

# Colloidal Glasses

Wilson C.K. Poon

## Abstract

This article reviews recent advances in understanding amorphous glassy states in dense colloidal suspensions with or without short-range interparticle attractions. Experiments, theory, and simulation show that two kinds of glassy states are possible, dominated respectively by repulsion and attraction. Under suitable conditions, a small change in the interparticle potential can lead to a transition between these two kinds of colloidal glasses that entails sharp changes in material properties such as the shear modulus. This may provide novel routes for fine-tuning the properties of industrial pastes and slurries.

**Keywords:** colloids, glasses, metastability, nonergodicity, rheology, sticky hard spheres.

## Introduction

Understanding the vitreous, or glassy, state of matter is one of the “grand challenges” of 21st century materials science. Glasses in traditional atomic, small-molecule, and polymeric materials are well known. Vitrification is also important in biology as a means of preserving life under extreme conditions (e.g., in seeds). In all of these cases, we are speaking of *structural* glasses involving frozen-in disorder in the spatial arrangement of constituent atoms and molecules. There are also “glasses” in which the frozen-in disorder is not primarily structural, for example, “spin glasses,” in which the disorder is of a magnetic kind. Despite much commonality among them, it is unknown whether a unified description of all of these glasses is possible (e.g., how fundamental is the difference between annealed and quenched disorder in structural and spin glasses, respectively?)

The study of structural colloidal glasses did not really get off the ground until the mid-1980s, but it has blossomed tremendously since then. Some of the results have corroborated and clarified our existing understanding of glasses in noncolloidal systems. In other cases, novel phenomena that may well be unique to colloids have been discovered, challenging any conceptual framework that seeks a generic understanding of glasses. In this article, I will review this research in colloidal glasses.

## Glass Transition Due to Crowding

Although there had been speculation about a hard-sphere glass transition since at least Bernal’s pioneering work on sphere packing in the 1960s, it was the mode cou-

pling theory (MCT) calculations of Götze and collaborators in the 1980s<sup>1</sup> and the experiments of Pusey and van Meegen<sup>2,3</sup> that put this phenomenon on a firm footing.

The equilibrium phase behavior of  $N$  hard spheres of radius  $R$  in volume  $V$  depends only on the volume fraction,

$$\phi = \frac{4}{3}\pi R^3(N/V). \quad (1)$$

Below  $\phi = 0.494$ , the lowest free-energy state is a fluid, a disorderly arrangement of particles that can individually explore all of  $V$  (the system is “ergodic”). From  $\phi = 0.545$  up to close-packing ( $\phi \approx 0.74$ ), the equilibrium state is crystalline. Fluid and crystal coexist for  $0.494 < \phi < 0.545$ .

Pusey and van Meegen found<sup>2</sup> that suspensions of poly(methyl methacrylate) (PMMA) particles, stabilized by a thin layer of grafted polymer “hairs,” display precisely this behavior, except that above  $\phi \approx 0.58$ , samples that should crystallize failed to do so; rather, they remained amorphous for months to years. Inspired by MCT calculations, the researchers performed dynamic light scattering (DLS) experiments to show that this failure to crystallize could be attributed to the particles being trapped in a glassy state.<sup>3</sup> DLS measures the intermediate scattering function  $f(q,t)$ , which gives information about the decay in time  $t$  of spontaneous density fluctuations with wavelength  $2\pi/q$ , normalized such that  $f(q,0) = 1$ . In an *ergodic* system, density fluctuations decay completely, and  $f(q,\infty) = 0$ . In a *nonergodic*, or *glassy*, system, however,  $f(q,\infty) > 0$ . Pusey

and van Meegen found that in hard-sphere colloids at  $\phi \approx 0.58$  or above,  $f(q,t)$  remained finite within their experimental time window.

MCT, which is a scheme for solving an approximate equation of motion for  $f(q,t)$  requiring only the static structure factor  $S(q)$  as input,<sup>4</sup> predicts a hard-sphere glass transition at volume fraction  $\phi_g \approx 0.52$ . The precise value varies, depending on the  $S(q)$  used and the form of  $f(q,t)$  in the vicinity of this transition. Pusey and van Meegen’s experiments suggest that  $\phi_g \approx 0.58$ . Their initial DLS results, together with subsequent detailed measurements by van Meegen,<sup>5</sup> show that MCT predicts  $f(q,t)$  accurately, provided that the theoretical  $\phi$  is scaled by  $0.58/0.52 = 1.12$ .

MCT calculations, together with DLS experiments, suggest that the glass transition in hard spheres is due to crowding. In a dense hard-sphere fluid, each particle is surrounded at any one instance by a “cage” of 10 or so neighbors (Figure 1). Each particle forming the cage is itself caged by its own neighbors. Thus, as  $\phi$  increases, rearrangements need to be more and more cooperative, and the identity of each particle’s cage of neighbors persists for longer and longer. At  $\phi_g \approx 0.58$ , the cage becomes effectively permanent. The particles cannot undergo long-range diffusion, and the system becomes nonergodic—a glass is formed. The recent confocal microscopy experiments of Weeks and collaborators have given us perhaps the first real-space picture of such “cage rattling.”<sup>6</sup>

Pusey and van Meegen used particles that were monodisperse enough to crystallize. If the polydispersity  $\sigma$ , which is equal to the size standard deviation normalized by the mean, is above  $\sim 10\%$ , crystallization is not observed as  $\phi$  increases beyond  $\sim 0.5$ . The fluid state re-

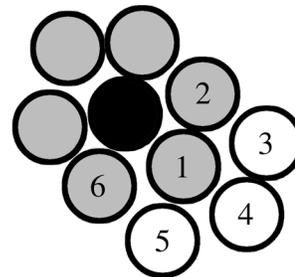


Figure 1. Schematic two-dimensional representation of a particle (solid circle) in a dense hard-sphere fluid being “caged” by its neighbors (grey circles). Each particle in the cage is also caged by its own cage of neighbors (e.g., particle 1 is caged by the black particle and particles 2–6).

mains ergodic until a transition to nonergodicity occurs at  $\phi \approx 0.6$ , the precise value being dependent on  $\sigma$ . Indeed, there is a suggestion (based on simulations) that monodisperse hard spheres always crystallize, and the experimental glass transition is due to polydispersity suppressing the crystallization.

### Glass Transitions in Sticky Colloids

Interparticle attractions with a range ( $\delta$ ) significantly smaller than the particle diameter ( $2R$ ) are ubiquitous in colloids, with values of the dimensionless range of the interparticle attraction  $\lambda = \delta/2R < 0.1$  not being uncommon. How does such a short-range attraction change the caging scenario described in the last section? Results we published in 1993<sup>7</sup> suggested that interesting physics should emerge from investigating this question. We “turned on” a short-range attraction between PMMA colloids by adding nonadsorbing linear polystyrene.<sup>8</sup> The exclusion of polymer from the region between two nearby colloids results in a net osmotic force, pushing them together (Figure 2a). The range and depth of this effective “depletion” attraction scale as the concentration and size, respectively, of the linear polymer (Figure 2b). In particular, the range  $\delta$  is roughly twice the radius of gyration ( $r_g$ ) of the polymers, that is,  $\lambda \approx r_g/R$ . Surprisingly, we found that turning on an attraction with  $\lambda \approx 0.08$  melted the hard-sphere glass into an ergodic fluid (which, because of low polydispersity, subsequently crystallized).

But it was MCT calculations published independently in 1999 by Bergenholtz and Fuchs<sup>9</sup> and Sciortino and collaborators<sup>10</sup> that started a recent surge of interest. These calculations predict two qualitatively distinct kinds of glasses in hard spheres with short-range attraction, separated by a reentrant glass-transition line. Experiments by Pham<sup>11</sup> in our group using PMMA colloids and nonadsorbing linear polystyrene with  $\lambda \approx 0.08$  confirmed this prediction (Figure 3). Consider, for example, samples with  $\phi \approx 0.6$ . The sample with no polymer (concentration  $c_p = 0$ , solid blue circles) is a hard-sphere glass. Adding sufficient polymer ( $c_p \approx 1 \text{ mg/cm}^3$ ) induces enough attraction to give an ergodic fluid that eventually crystallized (inverted green triangles). At  $c_p \approx 2.5 \text{ mg/cm}^3$  or higher, however, crystallization again failed to occur (solid red squares). Instead, these samples remained in amorphous states. DLS showed that the particles in these states were far more localized in space than in the hard-sphere glasses: they represent a qualitatively new kind of glass.

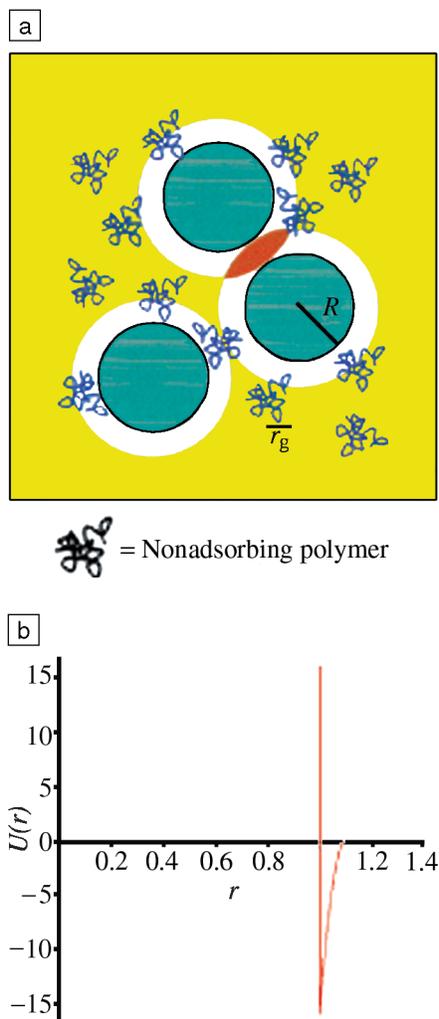


Figure 2. (a) Schematic illustration of the polymer-induced depletion attraction between hard spheres. The centers of mass of the polymer coils (radius of gyration  $r_g$ ) are excluded from the thin shell surrounding each particle. There is no polymer in the lens-shaped overlapping region between two nearby particles; this leads to a net osmotic force, pushing them together. (b) The depletion potential  $U(r)$  for a polymer that is  $\sim 10\%$  the size of the colloids (diameter = 1, so that the dimensionless range of the interparticle attraction is  $\lambda \approx 0.1$ ).

MCT and DLS suggest a heuristic picture for these observations<sup>11</sup> (Figure 3). In the “repulsion-dominated” hard-sphere glass, particles are caged by their neighbors. There is a characteristic length scale  $L$  over which each particle can “rattle” in its cage (analogous to the Lindemann length in melting). A little short-range attraction clusters the particles in the cage and opens up holes, ultimately melting the

glass and restoring ergodicity. Increasing the attraction further gives an “attraction-dominated” glass—particles are now localized within  $\delta$ , the width of the narrow interparticle attraction. Simulations<sup>11,12</sup> confirm this picture.

The MCT reentrant glass-transition line<sup>11</sup> is shown in Figure 3. The agreement with data is striking, given that all parameters were taken from experiments with the only adjustment being a volume fraction scaling to correct for the MCT  $\phi_g$  for hard spheres. To the right of the “cusp,” MCT predicts a glass-glass transition (double-headed arrow in Figure 3), where various physical properties should change abruptly. The distinction between the two kinds of glasses vanishes at a point known as the  $A_3$  singularity. Qualitatively, this is where the two length scales of the problem become equal; in the notation introduced in Figure 3,  $L \approx \delta$ . (MCT also predicts that the reentrant glass transition disappears when  $\delta$  becomes large enough; crudely, when  $L \approx \delta$  at the hard-sphere glass transition.) Finally, DLS has confirmed many qualitative features of the MCT prediction of  $f(q,t)$ .<sup>13</sup>

Significantly, the phenomenology shown in Figure 3 also occurs in other systems. First, Bartsch and colleagues have seen reentrant behavior in swollen polystyrene micronetwork spheres, with linear polystyrene inducing a depletion attraction.<sup>14</sup> Second, Mallamace and collaborators<sup>15</sup> studied micelles of Pluronic L64, a commercial triblock copolymer made of poly(ethylene oxide) and poly(propylene oxide):  $(\text{PEO})_{15}(\text{PPO})_{30}(\text{PEO})_{15}$ . Since PPO is more hydrophobic than PEO, Pluronic L64 self-assembles into micelles, each with a PPO core and a PEO corona. When the temperature increases, the decreasing solvency of water for PEO leads to an increasing short-range attraction between the micelles. These authors found evidence of a sharp transition between repulsive and attractive glasses.

A third system was studied by Mourchid and colleagues.<sup>16</sup> The diblock copolymer they investigated was prepared from polystyrene poly(ethyl acrylate) (PS-PEA) diblocks by partially hydrolyzing the PEA to poly(acrylic acid) (PAA). The resultant diblock again self-assembles into micelles in water, each with a PS core and an ionized PAA corona. The unhydrolyzed EA monomers in the corona act as hydrophobic “stickers,” giving rise to a short-range attraction between two micelles. The strength of the stickers is tuned by altering the fraction  $f$  of hydrolyzed EA stickers. Significantly, these authors found that the shear modulus  $G'$  was a non-monotonic function of  $f$  (Figure 4). Turning on an attraction

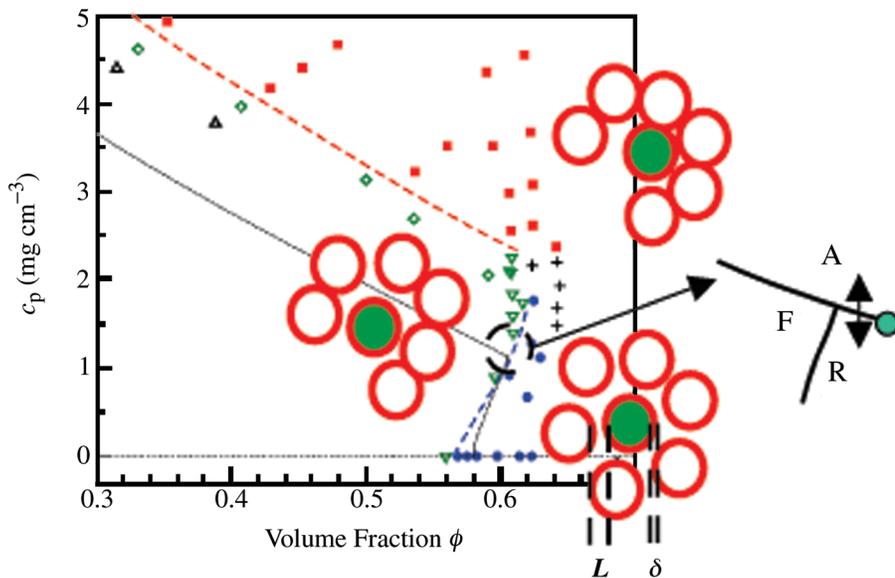


Figure 3. Equilibrium and nonequilibrium behavior of a colloid (volume fraction  $\phi$ ) and polymer (concentration  $c_p$ ) mixture with the dimensionless range of the depletion attraction  $\lambda = 0.08$ . Open symbols represent samples that reached thermal equilibrium: fluid (black triangles), fluid–crystal coexistence (green diamonds), and fully crystallized (inverted green triangles). Other samples did not reach thermal equilibrium and failed to crystallize; some showed characteristics of repulsion-driven glasses (solid circles), some showed those of attraction-driven glasses (solid squares), and some showed both (plus signs). Dashed curves are guides to the eye, indicating where crystallization ceased. Superimposed on the graph are schematic drawings of particles, showing the range of the attractive potential  $\delta$ . From bottom to top: caging in repulsion-driven glasses ( $L$  = cage length), clustering of cages due to attraction, and trapping of particles by nearest-neighbor potential wells in attraction-driven glasses. The continuous line is the reentrant glass-transition line predicted by mode coupling theory. The enlarged schematic on the far right shows the details of the “cusp”: to the right of the reentrant region separating attractive glass (A), fluid (F), and repulsive glass (R), there is a sharp glass–glass transition (double-headed arrow); the solid dot is the point known as the  $A_3$  singularity, beyond which one can move from a repulsive to an attractive glass continuously.

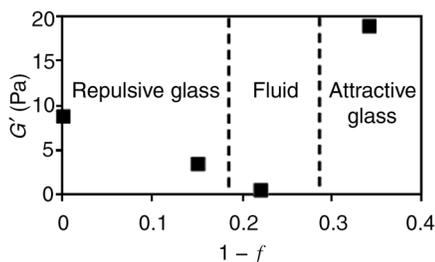


Figure 4. The low-frequency storage modulus  $G'$  of polystyrene poly(acrylic acid) (PS-PAA) micelles (block molecular weights, 2000–14,000 g/mol) with ethyl acrylate (EA) “stickers” in the PAA corona, versus  $1-f$ , the fraction of hydrophobic EA monomers remaining in the corona. The “stickiness” between two micelles increases with  $1-f$ . The data points are replotted from Reference 16. The vertical dotted lines indicate approximately where one may expect the transitions from repulsive glass to fluid to attractive glass.

(decreasing  $f$  from 1) weakens the hard-sphere glass, turns it into an ergodic fluid ( $G' \approx 0$ ), and then generates an attractive glass with a  $G'$  significantly higher than those shown by repulsive glasses. The differing elastic moduli of the two kinds of glasses has been predicted by MCT.<sup>17</sup> Thus, the reentrant glass transition offers a sensitive way of tuning the properties of dense colloidal systems by relatively small changes in external conditions.<sup>18</sup>

The intermediate scattering function  $f(q,t)$  has been measured in all four systems mentioned here. MCT predicts<sup>17,19</sup> and simulations confirm<sup>12,20</sup> that near the “cusp” of the reentrant glass transition, the dynamics should be very stretched out; indeed, part of  $f(q,t)$  should scale as the logarithm of  $t$ . One example of such “log-time” dynamics is shown in Figure 5. Such dynamics have also been observed in the other three systems introduced here.<sup>13–16</sup> This is a strong piece of evidence pointing to generic physics at work.

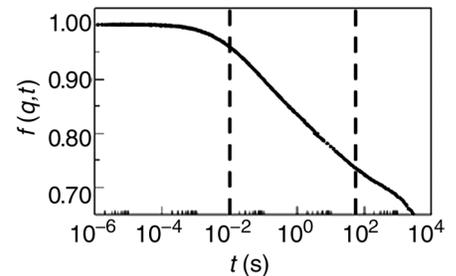


Figure 5. A typical intermediate scattering function,  $f(q,t)$ , showing log-time dynamics. This sample is the lowest “+” data point in Figure 3.  $f(q,t)$  is normalized to unity at  $t = 0$  and decays to zero for ergodic samples. This  $f(q,t)$  is linear in the logarithm of time between the dotted lines. Note that even after  $10^4$  s, it has only decayed down to  $\sim 0.65$ . (Taken from Reference 13.)

## Conclusions

The study of colloidal glasses has come a long way since its modest beginnings in the mid-1980s. The field is entering an exciting phase in which experiment, theory, and simulation combine to give an unprecedentedly detailed view of glass transitions in hard spheres on their own or with short-range attraction. Despite much progress, however, many important puzzles and challenges remain. To conclude, I will describe these briefly.

Perhaps a good place to start is the theory to which I have repeatedly appealed throughout this review: mode coupling theory (MCT). This is currently the theory of choice for experimentalists working in colloidal glasses because it uniquely gives precise predictions of many of the quantities most accessible to experimental measurement. Moreover, once certain experimental information is given, the theory has no fitting parameters; a stark confrontation of measurements and prediction is possible.

The MCT glass transition is formally a mathematical singularity, where the relaxation time (and other quantities) diverge. It is well known from the study of atomic, molecular, and polymeric glasses that this singularity is due to the theory’s neglect of *activated processes*, so that in practice (where processes like activated “hopping” do occur), the singularity and its associated divergences are avoided. Recent work suggests that such processes are important in attractive glasses<sup>21</sup> and perhaps even in hard-sphere glasses.<sup>22</sup> Undoubtedly, future experiments focusing on these processes will stimulate theoretical advances, whether in extending MCT or in developing other frameworks. The relationship

between activated processes and “aging” will also be a fruitful field of investigation.

The theme of dynamic heterogeneities is gaining prominence in glass studies. For example, Week’s confocal images of a repulsive colloid near the glass transition<sup>6</sup> show that fast-moving particles occur in clusters. It is possible that a recent attempt at moving beyond MCT for hard spheres succeeded in improving the predicted  $\phi_g$  from  $\sim 0.52$  to  $\sim 0.549$  (compared with the experimental  $\phi_g \approx 0.58$ ), partly because it takes some account of such heterogeneities (essentially, by not factorizing a pair-density correlation function into a product of two density correlation functions).<sup>23</sup> Some theories now start explicitly with dynamic heterogeneities.<sup>24</sup> The experimental investigation of such heterogeneities (e.g., by confocal microscopy) in sticky-sphere systems and the related phenomenon of intermittent dynamics (whereby relaxation occurs in bursts)<sup>25</sup> should prove fruitful.

Perhaps the most important result reviewed here for materials applications is the sensitivity of rheological properties to external conditions (e.g., see Figure 4). MCT has recently been extended to deal with sheared suspensions;<sup>26</sup> an alternative approach, known as soft glassy rheology, may also be used.<sup>27</sup> In this approach, the presence of “traps” on multiple energy scales controls the dynamics. A detailed study of mechanical properties in the vicinity of the reentrant glass transition should yield important results for applications and for discriminating between theories.

It is well known that colloids with short-range attraction form ramified (or “fractal”) gels at low volume fractions. The nature of these gels, and their relation (if any) with repulsive/attractive glasses, is an active area of research. If the suggestion is correct that such gels are glasses of large fractal clusters,<sup>28,29</sup> then the phenomenology discussed in this review may have wide applicability.

Finally, space has precluded treatment of glasses in systems with soft repulsive interactions, for example, star polymers<sup>30</sup>

and charged colloids,<sup>31</sup> where, in the latter case, measured  $f(q,t)$  compares well with MCT. Research in these materials is also well under way, but further advances in understanding can definitely be expected.

## References

1. U. Bengtzelius, W. Götze, and A. Sjölander, *J. Phys. C* **17** (1984) p. 5915.
2. P.N. Pusey and W. van Meegen, *Nature* **320** (1986) p. 340.
3. P.N. Pusey and W. van Meegen, *Phys. Rev. Lett.* **59** (1987) p. 2083.
4. The MCT literature is mostly very mathematical. For a less extensively mathematical review, see W. Götze and Sjölander, *Rep. Prog. Phys.* **55** (1992) p. 241. For brief critical introductions, see K. Kawasaki and B. Kim, *J. Phys.: Condens. Matter* **14** (2002) p. 2265; and M.E. Cates, “Arrest and Flow of Colloidal Glasses,” arXiv.org e-print archive, <http://arxiv.org/abs/cond-mat/0211066> (accessed December 2003).
5. W. van Meegen and S.M. Underwood, *Phys. Rev. E* **49** (1994) p. 4206.
6. E.R. Weeks, J.C. Crocker, A.C. Levitt, A. Schofield, and D.A. Weitz, *Science* **287** (2000) p. 627.
7. W.C.K. Poon, J.S. Selje, M.B. Robertson, S.M. Ilett, A.D. Pirie, and P.N. Pusey, *J. Phys. II* **3** (1993) p. 1075.
8. For a review of this model system, see W.C.K. Poon, *J. Phys.: Condens. Matter* **14** (2002) p. R859.
9. J. Bergenholtz and M. Fuchs, *Phys. Rev. E* **59** (1999) p. 5706.
10. L. Fabbian, W. Götze, F. Sciortino, P. Tartaglia, and F. Thiery, *Phys. Rev. E* **59** (1999) p. R1347; L. Fabbian, W. Götze, F. Sciortino, P. Tartaglia, and F. Thiery, *Phys. Rev. E* **60** (1999) p. 2430.
11. K.N. Pham, A.M. Puertas, J. Bergenholtz, S.U. Egelhaaf, A. Moussaïd, P.N. Pusey, A.B. Schofield, M.E. Cates, M. Fuchs, and W.C.K. Poon, *Science* **296** (2002) p. 104.
12. A.M. Puertas, M. Fuchs, and M.E. Cates, *Phys. Rev. Lett.* **88** 098301 (2002).
13. K.N. Pham, S.U. Egelhaaf, P.N. Pusey, and W.C.K. Poon, “Glasses in Hard Spheres with Short-Range Attraction,” arXiv.org e-print archive, <http://arxiv.org/abs/cond-mat/0308250> (accessed December 2003).
14. T. Eckert and E. Bartsch, *Phys. Rev. Lett.* **89** 125701 (2002).
15. S.H. Chen, W.R. Chen, and F. Mallamace, *Science* **300** (2003) p. 619.
16. J. Grandjean and A. Mourchid, in *Self-Assembled Nanostructured Materials*, edited by Y. Lu, C.J. Brinker, M. Antonietti, and C. Bai (Mater. Res. Soc. Symp. Proc. **775**, Warrendale, PA, 2003) p. 231.
17. K. Dawson, G. Foffi, M. Fuchs, W. Götze, F. Sciortino, M. Sperl, P. Tartaglia, Th. Voigtmann, and E. Zaccarelli, *Phys. Rev. E* **63** 011401 (2001).
18. F. Sciortino, *Nat. Mater.* **1** (2002) p. 145.
19. M. Sperl and W. Götze, *Phys. Rev. E* **66** 011405 (2002).
20. F. Sciortino, P. Tartaglia, and E. Zaccarelli, “Logarithmic Relaxation in Dense Short-Range Attractive Colloids,” arXiv.org e-print archive, <http://arxiv.org/abs/cond-mat/0304192> (accessed December 2003).
21. E. Zaccarelli, G. Foffi, F. Sciortino, and P. Tartaglia, *Phys. Rev. Lett.* **91** 1083101 (2003).
22. K.S. Schweizer and E.J. Saltzman, *J. Chem. Phys.* **119** (2003) p. 1181.
23. G. Szamel, *Phys. Rev. Lett.* **90** 228301 (2003). However, using simulated (rather than analytic) structure factors in standard mode coupling theory gives  $\phi_g = 0.546$ ; G. Foffi, W. Götze, F. Sciortino, P. Tartaglia, and Th. Voigtmann, “Alpha-Relaxation Processes in Binary Hard-Sphere Mixtures,” arXiv.org e-print archive, <http://arxiv.org/abs/cond-mat/0309007> (accessed December 2003).
24. E. Donth, *J. Phys. I* **6** (1996) p. 1189; D. Long and F. Lequeux, *Eur. Phys. J. E* **4** (2001) p. 371; S. Merabia and D. Long, *Eur. Phys. J. E* **9** (2002) p. 195; J.P. Garrahan and D. Chandler, *Phys. Rev. Lett.* **89** 035704 (2002).
25. L. Cipelletti, H. Bissig, V. Trappe, P. Ballesta, and S. Mazoyer, *J. Phys.: Condens. Matter* **15** (2003) p. S257.
26. M. Fuchs and M.E. Cates, *Faraday Discuss.* **123** (2003) p. 267; M. Fuchs and M.E. Cates, *Phys. Rev. Lett.* **89** 248304 (2002).
27. S.M. Fielding, P. Sollich, and M.E. Cates, *J. Rheol.* **44** (2000) p. 323.
28. P.N. Segre, V. Prasad, A.B. Schofield, and D.A. Weitz, *Phys. Rev. Lett.* **86** (2001) p. 6042.
29. W.C.K. Poon, *Faraday Discuss.* **123** (2003) p. 95; K. Kroy, M.E. Cates, and W.C.K. Poon, “A cluster mode-coupling to weak gelation in attractive colloids,” arXiv.org e-print archive, <http://arxiv.org/abs/cond-mat/0310566> (accessed January 2004).
30. E. Stiakakis, D. Vlassopoulos, B. Loppinet, J. Roovers, and G. Meier, *Phys. Rev. E* **66** 051804 (2002).
31. C. Beck, W. Hartl, and R. Hempelmann, *J. Chem. Phys.* **111** (1999) p. 8209. □