Shape-designed frustration by local polymorphism in a near-equilibrium colloidal glass

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We show that hard, convex, lithographic, prismatic kite platelets, each having three 72° vertices and one 144° vertex, preferentially form a disordered and arrested 2D glass when concentrated quasi-statically in a monolayer while experiencing thermal Brownian fluctuations. By contrast with 2D systems of other hard convex shapes, such as squares, rhombs, and pentagons, which readily form crystals at high densities, 72° kites retain a liquid-like disordered structure that becomes frozen-in as their long-time translational and rotational diffusion become highly bounded, yielding a 2D colloidal glass. This robust glass-forming propensity arises from competition between highly diverse few-particle local polymeric configurations (LPCs) that have incommensurate features and symmetries. Thus, entropy maximization is consistent with the preservation of highly diverse LPCs en route to the arrested glass.

Although much is known about many different kinds of glassy materials, including entangled polymers, dispersions of hard particles at high densities, and spin glasses (1–7), no single universal mechanism for glass formation describes them all. When isotropic Brownian systems of hard shapes are compressed slowly, the development of long-range order, typical of equilibrium crystal or liquid crystal phases, can either occur or be suppressed. By contrast, fast quenching processes, such as cooling molecular liquids or osmotically compressing dispersions of hard colloids, are known to produce nonequilibrium glassy states even if the components could, in principle, form highly ordered equilibrium high-density phases through slower processes (8–13). For instance, hard spheres in three dimensions (3D) undergo a first-order crystallization disorder–order transition when slowly compressed, yet can also be forced into a disordered and arrested (i.e., nonergodic) glassy solid through a rapid quench in their volume fraction to a value that is near but below the point at which the spheres actually jam (4, 14–18). Other types of glasses can be formed through mechanisms such as attractive interactions or entanglements between constituent objects (1–3). Disordered glasses differ from disordered gels, because gels result from strong attractions between constituents compared with thermal energy, and gels typically have much larger local spatial inhomogeneities than glasses (19). Thus, dispersions of colloidal particles that are not highly attractive and have hard interactions can be model glassy systems. Molecular and colloidal glass formers have been classified according to the notion of fragility (2, 20), which involves relative differences in attractive interactions. Nevertheless, a general theory of the glass-forming propensity of hard Brownian particles as a function of shape remains elusive. Moreover, dense glassy states typically have a significant residual entropy (21), reflecting orientational and positional randomness of constituent particles. The role of residual entropy in the general context of entropy maximization (22, 23) of hard particle systems that are very slowly compressed has not been completely addressed.

Dispersed Brownian systems of hard particles in two dimensions (2D) are especially suited for providing insight into glass formation, because monodisperse hard disks in 2D still order even under very fast quenching (24), whereas quenched hard spheres in 3D readily form glassy states (5). A recent study of prolate ellipsoids has shown that rapid quenching of their density can frustrate crystallization in 2D (24); this rapid quench has been used to suppress the formation of large regions having liquid crystalline order and to cause nonequilibrium jamming of the ellipsoids. Thus, this study did not demonstrate the formation of a disordered glass under slow near-equilibrium compression. Simulations show that hard, elongated ellipses having aspect ratios (i.e., semimajor axis divided by semiminor axis) greater than 2.4 form nematic phases (25). In the limit of very high aspect ratios, dispersions of rod-like fd virus, when slowly compressed, have yielded liquid crystals that possess long-range orientational order and are therefore not glasses (26). Thus, elongated colloidal objects do not necessarily form disordered glasses under very slow compression in the presence of Brownian fluctuations. Consequently, the question of whether a glass of hard monodisperse particles can be created through a slow compression in the presence of thermal excitations remains unresolved.

The development of top-down lithographic production of stable dispersions of shape-designed particles (27, 28) that have nearly hard interactions opens up the possibility of experimentally exploring the glass-forming propensity of different shapes in monodisperse 2D Brownian systems. For a limited number of convex polygonal shapes, including triangles, squares, pentagons, and 72° rhombs that have all been quasi-statically compressed, all systems undergo a disorder–order transition from a spatially and orientationally disordered liquid-like phase, in which long-time rotational and translational diffusion of shapes still occurs, to a liquid crystal

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Significance

The origin of disorder in glasses is one of the most important unresolved questions in materials science. In many cases, for materials made of monodisperse components that are not attractive and have the capacity to crystallize, such as dispersions of colloidal hard spheres, the disorder is typically associated with rapid, out-of-equilibrium quenching of the density that causes components to jam into disordered configurations. By contrast, here we reveal that hard colloidal kite-shaped particles, which have the geometric capacity to crystallize, instead form a disordered glass when compressed very slowly and quasi-statically. We show that this glassy disorder results from a high diversity of different local configurations of kites, effectively masking the one global crystal phase.

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or a crystal phase possessing at least quasi–long-range order (29–32). Thus far, no empirical observations of 2D Brownian systems exist that show a disordered liquid phase being slowly compressed into a disordered glassy solid-like state. Simulations using hard 3D shapes have shown that a small number of polyhedral shapes have a strong tendency to form glasses in 3D, even when equilibration times are long (33). However, these simulation results are limited to a few examples, and a broad predictive theory of disorder–disorder and disorder–order transitions as a function of shape still does not exist for Brownian hard-particle systems. Thus, experimentally demonstrating even a single example of a monodisperse Brownian system of a hard compact shape, which has a strong tendency to form a glass under a near-equilibrium compression from a liquid, would establish an important reference point in the science of glass-forming systems.

**Results**

We design and lithographically fabricate monodisperse colloidal 72° kite particles composed of polymeric photoresist (Materials and Methods). Each “kite” is a four-sided convex polygonal prismatic platelet that has three 72° and one 144° internal angles (Fig. 1 A and B). Two shorter edges (length s = 1.8 ± 0.1 μm) are adjacent on either side of the 144° vertex, and two longer edges (length L = 2.9 ± 0.1 μm) are adjacent on either side of the 72° vertex opposite the 144° vertex. L/s is the golden ratio, so L and s are incommensurate. Each kite has a centerline of mirror symmetry between these two vertices and a pointing direction from its 144° vertex (i.e., tail) to its opposite 72° vertex (i.e., head). A kite’s center-of-mass (designated O) is not equidistant between these two opposite vertices. The average thickness of a kite is 1.4 ± 0.1 μm. When compressed in a plane, a system of many 72° kites could potentially form an alternating stripe crystal (ASX) that fully tiles space (Fig. 1C) based on a four-particle ASX local polymorphic configuration (LPC). We have purposefully designed the kites to enable the formation of dense five-particle LPCs, such as the pentagonal star, because 360°/5 = 72° (Fig. 1D). However, pentagonal LPCs are fundamentally incompatible with the sole four-particle ASX LPC, so they could potentially inhibit crystallization of the ASX phase even as the particle area fraction φA is raised quasi-statically.

Using anisotropic depletion attractions (34), we create and slowly compress a Brownian system of 72° kites in a rectangular optical cell suitable for viewing using an optical microscope (Fig. 1E; see also SI Appendix). Because kites have a higher edge roughness, compared with their facial roughness, a depletion agent having a diameter between these two roughness scales causes a significant attraction between the faces of the kite-platelets and the wall of the optical cell, whereas in-plane interactions between the kites remain effectively hard. We tilt the cell by about 5° from horizontal, causing kites to slowly move toward the lower portion of the cell by weak gravitational sedimentation as they also diffuse. We allow equilibration to occur over 7 months, which is more than 5 times longer than that used for other 2D systems of shapes which have formed liquid crystals or crystals after only a few weeks of similarly slow compression (30–32). As φA is increased quasi-statically, the average rotational and translational diffusion of individual kites becomes strongly restricted (i.e., bound), whereas the system of kites retains a disordered spatial structure and uniform distribution of pointing directions, as shown in Fig. 2 (see also SI Appendix, Figs. S1–S4). To obtain images and movies of the system of kites at different φA, we translate a single optical cell along its length in the microscope, focusing the objective lens on the monolayer. At the top of the 2D barometric column of kites, a dilute isotropic gaseous region exists. Below this, as the density increases, the structure of the kites remains disordered, and yet their diffusion is slowed in a single-phase fluid-like region (Movie S1). Fourier transforms (FTs) of real-space optical micrographs of dense systems of kites that have been concentrated from dilute φA show a uniform ring both at φA = 0.49 and φA ~ 0.59 (Fig. 2A and F).

Using center positions of kites determined from image analysis, we calculate the spatial pair correlation function g(r/L), where r is the center-to-center separation between pairs of particles, at each φA (Fig. 2 B and G). Irrespective of φA, g(r/L) exhibits only short-range order. However, by analyzing movies of the dynamics of the kites, we find that the time- and ensemble-averaged transnational mean-square displacement (MSD), <Δr²(t)>, and mean-square angular displacement (MSAD), <Δϕ²(t)>, where t represents time, change dramatically as φA is increased from 0.49 to 0.59 (Fig. 2 C and H). At φA ~ 0.49, <Δr²(t) > and <Δϕ²(t) > rise proportional to time at long times, corresponding to ergodic kite diffusion and a liquid-like viscous behavior. By contrast, at φA ~ 0.59, <Δr²(t) > and <Δϕ²(t) > instead exhibit saturation at long times, corresponding to highly restricted, nonergodic, bound diffusion. Such bound translational diffusion corresponds to an effectively infinite viscosity, characteristic of a glass, as a result of increased crowding. In the near-glass regime, we see heterogeneous dynamics and long-time relaxation of the system (see Movie S2 at φA = 0.53); we also observe that time-averaged MSDs of individual kites can depart significantly from the reported ensemble- and time-averaged MSDs. Collective fluctuations of thermally driven kites are evident at φA ~ 0.59 (Movie S3), so the kites are not jammed to the point of complete immobility by their neighbors. Instead, they form a high-density glassy state in which Brownian fluctuations are still present.

The pointing directions of the kites remain random as φA is increased from the liquid into the glassy regime, as shown by color-coded micrographs (Fig. 2 D and J). Consequently, the ensemble-averaged probability distribution of pointing angles, pA(θ), remains uniform as φA is raised from 0.49 to 0.59 (Fig. 2E and J). Thus, over a relatively small increase in φA, the Brownian motion of individual kites becomes highly restricted whereas their spatial distribution remains disordered and their angular distribution of pointing directions remains uniform. Thus, we
Voronoi analysis based on center positions of kites yields the effect of nearest neighbors on the flocking behavior of kites. Optical microscope images of dense kites: (A and F). No long-range order is evident in either image. (Scale bar, 10 μm.) (Insets) FTs of the images showing isotropic ring-like patterns. (White scale bar, 0.4 μm.) Spatial PCFs \( g(r/L) \), where \( r \) is the center-to-center separation: (B and G). Rapid decays in the peak heights for increasing \( r/L \) are seen in both. Ensemble- and time-averaged single-particle dynamics for translational and rotational motion, expressed by the MSD, \( \langle \Delta r^2(t) \rangle \), and MSAD, \( \langle \Delta \theta^2(t) \rangle \) (C and H). Translational and rotational long-time dynamics are diffusive liquid-like in C but strongly arrested and solid-like in H. Microscope images of kites that have been color-coded by their pointing directions, as determined through particle-tracking image analysis: (D and I); color wheel inset in D defines orientation. Long-range orientational order is not seen in either color-coded image, and the corresponding measured distributions of single-particle pointing directions, \( p_\theta(\theta) \), in E and J, are effectively uniform.

Identify \( \phi_A \sim 0.49 \) as being below and \( \phi_A \sim 0.59 \) as being above an area fraction associated with a glass transition, \( \phi_{A,g} \).

Voronoi analysis, based on the detected center positions of the kites, provides insight into the nature of how the average number of nearest neighbors around a given particle changes as \( \phi_A \) is increased. A color-coded Voronoi construction, displayed in Fig. 3A, at \( \phi_A \sim 0.59 \) above \( \phi_{A,g} \), reveals that very large populations of five and seven nearest neighbors persist into the glass regime, even as six nearest neighbors are the majority. Examples of local configurations of kites that have five, six, and seven nearest neighbors are shown in Fig. 3B. Limited spatial domains, populated primarily by alternating five and seven nearest neighbors, interrupt other local regions populated by six nearest neighbors in what resembles a quenched and frozen two-phase separated structure. These interpenetrating domains have a characteristic width that is less than about 5\( L \). To describe the system’s spatial structure more precisely, we have extended classic Voronoi analysis to create spatial conditional pair correlation functions (C-PCFs) that are conditional upon the number of nearest neighbors around a given particle (Fig. 3C). For example, to calculate the C-PCF represented by \( g_{5n}(r/L) \), we first identify kites that have only five nearest neighbors by Voronoi construction, and then compute an ensemble-averaged spatial PCF using only those particles that have five nearest neighbors. Very large differences are observed between \( g_{5n}(r/L) \), \( g_{6n}(r/L) \), and \( g_{7n}(r/L) \), corresponding to five, six, and seven nearest neighbors, respectively. In particular, the primary peaks in \( g_{5n} \) and \( g_{7n} \) occur at values of \( r/L \) that are incommensurate with the primary peak of \( g_{6n} \). This, in combination with the limited local spatial regions, leads to a rapid decay in the peaks of the total combined \( g(r/L) \) calculated without considering the number of Voronoi neighbors. We have also measured how the average probabilities associated with five, six, and seven nearest neighbors depends on \( \phi_A \) (Fig. 3D). Nearly equal populations of five and seven nearest neighbors, at about 20% each, coexist with a population of six nearest neighbors, at about 60%, for \( \phi_A > 0.48 \).

Although the single-particle distribution \( p_\theta(\theta) \) is uniform even up to large \( \phi_A \) in the arrested glassy regime, the distribution of relative angles, \( \psi \), between pairs of first (i.e., closest) nearest-neighbor kites has an interesting nonuniform structure that can be associated with certain favored local pair configurations, as shown in Fig. 4. Examples of the most frequently encountered nearest-neighbor pair configurations of kites, which result in
relative angles of 36°, 72°, and 180°, are shown in Fig. 4A. More than one pair configuration exists for each of these angles; among all configurations, the upper pair configurations shown for the pentagonal star (green) and ASX (red) effectively have the same minimal center-to-center distance of $r_{\text{min}} \sim 0.709L$. The relative-angle pair probability distribution is an even function, so we display the ensemble-averaged measured $p_{\psi_j}$ for several different $\phi_j$ both above and below $\phi_{2k}$ (Fig. 4B). For lower $\phi_j \sim 0.44$, $p_{\psi_j}$ has a plateau-like region between about 30° and 80° and a small peak around 180°. By contrast, at higher $\phi_j \sim 0.62$, the distribution shows enhanced probabilities of finding particles having relative orientations at 72° and 180°, while also retaining a significant population at around 36°. The same trends are found for relative angles calculated using second-nearest-neighbor pairs and third-nearest-neighbor pairs (SI Appendix, Fig. S5), although the above-identified features in the distributions are not as distinct. Thus, the local pair structures of relative pointing directions exhibit several peaks at incommensurate angles that would inhibittiling into a crystalline lattice. To emphasize this, we create a color-coded image of LPCs based on the relative orientations of first-nearest neighbors, as shown in Fig. 4C. The dominant configurations are 180° and 72°, like the two particular examples shown in Fig. 4D and E, respectively. In Fig. 4C, it is possible to identify some small domain-like regions, each having a width of at most about three or four particles, that share similar relative angles, but these regions do not necessarily have identical pair configurations because more than one local configuration is coded into a particular color. Thus, despite the nonuniform nature of $p_{\psi_j}$ above $\phi_{2k}$, the spatial distribution of relative pointing directions has at most short-range order, comparable to or smaller than the short-range order seen in the spatial $g(r/L)$ and the widths of interpenetrating domains in the Voronoi construction.

To identify the area fraction associated with the onset of glassy behavior more precisely, we calculate several relevant dimensionless parameters as a function of $\phi_A$ (SI Appendix, Fig. S6). In particular, the long-time power-law exponents, $\alpha_T$ and $\alpha_L$, of the MSD and MSAD, respectively, are effectively unity at lower $\phi_A$, corresponding to long-time diffusive dynamics characteristic of a liquid, whereas these decrease to zero for $\phi_A > 0.58$, corresponding to highly bound confinement characteristic of a solid. In addition, non-Gaussian parameters for translation and rotation (17, 35) increase as $\phi_A$ is raised to $\sim 0.57$ (SI Appendix, Figs. S6–S8), indicating dynamical heterogeneity (13) in the approach to the glass transition, and these subsequently decrease in the nonergodic glassy state. Thus, based on average single-particle translational and rotational dynamics, the ergodic to nonergodic glass transition in the 2D system of disordered uniform 72° kites occurs at about $\phi_{A_{\text{g}}} \sim 0.58$. Over the same range of $\phi_A$, both below and above $\phi_{A_{\text{g}}}$, the dimensionless spatial correlation length, $\xi/L$, remains small, corresponding to short-range order. By contrast, for other hard shapes that have been observed to crystallize in 2D as $\phi_A$ is raised, $\xi/L$ rises dramatically as the dense system develops long-range order, whereas the MSD becomes bounded and $\alpha_T$ approaches zero.

**Discussion**

The persistence of disorder that we have observed in this 2D Brownian system of 72° kites as it becomes nonergodic does not result from highly nonequilibrium rapid quenching and jamming. Instead, during slow compression, the dense disordered system of kites contains a diverse set of fluctuating local polymorphic configurations that remain near-equilibrium. The structure of this set near $\phi_{A_{\text{g}}}$ is overwhelmingly likely to be disordered, because the shapes, sizes, and symmetries of neighboring LPCs, which have randomly formed during compression, are incommensurate and not necessarily have identical pairing relationships.

The designed shape of 72° kites leads to an extremely diverse set of single-particle LPCs. To generate this set, we position several additional kites at or near the central point, and these subsequently decrease in the nonergodic glassy state. Thus, based on average single-particle translational and rotational dynamics, the ergodic to nonergodic glass transition in the 2D system of disordered uniform 72° kites occurs at about $\phi_{A_{\text{g}}} \sim 0.58$. Over the same range of $\phi_A$, both below and above $\phi_{A_{\text{g}}}$, the dimensionless spatial correlation length, $\xi/L$, remains small, corresponding to short-range order. By contrast, for other hard shapes that have been observed to crystallize in 2D as $\phi_A$ is raised, $\xi/L$ rises dramatically as the dense system develops long-range order, whereas the MSD becomes bounded and $\alpha_T$ approaches zero.

**Fig. 4.** Image analysis yields the relative pointing angle $\psi$ between adjacent kites that are first-nearest neighbors (fnn) at $\phi_A \sim 0.62$. (A) Color-coded schematics and example microscope images depicting $\phi_A \sim 36°$ (blue), 72° (green), and 180° (red). (B) Observed fnn relative pointing angle probability distribution $p_{\psi_j}$. Ranges of angles displaying preferred relative pointing directions are color-coded as in A, i.e., [30°,45°] (blue), [55°,85°] (green), [165°,180°] (red). The measured distribution from $180°$ to $180°$ is symmetric about 0, so $p_{\psi_j}(\psi) \sim 0.58$. (C) Color-coded microscopic image showing the spatial distribution of $\psi$. Ranges of angles used for color coding are from B; gray is used for kites that do not have $\psi$ in any colored range of angles (i.e., corresponding to the black points in the plot at $\phi_A \sim 0.62$ in B). Examples of small, yet fully edge-commensurate, local dense packing configurations of kites are shown in (D) alternating stripe configuration (red), and (E) pentagonal star configuration (green), including both colored micrographs (Left) and corresponding schematics (Right).
pentagonal star, are shown in Fig. 4 D and E. The greater number of five-kite LPCs than four-kite LPCs implies that the dominant branching path (21) to the glassy state will be toward five-kite LPCs, away from four-kite LPCs. Thus, the full-tiling four-kite ASX LPC represents only one out of many possible LPCs, and its observed occurrence as \( \phi_A \) approaches \( \phi_{A,g} \) is correspondingly low.

As \( \phi_A \) of the system of hard kites is slowly increased, an extremely diverse set of fluctuating, interacting LPCs arises. We do not observe a significant rise in the population of the one highly specific four-kite LPC that is required to form the ASX phase. Instead, many five-kite LPCs, including the pentagonal star, persist as \( \phi_A \) nears and eventually exceeds \( \phi_{A,g} \). This persistently high density of five-kite LPCs in the system as \( \phi_A \) is raised, leading to five and seven nearest neighbors, is fundamentally incompatible with the formation of a long-range ASX crystal phase. To interpret our observations, we hypothesize that entropy maximization is consistent with a highly diverse set of fluctuating LPCs that coexist as \( \phi_A \) is slowly raised beyond a point at which dynamic arrest occurs. By considering few-kite LPCs, rather than individual kites, as the objects comprising the 2D system, entropy of mixing (22, 23) of these Brownian objects would cause diverse LPCs to be distributed throughout the system. Forward and backward reactions, some involving rotational rearrangements for the same local number of kites (blue arrows in Fig. 5) and others involving local topological changes in the local number of kites (red arrows in Fig. 5), are continuously occurring in the fluctuating system as \( \phi_A \) is slowly increased. Eventually, as \( \phi_A \) becomes large enough, rotational and translational fluctuations become bounded at long times and the rate constants associated with interconversion reactions between different LPCs vanish. Only very large-scale collective density fluctuations could then enable reorientations and isolated topological changes, and such fluctuations become extremely improbable when \( \phi_A \) exceeds \( \phi_{A,g} \), so the system becomes fully arrested into a glass.

A near-equilibrium colloidal glass is consistent with the principles of statistical mechanics (4); here, by purposefully designing a shape that creates a wide variety of incommensurate LPCs, crystallization is frustrated even under very slow compression, yielding a near-equilibrium 2D colloidal glass of hard 72° kites. Although no formal bonds exist between kites in any of the few-particle LPCs, these LPCs can be imagined to be analogous to different molecules that have complex structures and long lifetimes. Thus, a system of long-lived LPCs effectively has an entropy of mixing that favors evenly distributed spatial and orientational arrangements of different LPCs. The notion of residual entropy (21, 25) of these LPCs can also play an important role. Certain molecular systems, even as simple as carbon monoxide, when slowly cooled, retain rotationally random configurations even as they spatially crystallize, leading to a significant residual entropy (23, 36). By analogy, the single-kite distribution of orientation, \( p(\theta) \), remains uniform as \( \phi_A \) is raised through the glass transition; this retention of orientational randomness through \( \phi_{A,g} \) leads to a significant residual entropy in the glassy state. In effect, entropy maximization, when considered in terms of the probabilistic formulation of Gibbs and Shannon (21), preserves the local structural diversity of LPCs even through the glass transition into a highly arrested state. Thus, if one considers the residual entropy of LPCs, one would expect a variety of LPCs in different relative orientations and positions to continue to exist and intertransform as \( \phi_A \) is raised from the liquid-like state to higher densities where solidification effectively occurs, the viscosity diverges, diffusion becomes highly bounded, and the system becomes nonergodic. In applying the notions of entropy of mixing and residual entropy, we emphasize that these are applied to small groups of particles that can be interpreted as LPCs, not to individual kites. Because any given individual particle could be taken as being a part of more than one LPC, many different nonunique sets of LPCs could equivalently be used to analyze a single high-density configuration of kite particles. Many different choices of sets of LPCs could be made to describe the same system of particles at a given instant; yet, for large systems, entropy maximization of all of these sets would yield the same entropy of mixing and residual entropy, regardless of the particular set that might have been chosen. Thus, the inherent design of a particular shape can create a highly diverse set of distinguishably different yet incommensurate LPCs, which in turn can create a collective form of entropy that preserves disorder even as the system’s density is raised through the glass transition.

Strikingly, the incommensurate symmetries and perimeters of widely diverse LPCs, effectively created through the selective design of the kite’s shape, lead to glassy frustration and hide the global ASX phase up to and beyond a density corresponding to glassy solidification of the system, even for near-equilibrium compression. Expressed in different terms, a collective mixing entropy associated with different relative morphologies of a diverse
set of fluctuating few-particle LPCs cannot be neglected in comparison with the average configurational entropy of accessible microstates available to single particles constrained by hard interactions. This mixing entropy of few-particle LPCs, an emergent collective effect, suppresses ordering, whereas polyomorphically diversity, as well as randomness in relative positions and orientations of LPCs throughout the system, is preserved as the density is slowly raised. This mechanism of glass formation under slow compression of hard convex objects, which have been shape-designed to create topologically diverse local polymorphism, is fundamentally different from other mechanisms that promote disorder, including rapid quenching to trap a large density of defects, entanglement, and strong interparticle attractions that inhibit rearrangements.

Conclusion

We have demonstrated that it is possible to create a monodisperse system of a single compact convex shape that can, in principle, order into a space-filling crystal, yet does not because of the extreme diversity and incommensurate nature of few-particle LPCs, even when the applied compression is very slow, quasi-static, and near-equilibrium. The system of hard 72° kites that we have investigated here provides a key example of glass formation that does not arise from interparticle entanglements or attractive interactions. This mechanism is also different from trapping large numbers of defects in a system through a rapid quench that jams particles together. Instead, our experiments indicate that a different mechanism, extremely diverse polymorphism of topologically different LPCs, favors glass formation. As a consequence, the global ASX phase remains hidden by a maze of forward and backward reactions that suppresses growth of the ASX phase, and the kites remain disordered even as ϕ_{AS} is raised beyond the point of rotational and translational arrest, leading to a near-equilibrium glass. We believe that this mechanism is likely to be present for certain other shapes than the particular 72° kites that we have shown here. Thus, when designing shapes of particles to control their self-organized structures as the density is slowly raised from the fluid regime, considering the diversity, symmetry, topology, and commensurability of few-particle LPCs, not just the maximum-density tiling configuration, is worthwhile.

Materials and Methods

Sample Preparation. Uniform kite platelets are fabricated from a 1.4 × 0.1-μm layer of SU-8 polymer by stepper photolithography (Ultratech i-line XLS, 5:1 reduction), released into aqueous solution, and stabilized against aggregation by adsorbed SDS (1 mM). We prepare 2D Brownian systems using anisotropic depletion attractions and compress them slowly in the same manner as has been described for squares and other particles (see Materials and Methods in ref. 30, see also SI Appendix). A monolayer of a certain particle type achieves a steady state when the particle area fraction ϕ_{AS} as a function of distance (i.e., density profile) along the microcapillary stops changing, as measured by bright-field optical microscopy (40× long-working distance objective). However, by contrast with prior experiments, in which the waiting time for equilibrating this concentration profile usually takes several weeks and during which for crystals or liquid crystals form, for the 2D kite system, we wait a much longer time of 7 months for equilibration to provide ample time for long-range order to develop, if possible. About 1,000 kite particles are observed in a single microscopic field of view (118 μm × 89 μm) at high ϕ_{AS}. All values of ϕ_{AS} are calculated using particle center locations, determined by tracking software, and the average measured size of the kites, determined by scanning electron microscopy.

Quantitative Video Analysis. We have written enhanced video particle-tracking microscopy software that improves on existing routines for spheres and disks by detecting both the centers and vertices of all kites in successive video frames, providing both positional and orientational trajectories. Ensemble-averaged spatial, orientational, and dynamical correlation functions, as well as order parameters, are then calculated based on these trajectories (see more details in SI Appendix).

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