Observation of the Disorder-Induced Crystal-to-Glass Transition

Peter Yunker  
*University of Pennsylvania*, pyunker@sas.upenn.edu

Zexin Zhang  
*University of Pennsylvania*

Arjun G. Yodh  
*University of Pennsylvania*

Follow this and additional works at: [https://repository.upenn.edu/physics_papers](https://repository.upenn.edu/physics_papers)

Part of the Physics Commons

**Recommended Citation**


**Suggested Citation:**


© The American Physical Society  
[http://dx.doi.org/10.1103/PhysRevLett.104.015701](http://dx.doi.org/10.1103/PhysRevLett.104.015701)

This paper is posted at ScholarlyCommons. [https://repository.upenn.edu/physics_papers/25](https://repository.upenn.edu/physics_papers/25)  
For more information, please contact repository@pobox.upenn.edu.
Observation of the Disorder-Induced Crystal-to-Glass Transition

Abstract
The role of frustration and quenched disorder in driving the transformation of a crystal into a glass is investigated in quasi-two-dimensional binary colloidal suspensions. Frustration is induced by added smaller particles. The crystal-glass transition is measured to differ from the liquid-glass transition in quantitative and qualitative ways. The crystal-glass transition bears structural signatures similar to those of the crystal-fluid transition: at the transition point, the persistence of orientational order decreases sharply from quasilong range to short range, and the orientational order susceptibility exhibits a maximum. The crystal-glass transition also features a sharp variation in particle dynamics: at the transition point, dynamic heterogeneity grows rapidly, and a dynamic correlation length scale increases abruptly.

Disciplines
Physical Sciences and Mathematics | Physics

Comments
Suggested Citation:

© The American Physical Society
http://dx.doi.org/10.1103/PhysRevLett.104.015701
Observation of the Disorder-Induced Crystal-to-Glass Transition

Peter Yunker,1 Zexin Zhang,1,2 and A. G. Yodh1

1Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA
2Complex Assemblies of Soft Matter, CNRS-Rhodia–UPenn UMI 3254, Bristol Pennsylvania 19007, USA

(Received 30 October 2009; revised manuscript received 9 December 2009; published 8 January 2010)

The role of frustration and quenched disorder in driving the transformation of a crystal into a glass is investigated in quasi-two-dimensional binary colloidal suspensions. Frustration is induced by added smaller particles. The crystal-glass transition is measured to differ from the liquid-glass transition in quantitative and qualitative ways. The crystal-glass transition bears structural signatures similar to those of the crystal-fluid transition: at the transition point, the persistence of orientational order decreases sharply from quasilong range to short range, and the orientational order susceptibility exhibits a maximum. The crystal-glass transition also features a sharp variation in particle dynamics: at the transition point, dynamic heterogeneity grows rapidly, and a dynamic correlation length scale increases abruptly.

Disorder plays a critical role in traditional melting and freezing phenomena and in the formation of glasses. Melting from crystal to fluid, for example, is a sharp transition accompanied by loss of orientational and translational order and by a dramatic decrease in flow resistance and rearrangement time scale [1]. By contrast, orientational and translational order do not change significantly at the liquid-to-glass transition, even as viscosity and rearrangement time scale diverge [2]; nevertheless, frozen-in residual disorder is critical for glass formation. An interesting, less-studied but closely related problem concerns the role played by frustration and disorder in driving the transformation of a crystal to a glass. Herein we describe experiments which explore this transition, from crystalline solid to glass as a function of quenched disorder. The resultant glassy phases acquire typical properties such as dynamic heterogeneity [6–9] and disorder, but the crystal-to-glass transition is quite sharp, exhibiting features often associated with melting.

Investigations of glass transitions and structural arrest are of broad interest, in part because the new concepts thus generated affect understanding of a wide variety of materials across a wide swath of scientific communities [6,8–12], including molecular [13], colloidal [9], granular [14], and polymeric [15] glasses. The experiments reported in this contribution relate closely to studies exploring how polydispersity prevents crystallization [16]. Our investigation, however, differs from the above in important ways: single-particle spatial resolution, for example, permits quantitative exploration of orientational order and dynamic heterogeneity as a function of packing fraction and disorder across the crystal-glass transition.

The experiments employ temperature-dependent nearly hard-sphere binary colloidal suspensions composed of two particle sizes with substantially different diameters [12,17]. The number fraction of the smaller diameter “dopant” particles is varied from 0.0 to 0.5, and the area fraction of the two-dimensional (2D) suspension is varied from ~0.75 to ~0.90 at each dopant concentration. This approach enables us to trace sample evolution as function of increasing quenched disorder at fixed area fraction. Structural correlations associated with orientational order and dynamic correlations associated with particle rearrangements are measured. The path from crystal to glass is marked by a sharp drop in structural correlations and a sudden jump in dynamical correlations. The crystal-glass transition bears structural signatures similar to the crystal-fluid transition [1,18]: the orientational order correlation function changes form abruptly from quasilong range to short range at the transition point, and the orientational order susceptibility exhibits a maximum at the transition point. A similarly sharp transition from homogeneous to heterogeneous dynamics accompanies these structural changes; in particular, domains of correlated particle rearrangements (i.e., dynamic heterogeneity) appear to turn on suddenly, and a dynamic correlation length scale increases sharply from ~2 to ~6 particle diameters across the transition point. The crystal-to-glass transition is thus measured to differ from the liquid-to-glass transition in qualitative and quantitative ways.

Binary mixtures of repulsive particles have been used as model glasses in experiment [12,17,19] and simulation [10,20,21]. The present experiment employs aqueous suspensions of micron-size poly(N-isopropyl acrylamide) microgel colloidal spheres (i.e., NIPA particles), whose diameters increase as temperature is reduced [22]. The particles are very similar to those used in recent phase transformation experiments and are described therein [12,17,18,23]. A binary mixture of NIPA particles is sandwiched between two glass cover slips, creating a quasi-2D system. The sample consists of a mixture of NIPA spheres with small and large diameters, $D_S = 1.09 \, \mu m$ and $D_L = 1.55 \, \mu m$, respectively, at temperature $T = 28.0^\circ C$. The polydispersity of each particle type is ~3%, and the par-

DOI: 10.1103/PhysRevLett.104.015701 PACS numbers: 64.70.kj, 61.43.Fs, 64.70.pv, 82.70.Dd
particle interaction potentials are short-range repulsive with a soft tail [18].

We synthesized many bidisperse suspensions with varying small particle number fractions, \( n_S \) (i.e., \( n_S = 0.00, 0.01, 0.02, 0.04, 0.05, 0.07, 0.10, 0.15, 0.20, 0.28, 0.50 \)). By adjusting the sample temperature using a microscope objective heater (BiOptechs), the area fraction \( \phi_A \) was readily increased from \( \phi_A \approx 0.75 \) to \( \phi_A \approx 0.90 \) with a step size of \( \approx 0.01 \) in \( \phi_A \). Figure 1 summarizes \( n_S \) and \( \phi_A \) in every sample. Trajectories with varying \( n_S \) and fixed \( \phi_A \) can be constructed by following a horizontal line across the diagram. Data were collected at each \( \phi_A/n_S \) combination for 3000 s at a video rate of 3 frames per second. The field of view was 60 \( \mu \)m by 80 \( \mu \)m and contained \( \approx 2000 \) particles.

Orientational order is characterized by the bond orientational order parameter: \( \psi_6 = \frac{1}{N_{tot}CN} \sum_{i=1}^{N_{tot}} \sum_{k=1}^{CN} | e^{i \theta_{ik}} | \), where \( \theta_{ik} \) is the angle between the \( x \) axis and the \( j-k \) bond between particles \( j \) and \( k \), \( CN \) is the coordination number of particle \( j \), and \( N_{tot} \) is the total number of particles. The value of \( \psi_6 \) at \( \phi_A = 0.85 \) is plotted as a function of \( n_S \) in Fig. 2(b). As \( n_S \) increases from 0, \( \psi_6 \) decays as a power law. Additionally, the areal density of free disclinations \( N_D \) was measured to increase sharply and then stabilize for larger \( n_S \) [Fig. 2(c)]. Breakup of dislocations (free and bound) into free disclinations is typically associated with formation of the liquid phase [1,18].

To characterize the spatial persistence of orientational order, the correlation function \( g_6(r = |r_i - r_j|) = \langle \psi_6^*(r_i) \psi_6(r_j) \rangle \), where \( r_i \) and \( r_j \) are the positions of particles \( i \) and \( j \), is derived from the data [Fig. 2(d)]. Two distinct regimes corresponding to crystal and glass are quantitatively identified: \( g_6 \approx r^{-\eta} \) (quasilong range) for the crystalline state (\( n_S < 0.02 \)) and \( g_6 \approx e^{-r/\xi_6} \) (short range) for the glass state (\( n_S \gtrsim 0.02 \)). By contrast, \( g_6 \) changes very little across the liquid-to-glass transition [2].

Temporal fluctuations in \( \psi_6 \) are characterized by the susceptibility: \( \chi_6 = N_{tot} \langle (\psi_6)^2 \rangle - \langle \psi_6 \rangle^2 \), where \( \psi_6 \) is the average of \( \psi_6 \) within one image frame \( \langle \psi_6 \rangle = \frac{1}{N_{tot}} \sum_{i=1}^{N_{tot}} | \psi_6(i) | \), and angle brackets indicate average over time [see Fig. 2(a)]. To ameliorate finite-size effects, \( \chi_6 \) is calculated in multiple sub-boxes containing different numbers of particles and is then extrapolated to the infinite size limit [18] (see supplemental material [24]). Interestingly, this susceptibility reaches its maximum at \( n_S = 0.02 \), the same value of \( n_S \) that marks the change from quasilong-range orientational order to short-range orientational order [i.e., the dashed line in Figs. 2(a)–2(c)]. Thus the variation of both the correlation length and the orientational order susceptibility, \( \chi_6 \), suggests a sharp transition between crystal (ordered) and glass (disordered) states as a function of quenched disorder.

The sharp decrease in orientational order correlation length, the peak in \( \chi_6 \) (\( \psi_6 \) susceptibility), and the increase in defects (free disclinations) associated with the liquid state are all reminiscent of the crystal-liquid transition [1,18], suggesting a distinct transition from crystal to glass via increasing quenched disorder [5]. This result stands in contrast to the transition from liquid to glass, where

![FIG. 1](color online). Diagram summarizing all collected data. The crystalline phase is plotted with triangles, the glass phase is plotted with crosses, and the liquid phase is plotted with squares. Data presented in the remainder of the Letter come from points touching the dashed line. Experimental microscope images of sample subregions are displayed from suspensions with \( n_S = 0.01 \), \( \phi_A = 0.89 \) (crystal), \( n_S = 0.28 \), \( \phi_A = 0.90 \) (glass), and \( n_S = 0.28 \), \( \phi_A = 0.79 \) (liquid).

![FIG. 2](color online). (a) The bond orientational order parameter (\( \psi_6 \)) susceptibility, \( \chi_6 \), versus \( n_S \), at area fraction \( \phi_A = 0.85 \). The dashed line marks \( n_S = 0.02 \), the point where \( \chi_6 \) reaches its maximum value. The solid line guides the eye. (b) \( \psi_6 \) versus \( n_S \), at area fraction \( \phi_A = 0.85 \). The solid line is a power law fit. (c) Free disclination density \( N_D \), the number of disclinations per \( \mu m^2 \), versus \( n_S \) at \( \phi_A = 0.85 \). The solid line guides the eye. (d) Envelope of the local maxima of the orientational order spatial correlation functions \( g_6(r) \) for \( n_S = 0.00, 0.01, 0.02, 0.05, 0.11, 0.20, 0.28, 0.50 \), and packing fraction \( \phi_A = 0.85 \). The complete (oscillating) \( g_6 \) is shown for \( n_S = 0.01 \) (dashed line).
changes in structural correlations are not observed [2]. Thus the present system appears to be an excellent new model for study of the relationship between structural order and glass dynamics (e.g., dynamic heterogeneity).

To explore dynamical variations with $n_s$, we first compute the two-point self-correlation function: $Q_2(d_L, \Delta t) = \frac{1}{N_{tot}} \sum_{i=1}^{N_{tot}} \exp(-\Delta r_i^2/2d_L^2)$ [25]. Here $d_L$ is a preselected length scale to be probed and $\Delta r_i$ is the distance particle $i$ moves in time $\Delta t$. If a particle moves a distance smaller than $d_L$, $Q_2$ will be close to 1; if a particle moves a distance greater than $d_L$, $Q_2$ will be close to 0. Plots of $Q_2$ for $d_L = 0.05 \ \mu m$ are given in Fig. 3(a). For the crystalline states ($n_s < 0.02$), $Q_2$ plateaus and does not decay within the experimental window. Conversely, for glass states, $Q_2$ decays within the observed time frame, due to the rearrangement of particle cages as the particles seek new configurations. This effect was first noted in [4].

The emergence of domains of correlated rearrangements is central to many different properties of glasses [6–9]. This so-called dynamic heterogeneity is characterized by temporal fluctuations in $Q_2$, and these fluctuations are commonly quantified by the dynamical susceptibility $\chi_4(d_L, \Delta t) = N_{tot} (Q_2(d_L, \Delta t)^2 - \langle Q_2(d_L, \Delta t) \rangle^2)$, as a function of length scale $d_L$ and time scale $\Delta t$. The variation of $\chi_4$ with $n_s$, at the value of $d_L$ that maximizes the peak in $\chi_4$, is plotted in Fig. 3(b) for $\phi_A = 0.85$ and $n_s = 0.0, 0.01, 0.025, 0.07$, and 0.16. For $n_s > 0.02$, $\chi_4$ exhibits a peak similar to that found in previous works [8,25–28]. Conversely, $\chi_4$ is small and flat for samples with $n_s < 0.02$, as expected for crystalline systems.

![FIG. 3 (color online).](image)

(a) The two-point-correlation function $Q_2$, is plotted versus $\Delta t$, for $d_L = 0.05 \ \mu m$ and for $n_s = 0.00$ (solid squares), 0.01 (solid circles), 0.02 (open triangles), 0.07 (open squares), 0.16 (open circles). (b) The four-point dynamic susceptibility $\chi_4$ is plotted versus $\Delta t$, for the same values of $n_s$ as in (a); the value of $d_L$ is chosen to maximize peak height.

The maximum value of $\chi_4$ (i.e., $\chi_4^*$) is plotted in Fig. 4(a) for each $n_s$ at $\phi_A = 0.85$. In crystalline suspensions, $\chi_4^*$ is small ($\sim 1$). Once $n_s$ is increased beyond 0.02, however, $\chi_4^*$ jumps discontinuously to $\sim 35$. As $n_s$ is increased still further, $\chi_4^*$ remains fairly constant. This sharp change is absent in the liquid-glass transition [8,28]. For comparison we plot $\chi_4^*$ across the liquid-glass transition in this same experimental system as a function of particle area fraction at fixed dopant concentration $n_s = 0.25$ (i.e., along the vertical line with $n_s = 0.25$ in Fig. 1); $\chi_4^*$ increases continuously as packing fraction is increased [Fig. 4(b)], similar to [8,28].

$\chi_4^*$ can be related to the number of particles participating in a dynamically heterogeneous event [26]. The sudden variation of $\chi_4^*$ is thus indicative of a sudden increase in the size of domains of correlated rearranging particles as the system evolves from crystal to glass. When too much quenched disorder exists in the sample for crystallization to occur, the suspension is pushed out of equilibrium as it searches for a configuration to minimize its free energy. These search pathways are constrained by the suspension’s large packing fraction, and rearrangements must occur in a collective manner. Interestingly, once in the glass phase, further increasing $n_s$ moves $\chi_4^*$ to larger values of $d_L$ [Fig. 4(c)], implying relaxation events are more effective. However, $\chi_4^*$ itself does not increase significantly, thus implying the degree of quenched order has little effect on the domain size of collective rearrangements (see supplemental material [24]).

To further characterize the domain size of the correlated rearrangements, we derived spatial correlations of $1 - Q_2^2$.

![FIG. 4 (color online).](image)

(a) The maximum value of $\chi_4$, $\chi_4^*$, plotted versus the fraction of small particles $n_s$. The solid line is a linear fit, to guide the eye. The dashed line marks $n_s = 0.02$. Inset: Rearrangement correlation length $\xi_0$, versus $n_s$. The solid line is a linear fit to guide the eye. The dashed line marks $n_s = 0.02$. (b) $\chi_4^*$ plotted versus $\phi_A$ for $n_s = 0.25$. The solid line is a power law fit to guide the eye. (c) The maximum value of $\chi_4$ is plotted as a function of $d_L$ for four values of $n_s$. 

015701-3
yielding the rearrangement spatial correlation function:
\[ g_{Q_i}(r = |\mathbf{r}_i - \mathbf{r}_j|) = \langle (1 - Q_2^1(\mathbf{r}_i))(1 - Q_2^1(\mathbf{r}_j)) \rangle \]. Here \( Q_2^1 \) is calculated for values of \( d_L \) and \( \Delta t \) that maximize \( \chi_P \) and thus dynamic heterogeneity. Note that correlations of \( 1 - Q_2^1 \) relate to rearranging particles, i.e., particles moving farther than \( d_L \). These correlation functions are readily fit by decaying exponentials \( g_{Q_i} \propto \exp(-r/\xi_{Q_i}) \), and a correlation length \( \xi_{Q_i} \) is thus readily extracted [Fig. 4(a) inset]. For crystalline samples \( (n_S < 0.02) \), \( \xi_{Q_i} \propto 2D_L \), implying that when particles move large distances, only their nearest neighbors move large distances. For glass samples \( (n_S > 0.02) \), \( \xi_{Q_i} \propto 6D_L \), implying that when particles move large distances, they do so in a correlated manner involving many particles. The size of \( \xi_{Q_i} \) jumps sharply at \( n_S = 0.02 \), along with the discontinuous increase in \( \chi^*_4 \) (during the liquid-to-glass transition). \( \xi_{Q_i} \) follows the same continuous trend as \( \chi^*_4 \). Thus the onset of dynamic heterogeneity appears nearly discontinuously.

The dynamical transition from crystal to glass is thus characterized by a discontinuous jump in \( \chi^*_4 \), the maximum value of the dynamic susceptibility, and a discontinuous increase in spatial correlation decay length from \( \sim 2D_L \) to \( \sim 6D_L \). These results stand in contrast to the liquid-glass transition, during which dynamics change relatively more slowly and continuously. The rapid onset of glass dynamics occurs at the same value of \( n_S \) as the structural transition from crystal to glass. In other words, dynamic heterogeneity appears simultaneously with the disappearance of quasilong-range orientational order. To conclude, while the liquid-to-glass transition is somewhat ambiguous and often difficult to define, the crystal-to-glass transition with increasing quenched disorder appears sharp and unambiguously defined.

We thank Doug Durian, Piotr Habdas, Yilong Han, and Matt Lohr for useful discussions. We acknowledge the financial support of the National Science Foundation through DMR-080488 (A. G. Y.) and the PENN MRSEC DMR-0520020. Z. Z. gratefully acknowledges partial support from Rhodia.

S. I. Henderson, T. C. Mortensen, S. M. Underwood, and W. van Megen, Physica (Amsterdam) 233A, 102 (1996);
E. Zaccarelli et al., Phys. Rev. Lett. 103, 135704 (2009);