PHYSICAL REVIEW E **73**, 020503(R) (2006)

Dynamical perspective of the freezing transition of a suspension of hard spheres from the velocity autocorrelation function

W. van Megen
Department of Applied Physics, Royal Melbourne Institute of Technology, Melbourne, Victoria 3000, Australia
(Received 19 May 2005; revised manuscript received 7 December 2005; published 27 February 2006)

The velocity autocorrelation function of concentrated colloidal fluids of hard-sphere particles, measured by dynamic light scattering, decays to the experimental noise floor from below. The decay follows a stretched exponential function of delay time for the colloidal fluid in thermodynamic equilibrium, and a power law for the nonequilibrium, undercooled colloidal fluid. Consideration of this difference between the two states points to a possible dynamical mechanism of freezing.

DOI: 10.1103/PhysRevE.73.020503 PACS number(s): 64.70.Pf, 61.20.Ne, 82.70.Dd

The dynamics of suspensions of particles with hard-sphere-like interactions has been studied extensively, particularly by dynamic light scattering (DLS) [1,2]. The observed stretching of the time autocorrelation function of particle number density fluctuations, in the colloidal fluid, and the manner and extent to which these fluctuations arrest at the glass transition (GT) are quantitatively consistent with mode-coupling theory (MCT) [3–5]. This consistency supports the Markovian approximation, commonly invoked in considerations of the dynamics of suspensions, which holds that on the time scale of detectable particle excursions the suspending fluid acts as a white noise thermal bath [1,6]. Then, according to the idealized version of MCT of the GT at least [5], deviations of these excursions, and concomitant particle number density fluctuations, from the Markovian approximation—evident by the stretching just mentioned—are attributed to the (delayed) coupling of density fluctuations alone. From this perspective no distinction is made between the thermodynamically equilibrated and undercooled colloidal fluids, i.e., fluids whose volume fractions are, respectively, below and above the freezing volume fraction, 0.493, known for hard spheres [7]. From the standpoint of classical theory of crystallization [8], the freezing of the colloidal fluid into an opalescent crystal [9] is a kinetic process whereas, according to MCT, freezing into an amorphous, glassy solid is dynamical in origin. In other words, from the perspective of those theories, particularly successful in their ability to quantitatively describe experimental data pertaining to solidification of colloidal systems of hard spheres at least [2–4,10], freezing into a crystalline state and freezing into a glass occur by completely different and independent mechanisms.

Recent measurements and analyses [11,12] of the autocorrelation function of tagged particle density fluctuations, the self-intermediate scattering function (ISF), expose qualitative differences between equilibrated and undercooled colloidal fluids of hard spheres. This hint of the fluid's awareness of its traversal of the freezing volume fraction provides a motive to reexamine the above notions commonly applied in studies of the dynamics and freezing processes of colloids and also, to some extent, of simple liquids [6].

The quantity considered here is the velocity autocorrelation function (VAF). As reported previously [11] for the undercooled colloidal fluid, the VAF decays algebraically to zero from below. The additional data brought to bear in this communication exposes another difference between the equilibrated and undercooled colloidal fluids, a difference that leads to a possible dynamical mechanism by which freezing into the crystalline state is initiated.

The particles are polymer spheres, suspended in hydrocarbon liquids, and their mutual interactions are hard-sphere-like. Accordingly, the phase behavior exhibited by this suspension maps onto that known for the hard-sphere system; at equilibrium the coexisting colloidal fluid and crystal have volume fractions $\phi_f=0.494$ and $\phi_m \approx 0.54$ [9]. A spread of about 6% in the particle radius, relative to the mean, delays crystallization sufficiently [13] to allow measurement of the structure [14] and dynamical properties [3,14] of the undercooled colloidal fluid. The latter shows a glass transition at the volume fraction $\phi_g \approx 0.565$ [9,14]. Adding to the suspension of polymer spheres a small proportion of identically sized silica spheres, and adjusting the refractive index of the suspending liquid so as to suppress scattering from particle number density fluctuations, allows measurement of the self-ISF by DLS [15]. In the data below distances are expressed in units of the particle radius, $R=200$ nm, and delay times in units of the characteristic Brownian interval, $\tau_b=R^2/(6D_0)=0.021$ s, where D_0 is the diffusion coefficient of an isolated suspended particle. In these units the (dimensionless) mean-squared thermal velocity, $3kT/M$, where k is the Boltzmann constant, T the absolute temperature, and M the mass of the particles, has the value 4.2×10^6.

The VAF, $Z(\tau)$, is obtained by (numerical) differentiation of the self-ISF, $F_s(q,\tau)$ [6]

$$Z(\tau) = -\lim_{q\to 0}\frac{1}{q^2}\frac{d^2}{d\tau^2}F_s(q,\tau), \tag{1}$$

where q is the magnitude of the scattering vector. Typical results are shown in Fig. 1(a) for the colloidal fluid in thermodynamic equilibrium ($\phi<\phi_f$), and in Fig. 1(b), for the undercooled colloidal fluid ($\phi>\phi_f$). In both cases the VAF is seen to decay from below. A rough comparison of the magnitudes of the observed VAF with $Z(0)=3kT/M(=4.2\times10^6)$ shows just how feeble memory of the instantaneous thermal velocities is in the time window ac-

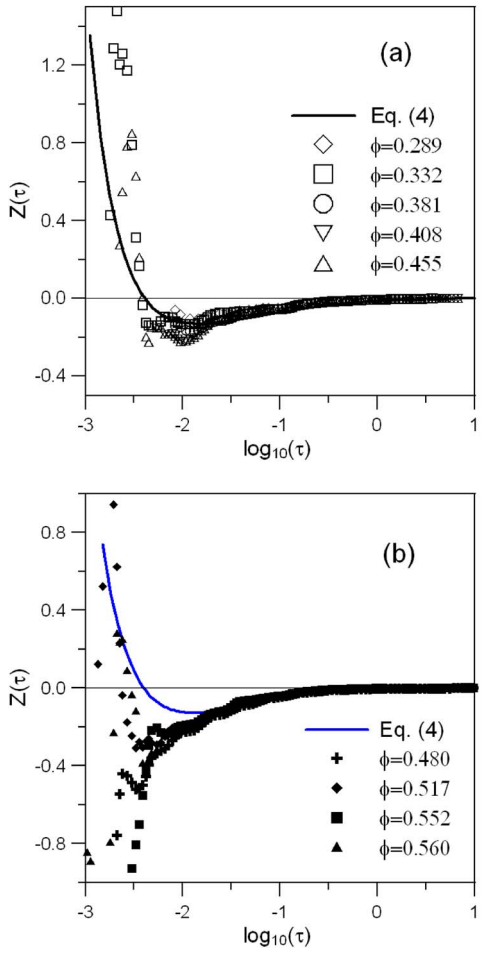

FIG. 1. (Color online) Velocity autocorrelation function, $Z(\tau)$, versus logarithm of delay time: (a) Colloidal fluid at a range of volume fractions in thermodynamic equilibrium, $\phi < \phi_f$. (b) Undercooled colloidal fluid at a range of volume fractions, $\phi > \phi_f$. (The oscillations evident for logarithm τ between about -2 and -1 are a consequence of the architecture of the real-time correlator and have no physical significance.)

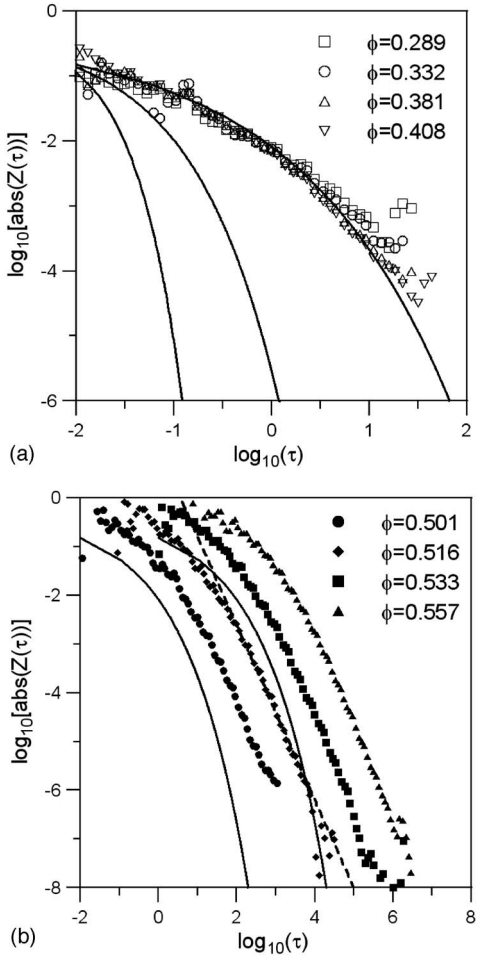

FIG. 2. Double logarithm plot of the VAF. (a) Colloidal fluid in thermodynamic equilibrium, $\phi < \phi_f$. The three solid curves are Eq. (2) for $B=0.45$, $\tau_d=0.007$ and, from left to right, $\zeta=1$, 0.5, 0.28. (b) Undercooled colloidal fluid, $\phi > \phi_f$. Each successive data set is translated along the abscissa by one unit. The solid curves are plotted for the same values of B, τ_d and $\zeta=0.28$, with one curve translated along the abscissa by two units. A straight (dashed) line with slope -1.8 is also drawn.

cessed in these experiments. Of course the positivity of the mean-squared velocity, $Z(0)$, dictates that $Z(\tau)$ passes through a minimum, whether or not thermodynamic equilibrium prevails. Indeed, minima can be discerned from experimental noise at $\tau_v \approx 10^{-2}$,for $\phi < \phi_f$ and also, but less convincingly, for $\phi > \phi_f$.

In dense molecular fluids the minimum in $Z(\tau)$ is attributed to backscatter of a molecule from its immediate "cage" of neighbors [6]. This is not the case here. As shown in Ref. 12, the time for a colloidal particle to diffuse a root-mean-squared distance equal to the average interparticle gap decreases with volume fraction, but it is also approximately two orders of magnitude larger than τ_v. Given their speed, sound modes being scattered from the neighbor cage must also be dismissed as a possible source of the minimum of the VAF.

The way in which the VAF decays to zero is seen more clearly with double logarithm plots shown in Fig. 2. Here a qualitative difference between the equilibrium and undercooled colloidal fluid is apparent.

In the equilibrium colloidal fluid [Fig. 2(a)] the measured long-time decay of $Z(\tau)$ can be described by the stretched exponential,

$$Z(\tau > \tau_v) = -B \exp\left[-\left(\frac{\tau}{\tau_d}\right)^s\right], \tag{2}$$

with $B=0.5\pm0.05$, $\zeta=0.28\pm0.02$, and $\tau_d=0.008\pm0.002$. For low volume fractions, $\phi<0.2$, it is difficult to discern the VAF from experimental noise. But for larger ϕ the VAF can be discerned quantitatively and, for these cases, no systematic variation of the parameters B, ζ, τ_d, or τ_v, with volume fraction is found. To indicate the significant degree of stretching shown by this part of the VAF, Eq. (2) is also plotted for $\zeta=1$ and 0.5.

Once the volume fraction exceeds the freezing value, Eq. (2) fails to describe the decay of the observed VAF for any value of ζ over any significant time window. As reported

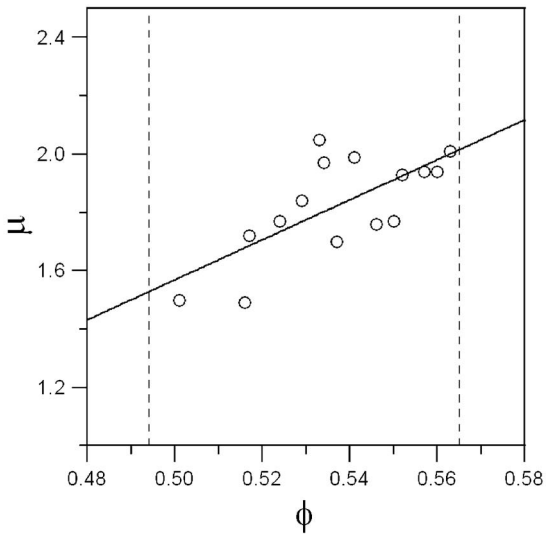

FIG. 3. Exponent of the power law fitted to the final decay of the VAF of the undercooled colloidal fluid. The two dashed vertical lines are drawn at ϕ_f and ϕ_g. The solid line is the line of best fit to these exponents.

previously [11] and illustrated in Fig. 2(b), in these cases the final decay of $Z(\tau)$ is approximated better by a power law,

$$Z(\tau) = -\left(\frac{\tau}{\tau_f}\right)^{-\mu}. \tag{3}$$

The scaling time, $\tau_f \approx 0.10$, shows no systematic variation with ϕ. However, linear regression of the long-time decays of these data exposes, as shown in Fig. 3, a weak variation of the index μ, from approximately 3/2 at ϕ_f to approximately 2 at ϕ_g.

The data of Fig. 1 show that the slow decay of the VAF is effected through loss of correlation of reversals of particle velocities. Figure 2 shows that this decay is qualitatively different in the equilibrated and undercooled colloidal fluids. Next we examine what can be inferred from these decays, as approximated by Eqs. (2) and (3), about the momentum and energy exchanges between the particles and the suspending liquid.

Equilibrium colloidal fluid. For delay times less than those around the minimum in $Z(\tau)$ the data clearly suffer too much noise for any direct quantitative analysis. Despite this, one can determine compatibility of these observations with a fully developed vorticity in the suspending liquid. As is now well established from computer simulation [16,17], experiment [18], and theory [19], a diffusing vorticity causes the VAF to decay (from above) in proportion to $\tau^{-3/2}$. Adding this term to the right-hand side of Eq. (2) gives

$$Z(\tau) = h\tau^{-3/2} - B\exp\left[-\left(\frac{\tau}{\tau_d}\right)^{\zeta}\right]. \tag{4}$$

The amplitude h derived from this in terms of the delay time, τ_v, at the minimum of $Z(\tau)$ is

$$h = \frac{2}{3}B\zeta\left(\frac{\tau_v}{\tau_d}\right)^{\zeta}\exp\left[-\left(\frac{\tau_v}{\tau_d}\right)^{\zeta}\right]\tau_v^{3/2}. \tag{5}$$

With the above values of B, ζ, τ_v, and τ_d one obtains $h = 6(\pm 2)\times 10^{-5}$. The large error in h derives mainly from the experimental uncertainty in τ_v. The theoretical expression for the amplitude, for an isolated particle in an unbounded fluid, is [19]

$$h_t = CkT\rho^{1/2}/3(\pi\eta)^{3/2}, \tag{6}$$

where ρ and η are the density and viscosity of the suspending liquid. By assuming the particles to be perfectly buoyant one obtains $h_t = C\times 1.2\times 10^{-4}$. The factor C accounts for the variation, between $\frac{1}{4}$ and 1, obtained in different theoretical approaches [19]. That is, the stretched exponential decay of the VAF, observed for the equilibrium colloidal fluid can be reconciled with the $(\tau^{-3/2})$ power law that expresses the effect of the fully developed vorticity, or incompressible flow, in an unbounded liquid in thermodynamic equilibrium. Moreover, as shown in Fig. 1(a), there is no quantitative inconsistency between the latter and the data.

The VAF obtained here as described by Eq. (4) is independent of the volume fraction, aside from the possibility that experimental noise disguises a systematic variation in the amplitude h of a factor two. By contrast, the (long-time) self-diffusion coefficient—the time integral of the VAF—decreases by almost two orders of magnitude between $\phi = 0$ and $\phi = \phi_f$ [15]. Thus, the diffusion coefficient is effectively determined by the manner by which $Z(\tau)$ decays from the mean-squared thermal velocity and crosses over to the form that manifests the diffusing vorticity. All this occurs on time scales shorter than those on which particle displacements are detected by DLS. In other words, on the experimental time scale all memory of inertial effects is lost and the particles have, in effect, been set adrift by the thermal forces and their movements are completely slaved to incompressible flow [the first term in Eq. (4)] and the (damped) compressible modes [the second term in Eq. (4)] in the liquid. Moreover, Eq. (4) implies that $Z(\tau)$ has a second crossing of the abscissa at $\tau \approx 200$, which is clearly outside the experimental window, and decays to zero asymptotically from above in proportion to $\tau^{-3/2}$. In this sense, the damped compressible modes are merely transient. Recent computer simulations on a system of ballistic hard spheres [17] show these features explicitly.

Undercooled colloidal fluid. As mentioned above, $Z(\tau)$ must pass through a minimum. However, for the undercooled fluid it is not possible to describe this minimum in terms of a crossover from a fully developed viscous response, expressed by the positive power law, $\tau^{-3/2}$, to an elastic response, expressed by another but negative power law, $-\tau^{-\mu}$, whose index $\mu \geqslant 3/2$. Thus, that part of the observed negative decay of the VAF that can be described by the said power law is incompatible with a fully developed vorticity. Of course the undercooled colloidal fluid, like any undercooled fluid, still flows. What is proposed here is that flow remains undeveloped because inertial effects have not fully dissipated. The undeveloped flow, or that part of the transverse momentum that does not diffuse, appears as a propa-

gating transverse momentum current. Coupling of these propagating transverse modes in the suspending liquid to the particles provides a path toward equilibrium. Compared with an undercooled fluid of hard spheres in a vacuum [17] this is a slow process because, given the mass difference between the particles and molecules of the suspending liquid, only very low frequency modes will be effective in this coupling. Indeed the colloidal crystals, of the type shown in Ref. [9], that ultimately form, quiver when gently tapped. In the undercooled fluid the mentioned coupling creates shear resistant assemblies of particles. The existence of such assemblies allows one to make sense of the enhanced resistance to flow and inability to attain the zero frequency limiting viscosity of very concentrated suspensions [20].

Conclusion. For the colloidal fluid in thermodynamic equilibrium inertial processes have relaxed on the time scale of particle displacements large enough to be detectable by DLS. Therefore, the fluctuations of the scattered light reflect the coupling of the particles to the (thermally activated) diffusing vorticity and damped elastic modes in the suspending liquid.

On the basis of the present data, these inferences cannot be extended to the undercooled colloidal fluid. In this case equilibrium is being established by the organization of particles so that they couple to the low frequency transverse momentum currents in the suspending liquid. The mechanism proposed here suggests a fundamental connection between the origin of crystal nuclei and the source of the enhanced resistance to flow in an undercooled fluid. In this sense freezing into a crystalline solid or an amorphous glass are both dynamical in origin and, as such, cannot be considered as completely unconnected processes.

My thanks go to Gary Bryant, Matthias Fuchs, Ignacio Pagonabarraga, Ian Snook, and Stephen Williams for their valuable comments on this work.

[1] P. N. Pusey, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991), p. 763.
[2] W. van Megen and S. M. Underwood, Langmuir **6**, 35 (1990).
[3] W. van Megen and S. M. Underwood, Phys. Rev. E **49**, 4206 (1994).
[4] W. Götze and L. Sjögren, Phys. Rev. A **43**, 5442 (1991); M. Sperl, Phys. Rev. E **71**, 060401 (2005).
[5] W. Götze, J. Phys.: Condens. Matter **11**, A1 (1999).
[6] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1886).
[7] W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1969).
[8] K. F. Kelton, Solid State Phys. **45**, 74 (1991).
[9] P. N. Pusey and W. van Megen, Nature (London) **320**, 340 (1986).
[10] J. L. Harland and W. van Megen, Phys. Rev. E **55**, 3054 (1997).
[11] W. van Megen, J. Phys.: Condens. Matter **14**, 7699 (2002).
[12] W. van Megen, T. C. Mortensen, and G. Bryant, Phys. Rev. E **72**, 031402 (2005); W. van Megen, *ibid.* **73**, 011401 (2006).
[13] S. I. Henderson and W. van Megen, Phys. Rev. Lett. **80**, 877 (1998).
[14] W. van Megen and P. N. Pusey, Phys. Rev. A **43**, 5429 (1991).
[15] W. van Megen *et al.*, Phys. Rev. E **58**, 6073 (1998).
[16] B. J. Alder and T. E. Wainright, Phys. Rev. A **1**, 18 (1970).
[17] S. R. Williams *et al.*, Phys. Rev. Lett. (to be published).
[18] G. L. Paul and P. N. Pusey, J. Phys. A **14**, 3301 (1981); K. Ohbayashi, T. Kohno, and H. Utiyama, Phys. Rev. A **27**, 2632 (1983); J. X. Zhu *et al.*, Phys. Rev. Lett. **68**, 2559 (1992).
[19] R. Zwanzig and M. Bixon, Phys. Rev. A **2**, 2005 (1970); A. Widom, *ibid.* **3**, 1394 (1971); T. S. Chow and J. J. Hermans, J. Chem. Phys. **56**, 3150 (1972); E. J. Hinch, J. Fluid Mech. **72**, 499 (1975).
[20] J. Mewis *et al.*, AIChE J. **35**, 415 (1989).