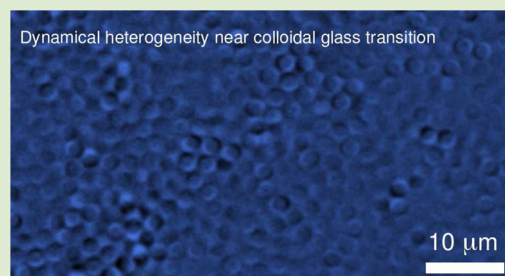


Introduction to the Colloidal Glass Transition

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ABSTRACT: 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 1980s. In this Viewpoint I summarize some of the intriguing behaviors of the glass transition in colloids and discuss open questions.



Glasses are an unusual 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 10 to 12 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 dissatisfying 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,¹ although this is not relevant for window glass.^{2,3}

In the 1980s, colloidal suspensions were introduced as model systems which had a glass transition.^{4–6} Colloidal suspensions are composed of small (10 nm to 10 μm 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;^{7,8} their structure is essentially unchanged at the glass transition;⁹ materials become dynamically heterogeneous as the transition is approached;^{10,11} confining colloidal samples modifies their glass transition.^{12,13} 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.^{14–18} Rather, a few representative experimental examples will be presented to demonstrate the advantages of colloids as a model system. A particular advantage is that their large size makes colloids directly observable with optical microscopy (see Figure 1) as well as indirectly observable with light scattering.¹⁹

Colloidal particles interact with one another with a variety of forces. This includes repulsive (such as electrostatic forces for charged particles) and attractive forces (such as the van der Waals force due to fluctuating electric dipole moments of the particles, which is quite strong at short-range). Discussing these

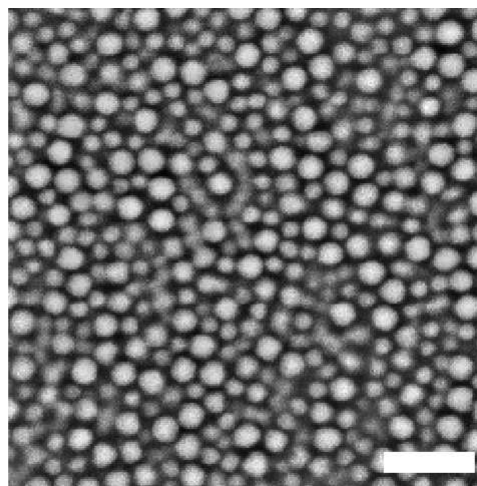


Figure 1. Confocal microscopy image of a bidisperse colloidal sample with particle radii 1.18 and 1.55 μm . The scale bar represents 10 μm . Reproduced with permission from ref 20. Copyright Royal Society of Chemistry 2011.

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forces is beyond the scope of this review; I will focus the discussion on purely repulsive colloidal particles. One important category is hard-sphere-like particles.⁵ 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. The polymer brush prevents the particles from approaching too closely. Frequently this polymer stabilizing layer is short (a length of 10–20 nm coating a particle of diameter $\sim 1 \mu\text{m}$)^{5,21} 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.^{22–26} 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. These soft particles can be soft in two senses. First, even if the particles themselves have hard cores, the interaction between their charges gives rise to a “softer” interaction in the sense of being a longer-range repulsion.²² Second, the particles themselves can be composed of soft hydrogels and thus easily deformable at high concentrations.^{24,27}

For hard-sphere-like particles, the control parameter is the volume fraction ϕ : 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.²⁸ With soft charged particles, samples can be glassy, even at relatively low volume fractions, due to long-range repulsions between the particles.⁴ For soft deformable particles, the notion of volume fraction may be useful at low concentrations, but at high concentration, particles can be strongly deformed and volume fraction becomes a less useful concept.^{24,27,29} 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,^{5,30–32} which is interesting in its own right.^{33–35} 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 Figure 1, much as is done in simulations.^{32,36,37}

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

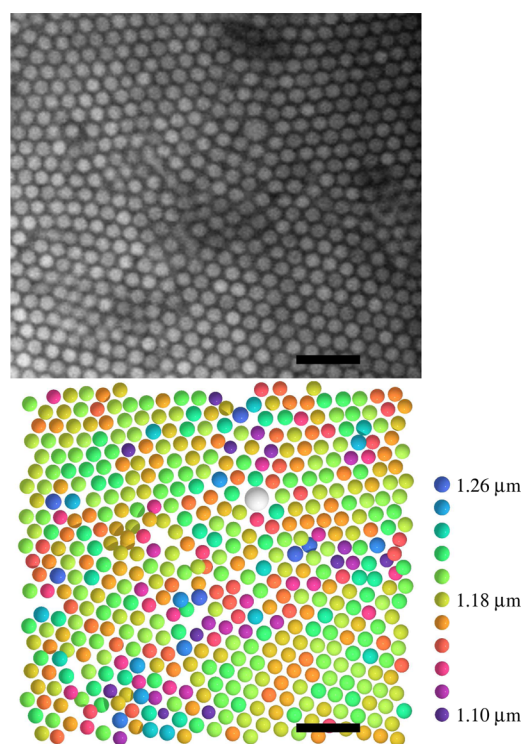


Figure 2. (Top) Confocal microscope image of a colloidal crystal. (Bottom) Rendered image of the same data, with the particles colored by their size, with the anomalous large particle shaded white. The legend indicates how the color corresponds to the particle radius. The particles have a mean radius of $1.18 \mu\text{m}$ 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 $10 \mu\text{m}$ 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 $2.2 \mu\text{m}$; not all the particles are perfectly coplanar. The data are from refs 10 and 38 and have a volume fraction $\phi = 0.46$.

sample to flow. The typical time scale for particles to diffuse their own radius is given by

$$\tau_D = \frac{a^2}{2D} = \frac{3\pi\eta a^3}{k_B T} \quad (1)$$

where a is the particle radius, D is the diffusion constant,^{39,40} η is the solvent viscosity, k_B is Boltzmann's constant, and T is the temperature.¹⁴ An example of a diffusing particle is shown in Figure 3, where the particle's position is marked with small filled circles at intervals of τ_D . For polystyrene particles in water, this time scale ranges from 0.8–800 ms for particles of radius $a = 100$ –1000 nm, which is the size range one typically sees for colloidal glass experiments. The a^3 dependence of τ_D allows 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 $10^5\tau_D$ is not an unreasonable amount of time to wait for an experiment to finish.^{41,42} The ability to undergo Brownian motion on experimentally reasonable time scales helps define the upper limit to colloidal particle diameters ($\sim 10 \mu\text{m}$).

While diffusion is also relevant for molecules in a small molecule glass former or polymers, colloids also have

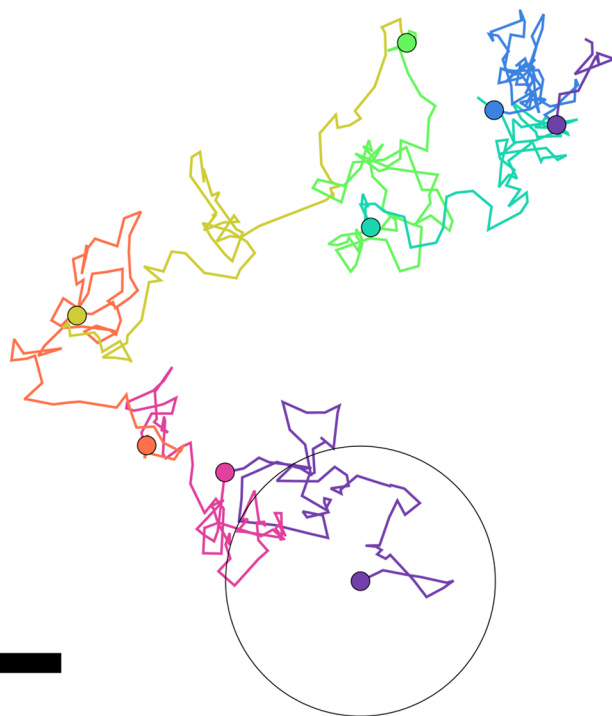


Figure 3. $8\tau_D = 155$ s duration trajectory of a colloidal particle with radius $a = 1.55 \mu\text{m}$ and diffusivity $D = 0.062 \mu\text{m}^2/\text{s}$. Segments of duration τ_D are indicated by color and separated by small filled circles. The large circular outline indicates the particle size. The scale bar is $1 \mu\text{m}$. This is from an experiment with a low particle concentration, far from the glass transition concentration.

hydrodynamic interactions due to the solvent.⁴³ Does this mean they're a poor model for glasses and you should stop reading this Viewpoint? Absolutely not. Of course, the solvent viscosity η_0 sets a viscosity scale for a colloidal suspension, much as τ_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.⁴³ On the other hand, the functional form of this viscosity growth in colloidal samples resembles the viscosity growth in more traditional glass-forming systems. For example, one experiment found their data were well-fit by

$$\frac{\eta}{\eta_0} = \exp\left(\frac{1.15\phi}{\phi - \phi_m}\right) \quad (2)$$

with $\phi_m = 0.638$ being a fitted maximum volume fraction.⁷ This equation is known as the Doolittle equation⁴⁴ and arises from considerations of free volume. For hard sphere colloids, free volume vanishes at the close packing volume fraction ϕ_m , where the particles are forced into contact. It is worth noting, however, that other functional forms can fit the experimental data.^{7,8} 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 viscosity, so the existence of 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.^{45–47}

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.^{48–50} 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.¹⁴ 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.⁵¹ This is reinforced by the observation that the glass transition temperature in polymers is independent of molecular weight (above some minimum molecular weight).^{52,53} Polymers generally have large viscosities and so even slowly cooled polymers have difficulty rearranging into a crystalline state. Polymers with stereoirregular 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.

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).^{54–56} 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.⁵⁷ These changes in the glass become exponentially slower as the sample ages; the amount of change between 10 and 100 min after the glass is formed would be similar to the amount of change between 10 and 100 h.⁵⁸

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.^{59–61} 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.^{24–26,29,61,62} This is 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 Figure 4. This is quite similar to the slow evolution of aging polymer samples.^{54,58} 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,⁶¹ as is also known to be the case for polymer glasses.⁶³

However, in either case colloidal aging is observed at constant concentration (constant volume), so this is distinctly

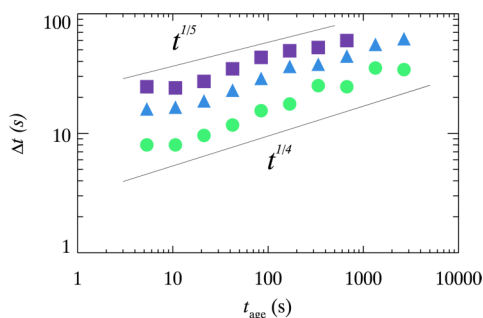


Figure 4. Time Δt needed for particles to move a certain distance as a function of the age of the sample. This is defined as $\langle |\bar{r}(t_{\text{age}} + \Delta t) - \bar{r}(t_{\text{age}})|^2 \rangle = L^2$, where the angle brackets are an average over all particles. The values of L^2 are 0.05, 0.10, and 0.20 μm^2 (circles, triangles, and squares, respectively). For the square symbols at large t_{age} , the experiment ended before the particles had diffused a distance L^2 . The sample is composed of particles with a mean radius of 1.18 μm and a volume fraction $\phi = 0.62$. The lines indicate power law growth with the exponents shown. The data are from ref 59.

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 few⁶⁴ or no changes.^{65,66} 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^{26,29,62} that mimic classic experiments by

Kovacs.⁶⁷ 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). The quantity measuring the response of the sample is δ , which relates to volume changes for polymers and relaxation time scale changes for colloids. When a sample ceases aging and thus reaches equilibrium for given conditions, δ is defined to be zero; thus, nonzero values of δ measure departures from equilibrium. For polymer glasses, Kovacs found that the sample that starts at a glassier state takes longer to evolve toward the final equilibrium, as shown in Figure 5b (bottom data).^{67,68} 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”. For colloids the asymmetry is weaker, as shown in Figure 5a for one sample. The two curves are not mirror images, and the initial magnitude of δ differs for all of the colloidal experiments, thus, exhibiting asymmetry. However, the approach toward the equilibrated final state takes the same time (~ 700 s in Figure 5a), an observation reproduced in two different colloidal samples by the McKenna group.^{26,29} Other experiments with these same samples suggest that the approach to equilibrium depends only weakly on the glassiness of the sample.²⁹ It may also be that the equilibration behavior for colloids is dominated by the final conditions rather than the initial conditions.

Another topic of interest related to aging is the memory effect, again first observed in polymers by Kovacs.⁶⁷ In these experiments, a sample is aged for a short time at one temperature allowing the departure from equilibrium δ to approach zero. Before δ reaches zero, the temperature is then changed to a different temperature for which the instantaneous δ is zero. Memory is manifested by the sample at the new

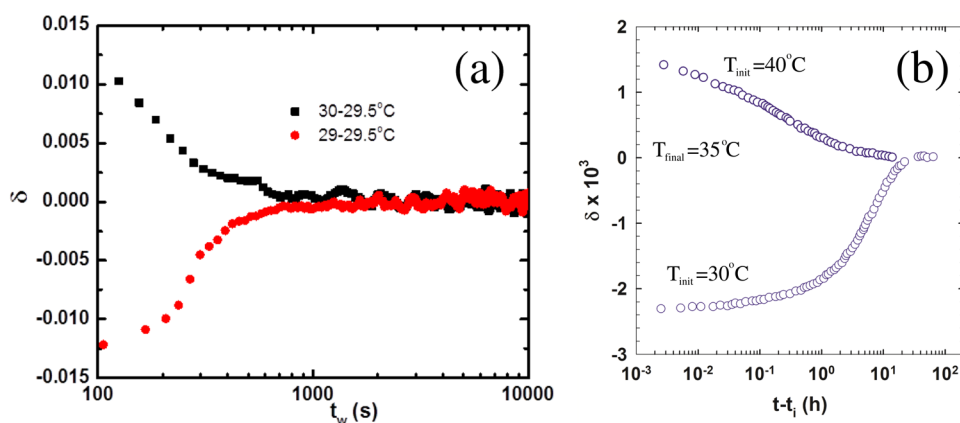


Figure 5. (a) Asymmetry of approach data from colloidal experiments using temperature sensitive particles. The temperature was adjusted from the initial temperature (as shown) to a final temperature of 29.5 °C. δ is termed the departure from equilibrium and is a measure of the out-of-equilibrium dynamics. (b) Asymmetry of approach data from polymer glass experiments by Kovacs,⁶⁷ as replotted by Zheng and McKenna.⁶⁸ A similar protocol was followed with temperature, with both experiments set to the same final temperature of 35 °C. Here δ is a measure of the out-of-equilibrium sample volume. (a) Reproduced with permission from Di, Peng, and McKenna, *J. Chem. Phys.* 2014, **140**, 054903. Copyright AIP publishing 2014. (b) Reproduced with permission from ref 68. Copyright ACS 2003.

temperature changing δ from zero for a while, before slowly equilibrating back to $\delta = 0$. The implication is that despite the sample having the correct equilibrium volume for the new temperature, in other respects it is clearly out of equilibrium and has “memory” of the previous temperature it had aged at. The McKenna group investigated the memory effect in colloids using their temperature-sensitive hydrogel particles and found little²⁶ or no²⁹ signature of memory. This is a qualitative difference between colloidal glasses and polymer glasses.

Turning back to colloidal samples in the liquid state, above I introduced τ_D (eq 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 eq 1, one might suspect that replacing the solvent viscosity η 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.^{21,69–72} This is known as the breakdown of the Stokes–Einstein relation between diffusion and viscosity as the glass transition is approached.^{73–75} Microscopically, this is likely due to dynamical heterogeneity. At any given moment, different regions within the sample have different diffusive time scales (spatial dynamical heterogeneity) and at different moments a given region has different dynamics (temporal heterogeneity). 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 the particles making large displacements at a given moment of time.^{76–79} A key observation is that the particles with large displacements were “cooperative” in that neighboring particles moved in similar directions.⁷⁹ For polymers, dynamical heterogeneity is observable by adding in dye probes or grafting dye probes to the polymer backbone.^{80–82} For example, ref 82 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.⁸³ 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.⁸⁴ Confocal microscopy allowed two different groups to study dynamical heterogeneity in three-dimensional colloidal samples,^{10,11} further confirming simulation results. Figure 6 shows an example taken from the data of ref 10. 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 polymers⁸¹ and small molecule liquids.⁸⁵ The Han group synthesized colloidal

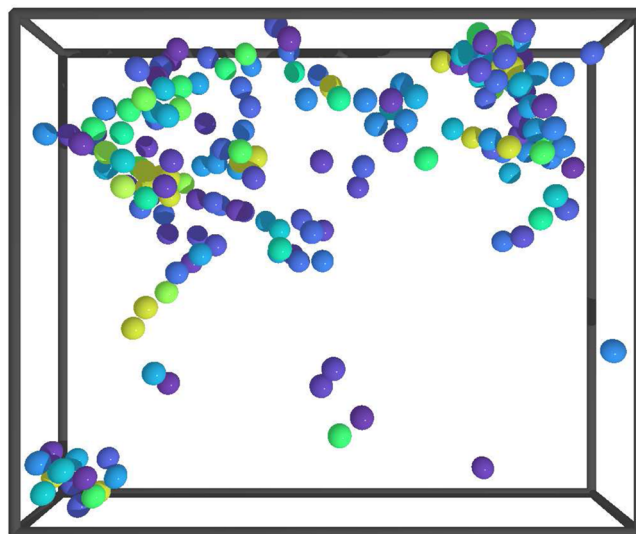


Figure 6. Rendering showing the positions of the most mobile colloidal particles at a particular time for a sample close to the colloidal glass transition. The particles have a radius of $1.18 \mu\text{m}$ and are drawn to scale. The pictured particles have displacements of at least $0.4 \mu\text{m}$ in the next 10 min, making them the top 5% most mobile particles. The color indicates relative mobility, with the darker blue particles having displacements $\sim 0.4 \mu\text{m}$ and the lighter particles moving as much as $\sim 1.0 \mu\text{m}$. Particles with smaller displacements are not pictured. The box is $60 \times 50 \times 10 \mu\text{m}^3$. The data are from ref 10 ($\phi = 0.52$).

ellipsoids with an aspect ratio of 6 (Figure 7a) and used sample chambers that confined these particles to a quasi-two-

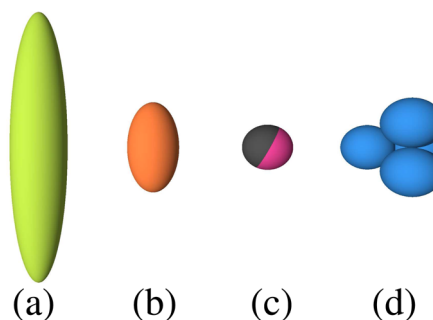


Figure 7. Illustrations of different particle shapes used in experiments to observe rotational diffusion. (a) Ellipsoid with aspect ratio 6.⁸⁶ (b) Ellipsoid with aspect ratio 2.⁸⁷ (c) Sphere with optical difference between two hemispheres.⁸⁹ (d) Tetrahedron composed of four joined spheres.⁹⁰

dimensional layer, allowing for easy visualization of translational and rotational motion of the ellipsoids.⁸⁶ 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 (Figure 7b).⁸⁷ In this experiment, the two glass transitions (rotation and translation) occurred at the same concentration. Later work that included both colloidal experiments and kinetic Monte Carlo simulations showed that the separation of the translational and rotational glass transitions occurred for all particles with aspect ratio $\gtrsim 2.5$.⁸⁸ In

all cases, 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,^{86,88} whereas there were more particles dually mobile for the smaller aspect ratio ellipsoids.^{87,88}

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 (Figure 7c).⁸⁹ 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 (Figure 7d) also added to samples of transparent spheres near the colloidal glass transition.⁹⁰ In this situation, the observations were the opposite of ref 89; both rotational and translational diffusion slowed dramatically, and in this experiment it was the rotational diffusion that was 50× slower than the translational diffusion at the highest concentration studied. Both of these experiments confirmed that the decoupling of translational and rotational diffusion from each other occurs on the single particle level, but they observed 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 90 could sterically "entangle" with the surrounding spheres. Both their rotational and translational motions 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 89 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.⁹¹ 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,⁹² for example, 1.4 for 2D simulations.⁹³ This prediction is also qualitatively consistent with the ellipsoid experiments discussed above, where ellipsoids with aspect ratio $\gtrsim 2.5$ have slower rotational dynamics than translational dynamics.^{86–88}

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.^{43,94} 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".

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 avoiding finite size effects.^{95,96} Experiments also study real materials which themselves might be of intrinsic interest: toothpaste is 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 challenges when comparing them to hard sphere simulations.²⁸ Some methods exist to measure pairwise interactions in colloidal experiments,⁹⁷ 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 conditions⁹⁸ or simulating behavior in four spatial dimensions.^{99,100}

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,^{78,79,101} hard particle simulations,¹⁰² soft particle simulations,^{76,77} polymer simulations,¹⁰³ hard-sphere-like colloids,^{10,11} and soft colloids,¹⁰⁴ all of which complement experiments done with small molecule glasses^{105–107} and polymer glasses.^{80,82,108} 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, particle shape is an intriguing parameter to play with for colloidal glasses, and there are many more shapes besides simple clusters of spheres or ellipsoids,¹⁰⁹ which may lead to a diversity of amorphous states.¹¹⁰ 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 or may not relate to the glass transition problem.¹¹¹ Since the late 1990s there was a conjecture that these problems were closely related;¹¹² recent simulations suggest that the similarities are more superficial than had been thought.^{111,113} Colloidal glass experiments by Basu et al. support the simulation results,¹¹⁴ 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.^{115,116} Recent experiments use 2D colloidal systems and holographic laser tweezers to duplicate some of these conditions,^{117,118} confirming many of the predictions. Given continuing advances in colloidal synthesis techniques¹⁰⁹ and other clever experimental techniques, fruitful conversations will long continue

between those interested in colloidal glasses and those interested in other types of glasses.

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