Colloids are suspensions of small solid particles in a liquid, and exhibit glassy behavior when the particle concentration is high. In these samples, the particles are roughly analogous to individual molecules in a traditional glass. This model system has been used to study the glass transition since the 1980's. In this Viewpoint we summarize some of the intriguing behaviors of the glass transition in colloids, and discuss open questions.

PACS numbers:

Glasses are an intriguing state of matter in that they share some similarities to both liquids and solids. Molten glass is a liquid and can flow easily, but as it cools its viscosity rises smoothly. In fact upon cooling by several tens of degrees, the viscosity grows by ten to twelve orders of magnitude. One rough definition of when a sample becomes a glass is when its viscosity is $10^{15}$ times that of water, simply because viscosities that are any larger become problematic to measure. At this point the sample remains as disordered as a liquid on the molecular scale, but macroscopically appears solid. This is perhaps a disatisfying situation, in that regular phase transitions are more obvious and well-defined as to the precise temperatures and pressures at which they occur. In contrast, the temperature required to form a glass depends on the cooling rate. Furthermore, one can note that if one waits decades flow can sometimes be observed \cite{1}, although this is not relevant for window glass \cite{2,3}.

Polymers easily form glasses. In part this is because the polymers entangle, which already causes interesting nontrivial flow properties even when a polymer sample isn’t glassy. More to the point, polymers generally have large viscosities and so even slowly cooled polymers have difficulty rearranging into a crystalline state. Polymers with stereo-irregular chemistry (random placement of side groups) further frustrate crystallization. For these reasons, when cooled polymers are quite likely to be trapped in a glassy state. Plastic materials are polymer glasses.

In the 1980's, colloidal suspensions were introduced as model systems which had a glass transition \cite{4-6}. Colloidal suspensions are composed of small (10 nm - 10 $\mu$m radius) solid particles in a liquid. Their glass transition is not as a function of temperature, but rather of concentration. At low concentration, particles undergo Brownian motion and diffuse through the sample freely. At higher concentrations, the particles pack together randomly (with a liquid-like structure), and macroscopically the sample viscosity grows dramatically as a function of concentration. Below the glass transition concentration, Brownian motion enables the sample to equilibrate, and the sample is still considered a liquid. Above the glass transition concentration, equilibration is no longer possible on experimental time scales, and macroscopically the sample has a yield stress like a regular elastic material.

Colloidal glasses share many similarities to “regular” glasses. For example, they have a strong growth of their viscosity as the glass transition is approached \cite{7}; their structure is essentially unchanged at the glass transition \cite{8}; materials become dynamically heterogeneous as the transition is approached \cite{9,10}; confining colloidal samples modifies their glass transition \cite{11,12}. This Viewpoint cannot describe all of the interesting glassy phenomena that have been studied with colloidal glasses, although the reader is invited to consult longer review articles \cite{13-17}. Rather, a few representative examples will be presented below that will highlight the advantages of colloids as a model system. A particular advantage is that their large size makes colloids directly observable with optical microscopy (see Fig. 1) as well as indirectly observable with light scattering \cite{18}.

Colloidal particles interact with one another with a variety of forces. This can include repulsive forces (such as electrostatic forces if the particles are charged) and
attractive forces (the van der Waals force due to fluctuating electric dipole moments of the particles, which is quite strong at short range). Discussing these forces is beyond the scope of this review, so accordingly I will focus the discussion on purely repulsive colloidal particles. One important category is hard-sphere-like particles \[2\]. Typically these are made by suspending the particles in a solvent that matches their index of refraction (thus reducing the van der Waals force), adding some sort of salt (thus screening the electrostatic forces), and coating the particles with a polymer brush layer. This polymer brush prevents the particles from approaching too closely, further preventing particles from sticking together due to the attractive van der Waals forces. Frequently this polymer stabilizing layer is short (a length of 10 - 20 nm coating a particle of diameter \(\sim 1 \text{ \mu m}\) \[5, 20\]) and so the particles can be treated as hard-sphere-like. The idea is that pairs of particles do not interact unless they are touching, at which point they are strongly repulsive.

A second important category is softer colloidal particles, which are typically charge stabilized. This means that ions disassociate from their surface, leaving their surface slightly charged with the counterions in the solvent, similar to polyelectrolytes. The like-charged particles repel each other, again preventing particles from getting close enough to each other to feel the van der Waals attraction. For hard-sphere-like particles, the control parameter is the volume fraction: the fraction of volume occupied by the particles, which of course is proportional to the particle concentration \[21\]. For softer particles, the control parameter is the concentration or number density \[21\]. To avoid confusion, this Viewpoint will use the word concentration to refer to the control parameter for colloidal samples. Glasses are found when the concentration is above the glass transition concentration, where that specific concentration depends on the sample details.

One other important consideration is the polydispersity of a colloidal suspension. Much like polymers, a batch of colloidal particles will have a range of sizes. The polydispersity is defined as the standard deviation of particle sizes divided by the mean size, using a number average; typical values are 5-8\%. Samples with a low polydispersity can organize into crystals \[5, 22, 24\], which is interesting in its own right \[22, 28\]. Figure 2 shows an image taken within a colloidal crystal; the color indicates the relative particle size. The crystalline regions tend to have mostly similar-sized particles, highlighting the importance of polydispersity. Often experimentalists who wish to study glass transition phenomena will use more highly polydisperse samples, or else a bidisperse mixture such as that shown in Fig. 1 much as is done in simulations \[24, 29\].

Another important experimental consideration is the particle size, which determines the particle diffusivity and therefore the relevant time scales of an experiment. Colloidal particles undergo Brownian motion due to thermal energy. In a liquid-like sample (below the glass transition concentration) Brownian motion allows the particles to rearrange, and macroscopically these rearrangements are what allows the sample to flow. The typical time scale for particles to diffuse their own radius is given by

\[
\tau_D = \frac{a^2}{2D} = \frac{3\pi \eta a^3}{k_B T},
\]

where \(a\) is the particle radius, \(D\) is the diffusion constant \[32, 33\], \(\eta\) is the solvent viscosity, \(k_B\) is Boltzmann’s constant, and \(T\) is the temperature \[13\]. An example of a diffusing particle is shown in Fig. 3 where the particle’s position is marked with small filled circles at intervals of \(\tau_D\). For polystyrene particles in water, this time scale ranges from 0.8 - 800 ms for particles of radius \(a = 100 \text{ nm}\) to \(a = 1 \text{ \mu m}\), which is the size range one typically sees for colloidal glass experiments. The \(a^3\) dependence of \(\tau_D\) al-

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**FIG. 2:** Top: Confocal microscope image of a colloidal crystal. Bottom: Rendered image of the same data, with the particles colored by their size, with the anomalous large particle shaded white. The legend indicates how the color corresponds to the particle radius. The particles have a mean radius of 1.18 \(\mu m\) and are drawn to scale. While the polydispersity is only 0.045, the particles that are smaller or larger than average tend to cluster in more disordered regions. In both panels, the scale bar is 10 \(\mu m\) and drawn at the same location in the sample. The sample was imaged in 3D and the rendered data are taken from a region of thickness 2.2 \(\mu m\); not all the particles are perfectly co-planar. The data are from Refs. \[4, 51\] and have volume fraction \(\phi = 0.46\).
The solvent viscosity sets a viscosity scale for a colloidal suspension, much as course, the solvent viscosity sets a viscosity scale for a colloidal suspension. The large circular outline indicates the particle size. The scale bar is 1 µm. This is from an experiment with a low particle concentration, far from the glass transition concentration.

This time scale to vary dramatically as the particle size is changed. Fundamentally, this sets a “clock speed” for a colloidal experiment. For example, one might state that near the glass transition the relaxation time scale grows by $10^5$, meaning that the relaxation time scale is $10^5\tau_D$, and one might wish to use particles of a size such that $10^5\tau_D$ isn’t an unreasonable amount of time to wait for an experiment to finish. The ability to undergo Brownian motion on experimentally reasonable time scales helps define the upper limit to colloidal particle diameters ($\sim 10 \ \mu m$).

While diffusion is also relevant for molecules in a small molecule glass former or a polymers, colloids also have hydrodynamic interactions due to the solvent viscosity. Does this mean they’re a poor model for glasses and you should stop reading this Viewpoint? Absolutely not. Of course, the solvent viscosity sets a viscosity scale for a colloidal suspension, much as $\tau_D$ sets a time scale for a colloidal experiment. When measuring the growth of the viscosity near the colloidal glass transition, one examines this growth relative to the solvent viscosity. Explaining the full rheological behavior requires understanding the hydrodynamic interactions. On the other hand, the functional form of this viscosity growth in colloidal samples resembles the viscosity growth in more traditional glass-forming systems. The glass transition is less a question about the rheological details of the liquid-like samples (which depends on hydrodynamics for colloids) and more a question about the dramatic increase in the zero-frequency viscosity. (The zero-frequency viscosity is the viscosity one would measure at very long times in an experiment with the smallest possible imposed stress.) In this sense of capturing the correct zero-frequency behavior, hydrodynamic interactions are not a limitation of colloids as a model system. One might also wonder if diffusive dynamics (as described in the previous paragraph) are a limitation, but several simulations have demonstrated that the long-time glassy dynamics are independent of the short time dynamics.

In fact, the dominant physics is the steric interaction of the colloidal particles: for a particle to move, other particles must move out of its way. Steric interactions are thought to be important for understanding liquids and glasses, and for example hard spheres are a simple well-studied model of atoms in liquids. The importance of steric interactions over other particle interaction details helps explain why similar behaviors are seen in computational glass models using Lennard-Jones particles, hard spheres, and soft spheres; and why these simulation results match colloidal experimental results with hard-sphere-like particles as well as softer particles. For that matter, in polymer glasses, the crowding of nearby monomers is quite important to understand their glassiness, and the fact that some of the monomers are linked together may be less crucial. This is reinforced by the observation that the glass transition temperature in polymers is independent of molecular weight (above some minimum molecular weight).

Turning now to the glass state itself: a glass is out of equilibrium. In general this is because the relaxation time scales in a glassy material exceed the experimental time scales. However, the properties of the sample do evolve with time, a process termed aging. In polymers, this manifests as physical aging, where it is observed that samples slowly become denser as time passes. One related consequence is that the gas permeability of a polymer glass decreases as the sample ages (which can be problematic for gas separation applications). The concept is that polymers rearrange to find better-packed configurations, thus decreasing the overall volume and closing some of the gaps where previously gas molecules could squeeze between. These changes in the glass become exponentially slower as the sample ages; the amount of change one sees between 10 minutes and 100 minutes after the glass is formed would be similar to the amount of change one sees between 10 hours and 100 hours.

Likewise glassy colloids exhibit aging phenomena, in that their properties slowly change with time. Typically this is examined by preparing a sample at a concentration such that it is glassy, then shear-melting the sample by vigorous stirring. After ending the stirring, the evolution of the sample is studied. This method is termed “shear-rejuvenation.” Alternatively, colloidal particles can be used for which their size is temperature-
controllable, and thus temperature can be used to induce the particles to pack into a glassy state \cite{54, 55}. This is more analogous to the traditional temperature quench of a polymer glass. With either preparation protocol, aging of a colloidal glass is then seen as particle motion slows with age. Slight motions occur in the sample (due to Brownian motion), and the time scale for these motions grows as the sample ages as shown in Fig. 6. This is quite similar to the slow evolution of aging polymer samples \cite{47, 51}. Experiments have shown that while aging is seen following either preparation protocol, the details of that aging differ between the two protocols even for the same final conditions \cite{54}, as is also known to be the case for polymer glasses \cite{58}.

However, in either case colloidal aging is observed at constant concentration (constant volume), so this is distinctly different from the physical aging of polymers. What then does it mean for a colloidal glass to age at constant volume? One idea is that aging is still the evolution of the sample toward a better packing of the particles. When the aging is initiated, the particles are in some configuration set by the preparation protocol, but this is not the equilibrium state. Brownian motion still occurs, and occasionally the particles rearrange in some way that brings them closer to an ideal equilibrium state. The closer the configuration is to the ideal state, the lower the driving force is toward that equilibrium state, and thus the dynamics should slow down. Unfortunately, a caveat is in order: while this conceptual picture is sensible, little data exist to support this story. Attempts to observe structural changes in aging colloidal samples have found few \cite{59} or no changes \cite{60, 61}. Despite the scarce direct evidence, this conceptual story must be true: the sample has no internal clock other than its structure, so the structure must evolve as the sample ages.

The McKenna group has used the temperature-sensitive colloids mentioned above to do a series of clever experiments on colloidal aging \cite{55–57} that mimic classic experiments by Kovacs \cite{62}. One such experiment studied the “asymmetry of approach” to the equilibrated glass state. In this experiment, the sample is prepared in a glassy state and allowed to age for some time. The sample conditions are then jumped to a different glassy state, and then studied as the sample evolves toward equilibrium at the new glassy state. This protocol is done twice, once with the initial state less glassy than the final state, and once with the initial state more glassy than the final state (more glassy in the sense of being at a higher concentration for the colloids, or at a lower temperature for the polymer glass). For the polymer glass, Kovacs found that the sample that starts at a glassier state takes longer to evolve toward the final equilibrium, as shown in Fig. 5 (b) \cite{62, 63}. This shows that the dynamics depend not only on the final temperature, but also on the structure and history of the glass. The difference in subsequent behavior between the initially less glassy and initially more glassy samples is why this is termed an “asymmetry of approach.” Surprisingly, for colloids this is not really seen, as shown in Fig. 5 (a) for one sample. The approach toward the equilibrated final state takes the same time, found in two different colloidal samples by the McKenna group \cite{52, 56}. Either the dynamics do not depend on the glassiness of the sample, or else the equilibration behavior is dominated by the final conditions rather than the initial conditions.

FIG. 4: The time $\Delta t$ needed for particles to move a certain distance as a function of the age of the sample. Specifically this is defined as $\langle |\vec{r}(t_{\text{age}} + \Delta t) - \vec{r}(t_{\text{age}})|^2 \rangle = L^2$ where the angle brackets are an average over all particles. The values of $L^2$ are 0.05, 0.10, and 0.20 $\mu$m$^2$ (circles, triangles, and squares respectively). For the square symbols at large $t_{\text{age}}$, the experiment concluded before the particles had diffused a radius of 1.18 $\mu$m. Direct evidence, this conceptual story must be true: the

$$\delta = \frac{L^2}{L_0^2}$$

is termed the departure from equilibrium and is a measure of the out-of-equilibrium dynamics. (b) Asymmetry of approach data from polymer glass experiments by Kovacs \cite{62}, as replotted by Zheng and McKenna \cite{64}. A similar protocol was followed with temperature, with both experiments set to the same final temperature of 35$^\circ$C. Here $\delta$ is a measure of the out-of-equilibrium sample volume. (a) Reproduced from Di, Peng, and McKenna, J. Chem. Phys. 140, 054903 (2014), with the permission of AIP publishing. (b) Reproduced from Zheng and McKenna, Macromol. 36, 2387 (2003) \cite{63}.
Above I introduced $\tau_D$ (Eqn. 1) as the time scale for particles to diffuse their own radius in a dilute sample. In a concentrated sample, it takes much longer for particles to diffuse their own radius; this is the slowing of dynamics that characterizes the approach to the glass transition. Likewise, the viscosity of colloidal samples grows dramatically as the glass transition is approached. Looking at Eqn. 1 one might suspect that replacing the solvent viscosity $\eta$ with the macroscopic sample viscosity $\eta(c)$ (at a particular concentration $c$) would produce the new diffusive time scale, and that the slowing of diffusion is a simple consequence of the growing viscosity. This, however, is not the case in glassy materials \cite{20, 64–67}. This is referred to as the breakdown of the Stokes-Einstein relation between diffusion and viscosity as the glass transition is approached \cite{68–70}. Microscopically, this is likely due to dynamical heterogeneity. At any given moment, different regions within the sample have different relaxation time scales (spatial dynamical heterogeneity) and at different moments a given region has different dynamics (temporal heterogeneity). Equivalently, diffusive motion has different instantaneous magnitudes in different regions. Slowing diffusion as the glass transition is approached is not just the sample slowing down; rather, diffusion takes place in a fundamentally different fashion.

Simulations in the 1990s first demonstrated dynamical heterogeneity by visualizing which particles were making large displacements at a given moment of time \cite{71, 72}. A key observation is that the particles with large displacements were “cooperative” in that neighboring particles moved in similar directions \cite{72}. For polymers, dynamical heterogeneity is observable by adding in dye probes, or perhaps grafting the dye probes to the polymer backbone \cite{73, 74}. For example, Ref. \cite{75} used polarized light to observe the fluorescence of single molecules and observed broad distributions of rotational and translational correlation time scales. For colloids, microscopy can be used to directly observe particle motion in a sample. In 1998 Kasper et al. first observed dynamical heterogeneity of probe particles in dense colloidal samples. Using 2D samples, Marcus et al. could observe all the particles in a region of the sample, and saw that mobile regions were cooperative similar to what the simulations had found. Confocal microscopy allowed two different groups to study dynamical heterogeneity in three-dimensional colloidal samples \cite{9, 10}, further confirming simulation results. Figure 6 shows an example taken from the data of Ref. \cite{9}. At the instant in time shown, the most mobile particles are drawn, with the lighter colors indicating the particles with the largest displacements. The mobile particles are clustered, leaving other regions with relatively immobile particles at this instant. At later times, different regions are mobile and immobile.

This discussion has focused on the translational diffusion of particles from one location to another; recent advances in colloidal particle synthesis methods have enabled striking observations of rotational diffusion. These experiments were motivated by prior experiments measuring rotational motion of probe molecules in supercooled samples of polymers \cite{76} and small molecule liquids \cite{77}. The Han group synthesized colloidal ellipsoids with an aspect ratio of 6 [Fig. 7(a)] and used sample chambers that confined these particles to a quasi-two-dimensional layer, allowing for easy visualization of translational and rotational motion of the ellipsoids \cite{80}. At moderate concentrations, their particles translate and rotate relatively easily. At higher concentrations, they found that the rotational motion underwent a glass transition, but that particles could still translate. At the highest concentrations, both types of motion were glassy. A related experiment was published two years later, using a quasi-two-dimensional layer and ellipsoids of aspect ratio two [Fig. 7(b)] \cite{81}. In this experiment, the two glass transitions (rotation and translation) occurred at the same concentration. In both experiments, as the glass transition(s) were approached, particles moved in cooperative groups – that is, both rotational and translational motion exhibited dynamical heterogeneity. For the large aspect ratio ellipsoids, the particles undergoing large rotations were usually different from those undergoing large translations \cite{80}, whereas there were more particles dually mobile for the smaller aspect ratio ellipsoids \cite{81}.

Two separate experiments examined rotational motion of tracers in three-dimensional colloidal samples, and found opposite effects. The first experiment used colloidal spheres which had been treated so their orientation could be seen in a microscope image [Fig. 7(c)] \cite{82}.
These were added to samples of transparent spheres close to the colloidal glass transition. While their translational motion slowed dramatically as the glass transition was approached, rotational motion only slowed modestly. In fact, their ratio changed by a factor of 100 at the highest concentration they studied, as compared to the dilute situation. Were diffusion simply a matter of the sample’s macroscopic viscosity, this ratio would have been independent of the concentration. The second experiment used tetrahedral clusters of spheres [Fig. 7(c)] also added to samples of transparent spheres near the colloidal glass transition [82]. In this situation, the observations were the opposite of Ref. [82]: both rotational and translational diffusion slowed dramatically, and in this experiment it was the rotational diffusion that was 50 times slower than the translational diffusion at the highest concentration studied. Both of these experiments confirm that the decoupling of translational and rotational diffusion from each other occurs on the single particle level, but they observe opposite directions of this decoupling.

Despite observing opposite effects, both of these experiments can be understood by recalling the basic physics discussed above. The tetrahedral clusters of Ref. [83] could sterically “entangle” with the surrounding spheres. Both their rotational and translational degrees of freedom required the surrounding particles to move and rearrange which is the motion that is known to be dynamically heterogeneous. In contrast, the spherical tracers of Ref. [82] interact sterically when they try to translate, but interact hydrodynamically when they rotate. That is, even if the background particles were completely motionless, the spherical tracers could still rotate, constrained only by a hydrodynamic drag from the surrounding motionless particles [84, 85]. At higher concentrations, these neighboring particles were closer to the tracers, so it is natural that rotational motion slowed down; but this hydrodynamic effect was far less significant than the steric hindrance of the translational motion. One can conjecture that upon gradually varying the probe particle shape from a sphere to an ellipsoid, steric hindrance of rotational motion would be gradually enhanced, and a crossover could be seen from fast rotational dynamics to slow, glassy rotational dynamics. Theoretical and computational predictions suggest that the aspect ratio of ellipsoids needs to be above some minimal value [86], for example 1.4 for 2D simulations [57]. This prediction is also qualitatively consistent with the ellipsoid experiments discussed above, where the aspect ratio 6 ellipsoids had slower rotational dynamics [81] and the aspect ratio 2 ellipsoids had identical translational and rotational dynamics [81].

Returning to broader questions about the scientific merits of colloidal glasses, this Viewpoint has argued that the colloidal glass transition is a good model with many similarities to the glass transition of polymers and small molecules. Of course, one needs to be aware of the advantages and disadvantages of any model. A useful comparison is between colloidal experiments and simulations. In general, simulations of colloids are done to understand situations where hydrodynamics are important [36, 37, 88]. Most typically these simulations aim to understand the rheological behavior of colloidal suspensions at moderate concentrations, and so the goal is not to understand the glass transition. Accordingly, there are relatively few simulations of “the colloidal glass transition” in comparison to the number of simulations aimed at “the glass transition.” As noted previously, there have been several studies that compared realistic molecular dynamics at short time scales with Brownian dynamics, all of which found that the short time scale dynamics have no influence on the long time scale behavior of interest [38, 40].

The comparison to make, then, is the strengths and weaknesses of colloidal glass transition experiments as compared to glass transition simulations. Experiments have the advantage of typically having $10^8 - 10^{10}$ particles in a sample, allowing for well-defined averages (when using light scattering) and at a minimum avoiding finite size effects [80, 90]. Experiments also study real materials which themselves might be of intrinsic interest: toothpaste is essentially a colloidal glass, for example. Simulations have the advantage that the particle interaction is completely specified. For example, even hard-sphere-like colloids are not truly hard spheres and there are real challenges when comparing them to hard sphere simulations [21]. Some methods exist to measure pairwise interactions in colloidal experiments [91], but one hopes that the conclusions from an experiment are not too sensitive to the exact details of the interparticle interactions. A final advantage of simulations is that certain useful tricks are easier with simulations, such as reproducing initial conditions [92] or simulating behavior in four spatial dimensions [93, 94].

In the end, much progress has been made when simulations of various types of particles agree with experimental results using various types of colloidal particles which in turn agree with experiments studying polymers or small...
molecules. For example, dynamical heterogeneity has been seen in Lennard-Jones simulations [73, 75, 95], hard particle simulations [96], soft particle simulations [71, 72], polymer simulations [97], hard-sphere-like colloids [8, 10], and soft colloids [98] – all of which complements experiments done with small molecule glasses [99, 101] and polymer glasses [76, 78, 102]. At this point it is clear that the presence dynamical heterogeneity does not depend on the system studied, and then each experiment or simulation contributes to a larger picture.

There are indeed several large pictures of current interest. As mentioned above, shape is an intriguing parameter to play with for colloidal glasses, and there are many more shapes besides simple clusters of spheres or ellipsoids [103] which may lead to a diversity of amorphous states [104]. Using complex shapes can lead to better understanding of how steric interactions determine the glassiness of small molecule glasses. Another current topic of interest is clarifying how packing problems (especially of athermal particles) may relate, or not, to the glass transition problem [105]. Since the late 90’s there was a conjecture that these problems were closely related [106]; recent simulations suggest that the similarities are more superficial than had been thought [107, 108]. Colloidal glass experiments by Basu et al. support the simulation results [108], but questions remain how packing structures and dynamics differ between thermal and athermal systems. To mention a final topic, simulations and theories of the glass transition often consider physically implausible situations that lead to interesting insights, such as freezing a subset of particles and observing how nearby particles are affected [109, 111]. Recent experiments use 2D colloidal systems and holographic laser tweezers to duplicate some of these conditions [112, 113], confirming many of the predictions. Given continuing advances in colloidal synthesis techniques [103] and other clever experimental techniques, it is likely that fruitful conversations will long continue between those interested in colloidal glasses and those interested in other types of glasses.

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[1] R. Edgeworth, B. J. Dalton, and T. Parnell, The pitch drop experiment, Euro. J. Phys., 5, 198–200 (1984).
[2] E. D. Zanotto, Do cathedral glasses flow?, Am. J. Phys., 66, 392–395 (1998).
[3] J. M. Pasachoff, Comment on do cathedral glasses flow?, by Edgar Dutra Zanotto [Am. J. Phys. 66 (5), 392395 (1998)], Am. J. Phys., 66, 1021 (1998).
[4] H. M. Lindsay and P. M. Chaikin, Elastic properties of colloidal crystals and glasses, J. Chem. Phys., 76, 3774–3781 (1982).
[5] P. N. Pusey and W. van Megen, Phase behaviour of concentrated suspensions of nearly hard colloidal spheres, Nature, 320, 340–342 (1986).
[6] P. N. Pusey and W. van Megen, Observation of a glass transition in suspensions of spherical colloidal particles, Phys. Rev. Lett., 59, 2083–2086 (1987).
[7] Z. Cheng, J. Zhu, P. M. Chaikin, S.-E. Phan, and W. B. Russel, Nature of the divergence in low shear viscosity of colloidal hard-sphere dispersions, Phys. Rev. E, 65, 041405 (2002).
[8] A. van Blaaderen and P. Wiltzius, Real-space structure of colloidal hard-sphere glasses, Science, 270, 1177–1179 (1995).
[9] E. R. Weeks, J. C. Crocker, A. C. Levitt, A. Schofield, and D. A. Weitz, Three-Dimensional direct imaging of structural relaxation near the colloidal glass transition, Science, 287, 627–631 (2000).
[10] W. K. Kege and A. van Blaaderen, Direct observation of dynamical heterogeneities in colloidal hard-sphere suspensions, Science, 287, 290–293 (2000).
[11] C. R. Nugent, K. V. Edmond, H. N. Patel, and E. R. Weeks, Colloidal glass transition observed in confinement, Phys. Rev. Lett., 99, 025702 (2007).
[12] B. Zhang and X. Cheng, Structures and dynamics of Glass-Forming colloidal liquids under spherical confinement, Phys. Rev. Lett., 116, 025702 (2016).
[13] G. L. Hunter and E. R. Weeks, The physics of the colloidal glass transition, Rep. Prog. Phys., 75, 066501 (2012).
[14] Y. M. Joshi, Dynamics of colloidal glasses and gels, Annual Review of Chemical and Biomolecular Engineering, 5, 181–202 (2014).
[15] P. N. Pusey, Colloidal glasses, J. Phys.: Condens. Matter, 20, 494202 (2008).
[16] F. Sciortino and P. Tartaglia, Glassy colloidal systems, Adv. Phys., 54, 471–524 (2005).
[17] S. Gokhale, A. K. Sood, and R. Ganapathy, Deconstructing the glass transition through critical experiments on colloids, Adv. Phys., 65, 363–452 (2016).
[18] F. Scheffold and R. Cerbino, New trends in light scattering, Curr. Op. Coll. Int. Sci., 12, 50–57 (2007).
[19] T. Narumi, S. V. Franklin, K. W. Desmond, M. Tokuyama, and E. R. Weeks, Spatial and temporal dynamical heterogeneities approaching the binary colloidal glass transition, Soft Matter, 7, 1472–1482 (2011).
[20] W. C. K. Poon, E. R. Weeks, and C. P. Royall, On measuring colloidal volume fractions, Soft Matter, 8, 21–30 (2012).
[21] C. P. Royall, W. C. K. Poon, and E. R. Weeks, In search of colloidal hard spheres, Soft Matter, 9, 17–27 (2013).
[22] S. I. Henderson and W. van Megen, Metastability and crystallization in suspensions of mixtures of hard spheres, Phys. Rev. Lett., 80, 877–880 (1998).
[23] H. J. Schöpe, G. Bryant, and W. van Megen, Effect of polydispersity on the crystallization kinetics of suspensions of colloidal hard spheres when approaching the glass transition, J. Chem. Phys., 127, 084505 (2007).
[24] P. N. Pusey, E. Zaccarelli, C. Valeriani, E. Sanz, W. C. K. Poon, and M. E. Cates, Hard spheres: crystallization and glass formation, Phil. Trans. Roy. Soc.
L. Berthier, D. Chandler, and J. P. Garrahan, Length
M. G. Mazza, N. Giovambattista, H. E. Stanley, and
S. F. Swallen and M. D. Ediger, Self-diffusion of the
M. M. Hurley and P. Harrowell, Non-Gaussian behav-
Y. Jung, J. P. Garrahan, and D. Chandler, Excitation
Y. Zheng and G. B. McKenna, Structural recovery in
C. Z. Liu and I. Oppenheim, Enhanced diffusion upon
M. D. Ediger, Spatially heterogeneous dynamics in super-
C. Z. Liu and I. Oppenheim, Enhanced diffusion upon
Y. Jung, J. P. Garrahan, and D. Chandler, Excitation
L. Berthier, D. Chandler, and J. P. Garrahan, Length
M. M. Hurley and P. Harrowell, Kinetic structure of a two-dimensional liquid, Phys. Rev. E, 52, 1694–1698 (1995).
M. M. Hurley and P. Harrowell, Non-Gaussian behavior and the dynamical complexity of particle motion in a dense two-dimensional liquid, J. Chem. Phys., 105, 10521–10526 (1996).
W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Dynamic heterogeneities in a supercooled Lennard-Jones liquid, Phys. Rev. Lett., 79, 2827–2830 (1997).
P. H. Poole, C. Donati, and S. C. Glotzer, Spatial correlations of particle displacements in a glass-forming liquid, Physica A, 261, 51–59 (1998).
C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Stringlike cooperative motion in a supercooled liquid, Phys. Rev. Lett., 80, 2338–2341 (1998).
M. T. Cicerone, F. R. Blackburn, and M. D. Ediger, Anomalous diffusion of probe molecules in poly styrene: Evidence for spatially heterogeneous segmental dynamics, Macromolecules, 28, 8224–8232 (1995).
D. B. Hall, D. D. Deppe, K. E. Hamilton, A. Dhinojwala, and J. M. Torkelson, Probe translational and rotational diffusion in polymers near Tg: Roles of probe size, shape, and secondary bonding in deviations from Debye-Stokes-Einstein scaling, J. Non-Cryst. Solids, 235–237, 48–56 (1998).
A. Schob, F. Cichos, J. Schuster, and C. von Borchyskowski, Reorientation and translation of individual dye molecules in a polymer matrix, Euro. Poly. J., 40, 1019–1026 (2004).
I. Chang, F. Fujara, B. Geil, G. Heuberger, T. Mangel, and H. Sillescu, Translational and rotational molecular motion in supercooled liquids studied by NMR and forced Rayleigh scattering, J. Non-Cryst. Solids, 172–174, 248–255 (1994).
Z. Zheng, F. Wang, and Y. Han, Glass transitions in Quasi-Two-dimensional suspensions of colloidal ellipsoids, Phys. Rev. Lett., 107, 065702 (2011).
C. K. Mishra, A. Rangarajan, and R. Ganapathy, Two-step glass transition induced by attractive interactions in quasi-two-dimensional suspensions of ellipsoidal particles, Phys. Rev. Lett., 110, 185301 (2013).
M. Kim, S. M. Anthony, S. C. Bae, and S. Granick, Colloidal rotation near the colloidal glass transition, J. Chem. Phys., 135, 054905 (2011).
K. V. Edmond, M. T. Elsesser, G. L. Hunter, D. J. Pine, and E. R. Weeks, Decoupling of rotational and translational diffusion in supercooled colloidal fluids, Proc. Nat. Acad. Sci., 109, 17891–17896 (2012).
A. J. Goldman, R. G. Cox, and H. Brenner, Slow viscous motion of a sphere parallel to a plane wall motion through a quiescent fluid, Chem. Eng. Sci., 22, 637–651 (1967).
A. Imperio, J. T. Padding, and W. J. Briels, Diffusion of spherical particles in microwaves, J. Chem. Phys., 134, 154904 (2011).
C. De Michele, R. Schilling, and F. Sciortino, Dynamics of uniaxial hard ellipsoids, Phys. Rev. Lett., 98, 265702 (2007).
T. Shen, C. Schreck, B. Chakraborty, D. E. Freed, and C. S. O’Hern, Structural relaxation in dense liquids composed of anisotropic particles, Phys. Rev. E, 86, 041303 (2012).
J. F. Brady and G. Bossis, Stokesian dynamics, Ann. Rev. Fluid Mech., 20, 111–157 (1988).
K. Kim and R. Yamamoto, Apparent finite-size effects in the dynamics of supercooled liquids, Phys. Rev. E, 61, R41–R44 (2000).
E. Flenner and G. Szamel, Fundamental differences between glassy dynamics in two and three dimensions, Nature Comm., 6, 7392 (2015).
S. Behrens and D. Grier, Pair interaction of charged colloidal spheres near a charged wall, Phys. Rev. E, 64, 050401 (2001).
A. Widmer-Cooper, P. Harrowell, and H. Fynnewever, How reproducible are dynamic heterogeneities in a supercooled liquid?, Phys. Rev. Lett., 93, 135701 (2004).
J. A. van Meel, D. Frenkel, and P. Charbonneau, Geometrical frustration: A study of four-dimensional hard spheres, Phys. Rev. E, 79, 030201(R) (2009).
S. Sengupta, S. Karmakar, C. Dasgupta, and S. Sastry, Adam-Gibbs relation for glass-forming liquids in two, three, and four dimensions, Phys. Rev. Lett., 109, 095705 (2012).
L. Berthier, Time and length scales in supercooled liquids, Phys. Rev. E, 69, 020201(R) (2004).
B. Doliva and A. Heuer, Cooperativity and spatial correlations near the glass transition: Computer simulation results for hard spheres and disks, Phys. Rev. E, 61, 6988–6908 (2000).
C. Bennemann, C. Donati, J. Baschnagel, and S. C. Glotzer, Growing range of correlated motion in a polymer melt on cooling towards the glass transition, Nature, 399, 246–249 (1999).
R. Colin, A. M. Alsayed, J.-C. Castaing, R. Goyal,
L. Hough, and B. Abou, Spatially heterogeneous dynamics in a thermosensitive soft suspension before and after the glass transition, *Soft Matter*, 7, 4504–4514 (2011).

[99] R. Böhmer, G. Hinze, G. Diezemann, B. Geil, and H. Sillescu, Dynamic heterogeneity in supercooled ortho-terphenyl studied by multidimensional deuteron NMR, *Europhys. Lett.*, 36, 55–60 (1996).

[100] M. T. Cicerone and M. D. Ediger, Relaxation of spatially heterogeneous dynamic domains in supercooled ortho-terphenyl, *J. Chem. Phys.*, 103, 5684–5692 (1995).

[101] M. T. Cicerone and M. D. Ediger, Enhanced translation of probe molecules in supercooled oterphenyl: Signature of spatially heterogeneous dynamics?, *J. Chem. Phys.*, 104, 7210–7218 (1996).

[102] K. Schmidt-Rohr and H. W. Spiess, Nature of nonexponential loss of correlation above the glass transition investigated by multidimensional NMR, *Phys. Rev. Lett.*, 66, 3020–3023 (1991).

[103] S. C. Glotzer and M. J. Solomon, Anisotropy of building blocks and their assembly into complex structures, *Nature Materials*, 6, 557–562 (2007).

[104] P. F. Damasceno, M. Engel, and S. C. Glotzer, Predictive self-assembly of polyhedra into complex structures, *Science*, 337, 453–457 (2012).

[105] A. Ikeda, L. Berthier, and P. Sollich, Unified study of glass and jamming rheology in soft particle systems, *Phys. Rev. Lett.*, 109, 018301 (2012).

[106] A. J. Liu and S. R. Nagel, Jamming is not just cool any more, *Nature*, 396, 21–22 (1998).

[107] A. Ikeda, L. Berthier, and P. Sollich, Disentangling glass and jamming physics in the rheology of soft materials, *Soft Matter*, 9, 7669–7683 (2013).

[108] A. Basu, Y. Xu, T. Still, P. E. Arratia, Z. Zhang, K. N. Nordstrom, J. M. Rieser, J. P. Gollub, D. J. Durian, and A. G. Yodh, Rheology of soft colloids across the onset of rigidity: scaling behavior, thermal, and non-thermal responses, *Soft Matter*, 10, 3027–3035 (2014).

[109] G. Biroli, J. P. Bouchaud, A. Cavagna, T. S. Grigera, and P. Verrocchio, Thermodynamic signature of growing amorphous order in glass-forming liquids, *Nat Phys*, 4, 771–775 (2008).

[110] C. Cammarota and G. Biroli, Ideal glass transitions by random pinning, *Proc. Nat. Acad. Sci.*, 109, 8850–8855 (2012).

[111] C. Cammarota, G. Gradinigo, and G. Biroli, Confinement as a tool to probe amorphous order, *Phys. Rev. Lett.*, 111, 107801 (2013).

[112] S. Gokhale, K. Hima Nagamanasa, R. Ganapathy, and A. K. Sood, Growing dynamical facilitation on approaching the random pinning colloidal glass transition, *Nature Comm.*, 5, 4685 (2014).

[113] K. Hima Nagamanasa, S. Gokhale, A. K. Sood, and R. Ganapathy, Direct measurements of growing amorphous order and non-monotonic dynamic correlations in a colloidal glass-former, *Nature Phys.*, 11, 403–408 (2015).