g^{(2)}(Q,\tau) = 1 + [cF(Q,\tau)/S(Q)]^2, \tag{2}$$

where c is an apparatus constant determined largely by the ratio of coherence area to detector area. Here the (coherent) dynamic structure factor for N particles is

$$F(Q,\tau) = \frac{1}{N} \sum_{j,k=1}^{N} \langle \exp i\mathbf{Q}\cdot[\mathbf{r}_j(0) - \mathbf{r}_k(\tau)]\rangle, \tag{3}$$

where $\mathbf{r}_j(t)$ is position of the jth particle at time t; $S(Q) \equiv F(Q,0)$ is the static structure factor.

With use of standard equipment, DLS measurements were made on samples A to H at scattering vector $Q_m \approx 2.14\times 10^5$ cm^{-1} corresponding to the main peaks in their structure factors. The samples were tumbled thoroughly and studied before significant crystallization was observed. Thus, for samples B to H, the measurements apply to the metastable-fluid or glassy phases and, for sample A, to the equilibrium-fluid phase. In addition, the coexisting equilibrium-fluid phase of sample C (designated C* in Table I) was studied after the sample had stood long enough, about one day, for phase separation to occur; i.e., for the crystallites formed to settle under gravity.

In Fig. 1 $\ln[cF(Q_m,\tau)/S(Q_m)]$, obtained from the measurements via Eqs. (1) and (2), is plotted against delay time τ. For samples A to E, a small $[\simeq(100\,\mu\text{m})^3]$ scattering volume was used, the detector accepted about one coherence area, and $c \approx 0.8$. For samples F to H, the larger scattering volume, discussed above, was used and $c \approx 1/\sqrt{10}$. In all cases the data show a relatively rapid initial decay, followed by a much slower decay at longer times. Estimates of the time constants T_L of the slower decays (listed in Table I) were obtained by fitting each set of data in Fig. 1 by the sum of two exponentials.

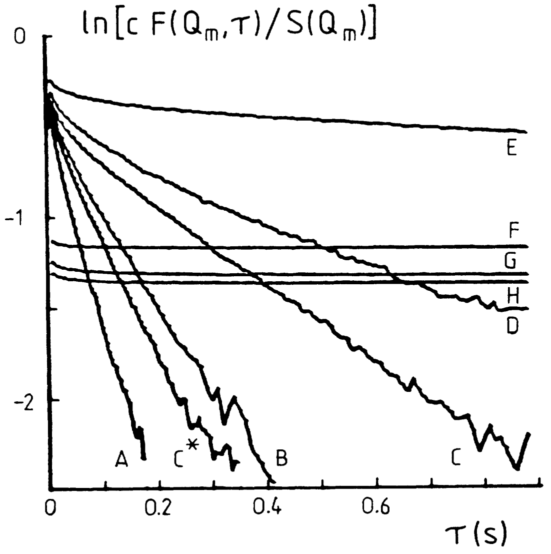

FIG. 1. Semilogarithmic plots of the dynamic structure factor $[cF(Q_m,\tau)/S(Q_m)]$, measured at the main peaks of the static structure factor, against delay time τ for suspensions of collodial spheres (samples A to H, see Table I). For the "nonergodic" samples F, G, H an enlarged scattering volume was used, leading to a reduced amplitude c (see text). Note (i) initial rapid and longer-time slow decays and (ii) marked divergence of the slow decay time with increasing concentration (A → H).

As is evident in both the figure and the table, T_L increases rapidly with particle concentration and increasingly steeply at the higher concentrations. Nevertheless, for samples A to E, these slowest decay times are still small enough that many complete fluctuations of the scattered light were sampled in the course of a 10^3-s experiment and the samples are effectively ergodic. By contrast, for samples F, G, and H, the slowest decay times exceeded 10^3 s so that these samples are nonergodic on the experimental time scale.[21]

Elsewhere we will give a more complete analysis of our data, which include measurements over broader ranges of delay times and scattering vectors, and a discussion of the applicability of simple-liquid theories to suspensions. The main aim here is to point out the qualitative agreement between our results and the theoretical predictions of Bengtzelius and co-workers[6,14] for hard-sphere and Lennard-Jones atomic liquids and the computer simulations of Ullo and Yip[15] on an atomic liquid with a truncated Lennard-Jones potential. These authors also found dynamic structure factors $F(Q_m,\tau)$ comprising two main features: An initial decay spanning 10%–20% of the amplitude of the correlation function, attributed to local particle motions, and a slower decay associated with larger-scale particle motions. The time constants of the slower decays increased with increasing concentration approaching, quite abruptly, an essentially infinite value, implying structural arrest, at a concentration ϕ_G associated with the glass transition.

An important feature of our findings is a correlation between the observed macroscopic phase behavior and the (microscopic) DLS results, namely that crystallization ceased to be observed at roughly the same concentration as that at which the relaxation times measured by DLS became extremely large. Thus, while the (ergodic) sample E ($\phi_E = 0.542$) crystallized completely within a few hours of mixing, sample F ($\phi_E = 0.554$), the first to show decay times exceeding 10^3 s, took several days for complete crystallization. The next sample (G, $\phi_E = 0.5655$) did not crystallize over several weeks. We can therefore identify a glass-transition concentration for our system at $\phi_G \approx 0.56$.

This experimental value of ϕ_G is somewhat larger than that, 0.52–0.54, found for hard spheres in the theory of Bengtzelius, Götze, and Sjölander.[6] By contrast, Woodcock's computer simulation of hard spheres[4] seems to indicate $\phi_G = 0.58$–0.60, through, because of run-time limitations, it is not currently possible to search directly in computer experiments for long-lived metastable states. In earlier experiments on larger PMMA spheres (diameter 650 nm) we observed homogeneously nucleated crystallization up to $\phi_E \approx 0.59$.[13] Though small, this difference in the ϕ_G values of the present (0.56) and earlier (> 0.59) experiments is larger than estimated experimental error and may be associated with slight differences in the interparticle potential and/or the particle-size distribution.

It is interesting that, despite the above-mentioned uncertainties, the glass transition occurs at a volume fraction well below that, 0.64, of the random close packing of spheres.[1,2,4] Above ϕ_G the colloidal glasses must be regarded as effectively solid and therefore able to support a finite shear stress.[22] Nevertheless, we observe the glasses (and the colloidal crystals) to be extremely fragile mechanically and easily "melted" by the application of small stresses to give flowing suspensions which exhibit pronounced shear thinning.[23]

Two other experimental studies[24,25] of the dynamic structure factor near glass transitions have been reported recently; these will be compared with the present work elsewhere.

Finally, it is perhaps worth repeating an inherent and obvious limitation of all experimental studies of the glass state: Once material relaxation times become much longer than experimental measurement times it is impossible to distinguish between long-lived metastability and true stability. Nevertheless, our observation of the rapid divergence of the decay time of $F(Q,\tau)$ essentially coincident with the macroscopically observed suppression of crystallization gives strong support to the existence of an operationally meaningful glass transition in simple systems.

One of us (P.N.P) benefitted greatly from discussions with C. A. Angell, U. Bengtzelius, A. Sjölander, and S. Yip at a meeting on the glass transition organized by P. A. Madden. We thank B. J. Ackerson and L. V. Woodcock for several valuable discussions and S. M. Underwood for preparing the particles used in this study. Another one of us (W.v.M.) is grateful to the Royal Signals and Radar Establishment for financial support during a study leave.

---

[a] Permanent address: Department of Applied Physics, Royal Melbourne Institute of Technology, Melbourne, Victoria, Australia.

[1] J. D. Bernal, Nature (London) **183**, 141 (1959), and **185**, 68 (1960), and Proc. Roy. Soc. London, Ser. A **280**, 299 (1964); J. D. Bernal and J. Mason, Nature (London) **188**, 910 (1960).

[2] G. D. Scott, Nature (London) **188**, 908 (1960), and **194**, 956 (1962), and **201**, 382 (1964), and J. Chem. Phys. **40**, 611 (1964).

[3] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959), and **34**, 120 (1961), and **52**, 3038 (1970), and Nature (London) **203**, 964 (1964); D. Turnbull, J. Phys. (Paris) Colloq. **35**, C4-1 (1974).

[4] For a review of computer experiments, see C. A. Angell, J. H. R. Clarke, and L. V. Woodcock, Adv. Chem. Phys. **48**, 397 (1981); the most complete computer study of the glass transition of hard spheres is that of L. V. Woodcock, Ann. N. Y. Acad. Sci. **37**, 274 (1981).

[5] E. Leutheusser, Phys. Rev. A **29**, 2765 (1984).

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

[7] S. P. Das, G. F. Mazenko, S. Ramaswamy, and J. J. Toner, Phys. Rev. Lett. **54**, 118 (1985); S. P. Das and G. F. Mazenko, Phys. Rev. A **34**, 2265 (1986).

[8] T. R. Kirkpatrick, Phys. Rev. A **31**, 939 (1985).

[9] T. Geszti, J. Phys. C **16**, 5805 (1983).

[10] For a recent general review of the glass transition, see J. Jäckle, Rep. Prog. Phys. **49**, 171 (1986).

[11] W. van Megen and I. Snook, Adv. Colloid. Interface Sci. **21**, 119 (1984); see various papers in Faraday Discuss. Chem. Soc. **76** (1983).

[12] W. Hess and R. Klein, Adv. Phys. **32**, 173 (1983); R. J. A. Tough, P. N. Pusey, H. N. W. Lekkerkerker, and C. van den Broeck, Mol. Phys. **59**, 595 (1986).

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

[14] U. Bengtzelius, Phys. Rev. A **34**, 5059 (1986).

[15] J. J. Ullo and S. Yip, Phys. Rev. Lett. **54**, 1509 (1985).

[16] Note that the lattice parameter, $\simeq 340$ nm, of our colloidal crystals is such that they give Bragg reflection of visible light. Thus direct visual observation provides unambiguous discrimination between crystalline and amorphous structures (Ref. 13).

[17] L. Antl, J. W. Goodwin, R. D. Hill, R. H. Ottewill, S. M. Owens, S. Papworth, and J. A. Waters, Colloid. Surf. **17**, 67 (1986).

[18] P. N. Pusey and W. van Megen, J. Chem. Phys. **80**, 3513 (1984).

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

[20] See, for example, P. N. Pusey, in *Photon Correlation Spectroscopy and Velocimetry,* edited by H. Z. Cummins and E. R. Pike (Plenum, New York, 1977), p. 45.

[21] For these samples the intensity correlation functions obtained from each of the ten measurements described in the text were also normalized individually. These individually normalized functions showed smaller amplitudes than the full ensemble average (obtained by subsequent normalization of ten summed correlation functions) indicating that only a restricted range of intensity fluctuations was sampled during a single measurement and thus implying the existence of decay times exceeding the duration of an experiment (10^3 s).

[22] Measurements of the shear modulus of a glass formed by a mixture of charge-stabilized colloids have been reported by H. M. Lindsay and P. M. Chaikin, J. Chem. Phys. **76**, 3774 (1982).

[23] Shear-induced melting of charge-stabilized colloidal crystals was described by B. J. Ackerson and N. A. Clark, Phys. Rev. Lett. **46**, 123 (1981).

[24] S. H. Chen and J. S. Huang, Phys. Rev. Lett. **55**, 1888 (1985).

[25] F. Mezei, W. Knaak, and B. Farago, Phys. Rev. Lett. **58**, 571 (1987).