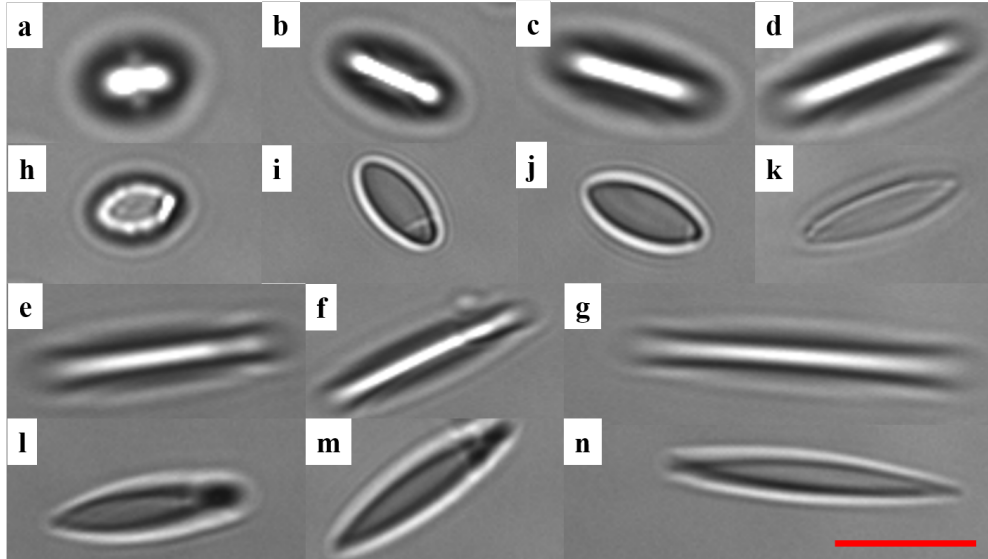


Supplementary Note 1: Experimental system and measurement

In this work ellipsoidal particles were fabricated using the method described in Supplementary Ref. [1]. We placed 0.5% Polymethyl Methacrylate (PMMA) spheres into a 12% aqueous Polyvinyl Alcohol (PVA) solution in a Petri dish. After the water in the PVA solution had evaporated, we stretched the PVA film at approximately 130°C. PMMA spheres embedded in the film can be simultaneously stretched because their glass transition temperatures are below 130°C. After the product had cooled to room temperature, we dissolved the PVA and obtained ellipsoids with 5% polydispersity. The clean ellipsoid solution was stabilised using 7 *millimole* Sodium Dodecyl Sulfate (SDS), after which the samples were sonicated and centrifuged.

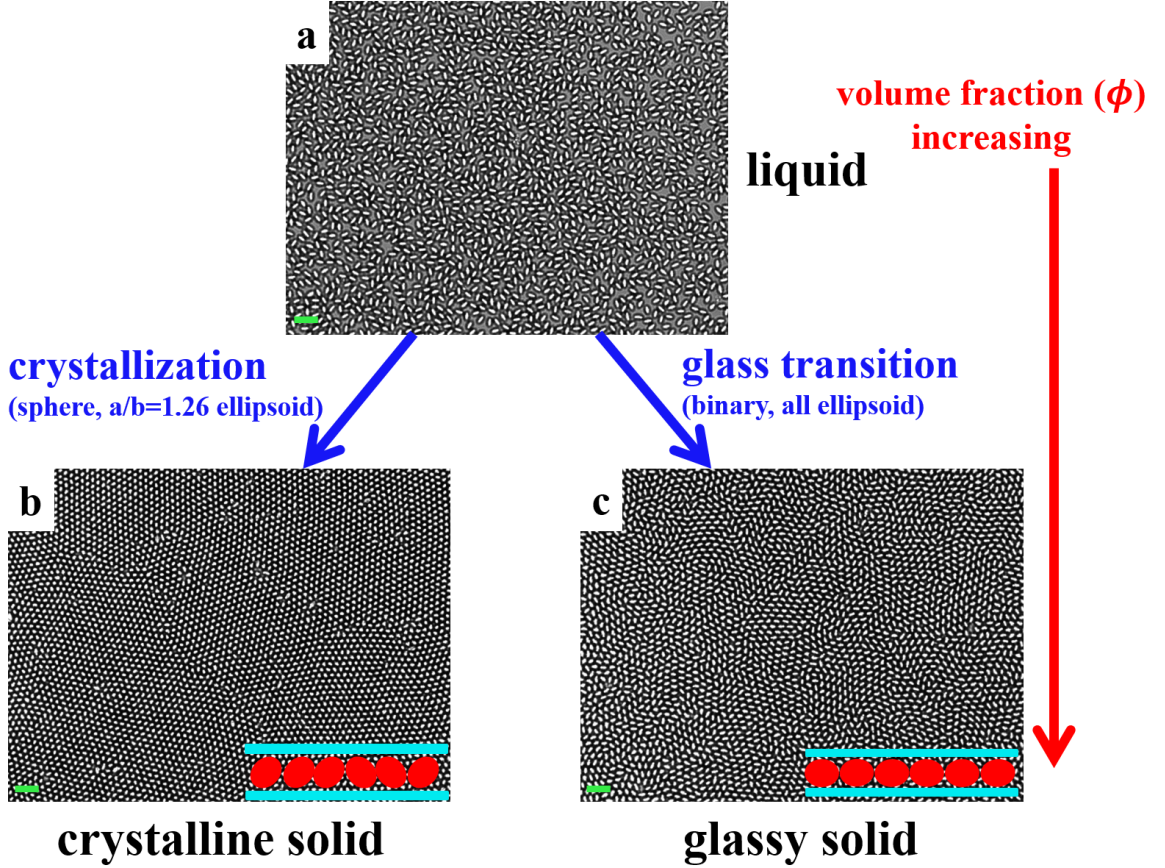


Supplementary Fig. 1: Contrast images of ellipsoids for particle tracking (**a-g**) and images that reflect the true aspect ratios of the particles (**h-n**). The scale bar is 3 μm .

The aspect ratios of the ellipsoids were calculated as follows. If the length of the PVA film was elongated by a factor of q , the long axis of the ellipsoid became $a = q\sigma$, where σ is the diameter of the spherical particles. The short axis b of the ellipsoid was then calculated using the fact that the volume of a particle was conserved before and after the stretching; that is, $\frac{4}{3}\pi(\sigma/2)^3 = \frac{4}{3}\pi(a/2)(b/2)^2$. The aspect ratio of the ellipsoids was then $p = a/b$.

The images of ellipsoids that are optimal for particle tracking (Supplementary Fig. 1a-g) differ from the images that accurately show the aspect ratios of the particles (lower panel of

Supplementary Fig. 1h-n). In our experiments, we adopted the images in the upper panel of Supplementary Fig. 1 for the purpose of image processing. Therefore, the ellipsoids in the raw images appear to have higher aspect ratios than their true values. The choice does not affect the precision of the mass-to-center positions and the angles calculated by the imaging tracking algorithm widely adopted in Supplementary Ref. [2–4].



Supplementary Fig. 2: Kinetic pathways of liquids upon cooling. As the volume fraction increases, a liquid in **a** either crystallises into **b** or transforms into a amorphous state in **c** via a glass transition. The scale bar is $10\ \mu\text{m}$.

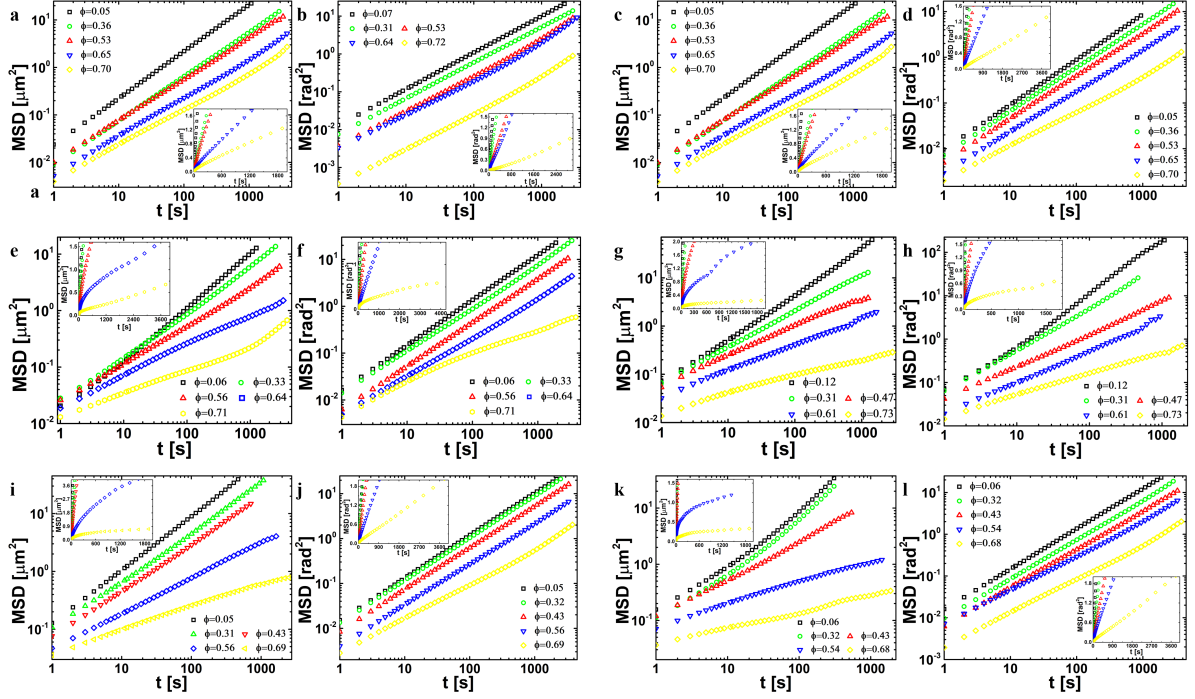
For binary spherical systems, we mixed $2.08\ \mu\text{m}$ and $2.74\ \mu\text{m}$ PMMA spheres with number ratio of 0.55 : 0.45. The ratio was chosen based on the standard Kob-Anderson model [5] and was proverbially chosen in colloidal experiments [6]. To ensure the homogeneous mixture of two types of spheres, we shook the sample for 1 min and horizontally settled it for 4 hours on the objective stage before recording data.

As discussed in the main text, a $p = 1.26$ ellipsoid (Fig. 2d) was able to take either the c-path (Fig. S2a, c) or g-path (Fig. S2a, d), depending on the separation of the two glass walls. For monolayer colloidal samples, the wall separation, h , usually satisfied the condition $b < h < 1.2b$, where b denotes the short axis of particles in the ellipsoidal systems. When h was close to b , the ellipsoids were strictly confined in the xy-plane (inset of Supplementary Fig. 2c). As ϕ increased, the incompatible motif ruined crystal symmetries. The formation of liquid crystal phases was also avoided due to higher charge density at the steeple of the particles [7]. When h approached to $1.2b$, however, the system had free space in which the ellipsoids tilted slightly in the z-direction (inset of Supplementary Fig. 2b). Consequently, under high ϕ , the additional rotational entropy in the z-direction tended to drive the system into the rotator phase [8], as illustrated in Supplementary Fig. 2b. Note that the $p = 1.26$ ellipsoids in Supplementary Fig. 2b appear smaller and more like spherical particles compared with those shown in Supplementary Fig. 2c because what we observed is illustrated as a xy-cross-section of tilted ellipsoids in Supplementary Fig. 2b. This observation clearly demonstrates that the ellipsoids were indeed tilted in the z-direction when both h and ϕ were relatively high.

Because the diffusion coefficients at low ϕ were sensitive to the separation between the glass walls, we recorded data for all area fractions within the same sample. To achieve this, we tilted the monolayers by a small angle of 0.5° . After equilibration for weeks, the sedimentation-diffusion equilibrium was well established [9]. Particle density was homogeneous within the field of view and no drift or flow was observed during the experiment period.

To obtain the diffusion coefficient, we first calculated the mean square displacement (MSD), $\Delta r^2(t) = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$, where $\mathbf{r}(t)$ and $\mathbf{r}(0)$ are the particles' positions at time t and 0 respectively and $\langle \rangle$ means the ensemble average. In accordance with previous 2D colloidal experiments [10], we found the particle movement was significantly caged in middle time scale (deviation of MSD from linear form in Supplementary Fig. 3) but eventually jump out of the cage in long time. We therefore fitted the MSD data in large time region into linear form and used the slope as the diffusion constant in the main text. The standard deviation of the fitted slope (scaled by D_0) served as the error of the diffusion coefficient in Fig. 2 and Supplementary Fig. 8.

The dramatic difference between the kinetic slowing down in translational and rotational

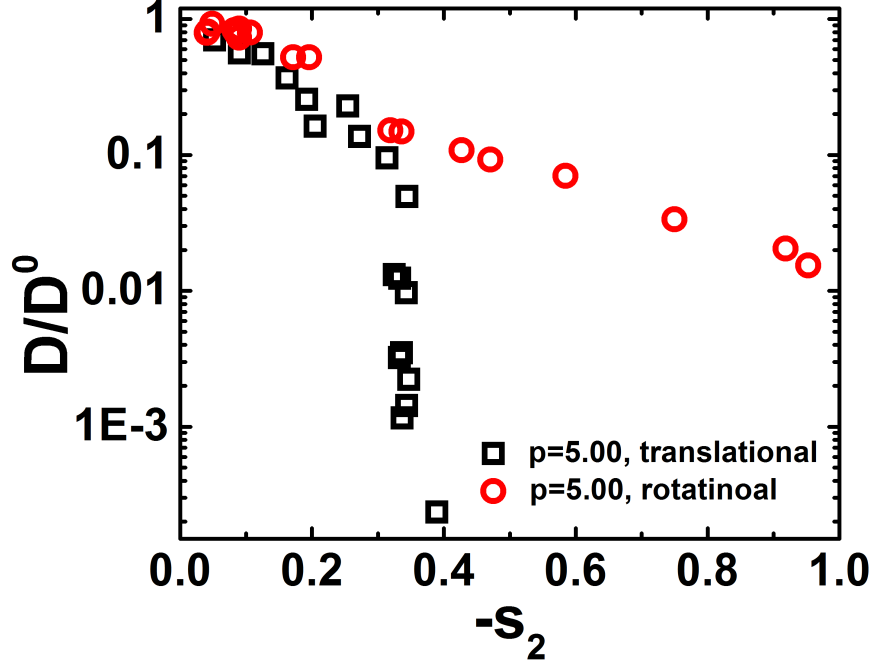


Supplementary Fig. 3: Mean square displacement in translational (**a**, $p = 1.60$, **c**, $p = 1.84$, **e**, $p = 2.68$, **g**, $p = 3.72$, **i**, $p = 5.00$ and **k**, $p = 7.06$ ellipsoids) and rotational (**b**, $p = 1.60$, **d**, $p = 1.84$, **f**, $p = 2.68$, **h**, $p = 3.72$, **j**, $p = 5.00$ and **l**, $p = 7.06$ ellipsoids) degrees of freedom in log-log scale. The **insets** are same data in linear scale.

motion can be more clearly exhibited by plotting the $D^T - s_2^T$ and $D^\theta - s_2^\theta$ together. As shown in Supplementary Fig. 4, the data points of $p = 5.00$ ellipsoids almost formed a straight line in semi-log plot for rotational degree of freedom, suggesting the exponential scaling was valid in the whole region with ϕ up to 0.64. While in the translational data, D^T started steeping down after $\phi_T = 0.25$. Why translation and rotation chose so distinct kinetic pathway for the slowing down remains to be explored in more details.

Supplementary Note 2: Dynamical heterogeneity and ϕ_T

In the main text of the article, we argue that the turning point of $D^T - s_2^T$ scaling was irrelevant to the dynamical heterogeneity (DH) by comparing the turning point (ϕ_T) with the onset of DH. We found that for ellipsoids with $p = 1.84, 2.68, 3.72, 5.00, 7.06$, ϕ_T was too small for any cluster to form within the system (Fig. 3). It can be simply judged from

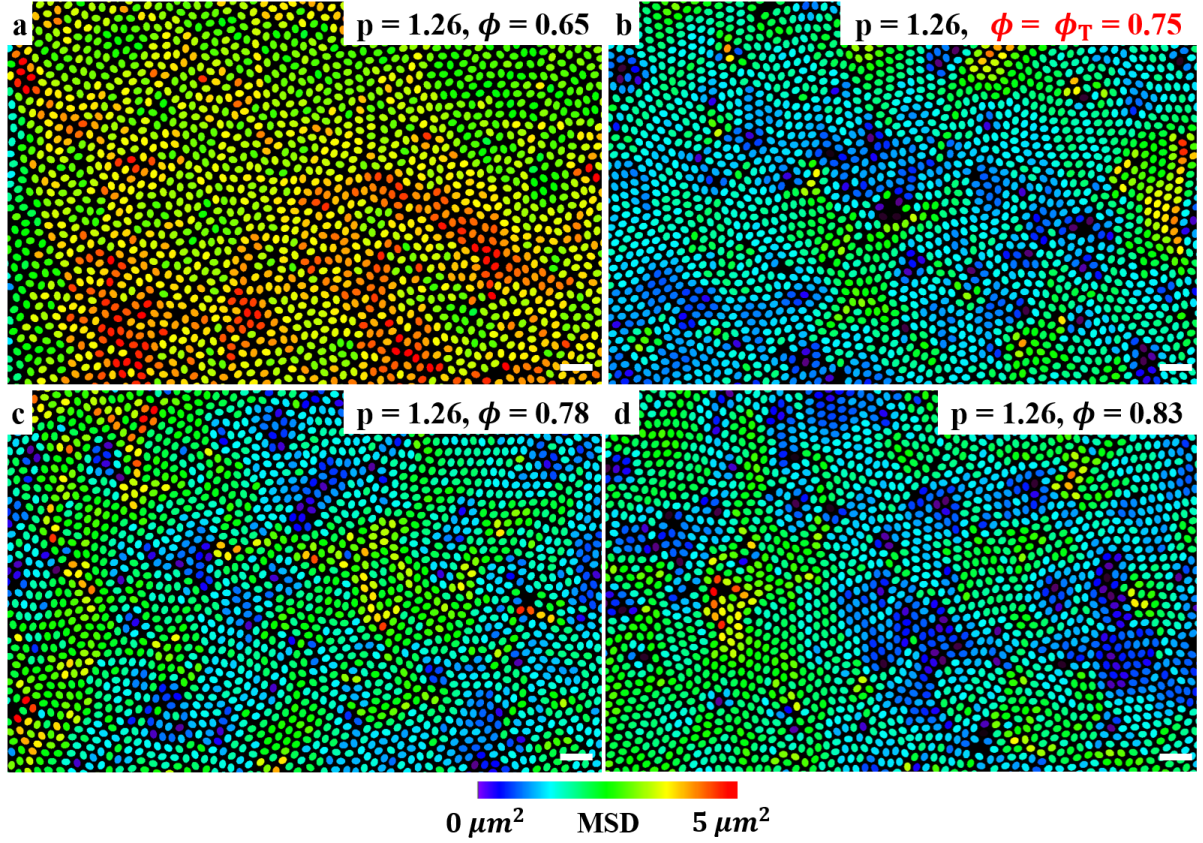


Supplementary Fig. 4: The diffusion coefficient of $p = 5.00$ ellipsoids as a function of two-body excess entropy in both translational and rotational degrees of freedom.

the raw images (Fig. 3d-h) that DH was not able to cause the turning in $D^T - s_2^T$ scaling in these systems. However, because ϕ_T values for binary and ellipsoids with $p = 1.26, 1.60$ were relatively high ($\phi_T = 0.72, 0.75$, and 0.53 , respectively), more analysis is required to rule out the role DH might have played in the turning of $D^T - s_2^T$ scaling in these three systems. Therefore, here, we discuss the relationship between DH and turning in $D^T - s_2^T$ scaling.

For $p = 1.26$ ellipsoids, DH occurred before the turning of $D^T - s_2^T$ scaling. At $\phi = 0.65$, particles with fast translational motion started to cluster and separated from slow particles in real space (Supplementary Fig. 5a). The length scale of the separated clusters grew observably with ϕ thereafter (Supplementary Fig. 5b-d). At $\phi_T = 0.75$, when the $D^T - s_2^T$ scaling had broken down, the characteristics of DH were unambiguously observable throughout the whole system (Supplementary Fig. 5b). Therefore, the occurrence of DH cannot have been responsible for the turning of $D^T - s_2^T$ scaling in $p = 1.26$ ellipsoids.

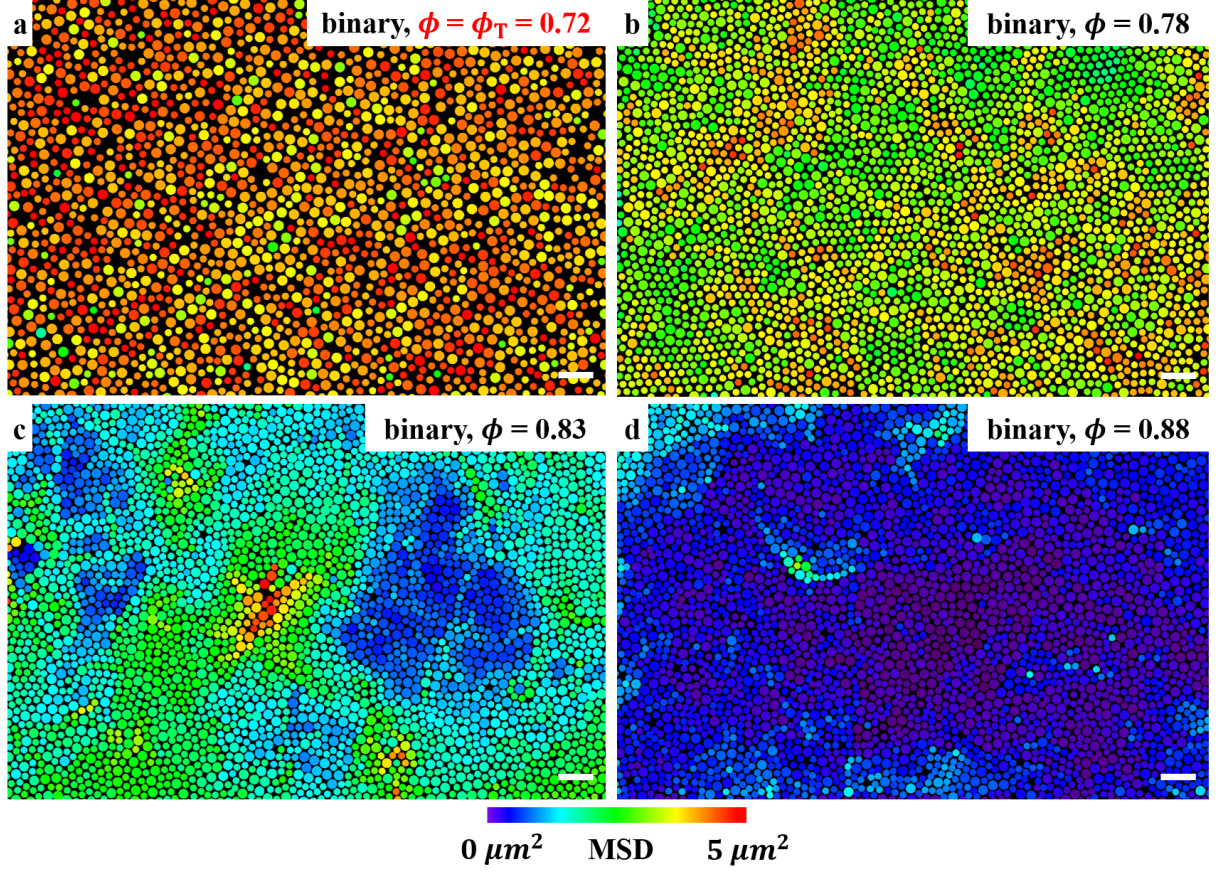
For binary spheres and $p = 1.60$ ellipsoids, DH occurred later than the turning of $D^T - s_2^T$ scaling. At ϕ_T , the distribution of particle mobility was completely homogeneous for both



Supplementary Fig. 5: Dynamical heterogeneity of $p = 1.26$ ellipsoids under **a** $\phi = 0.65$, **b** $\phi = \phi_T = 0.75$, **c** $\phi = 0.78$ and **d** $\phi = 0.83$. The color represents the value of the mean square displacement of a particle during 500 s. The scale bar is 10 μm .

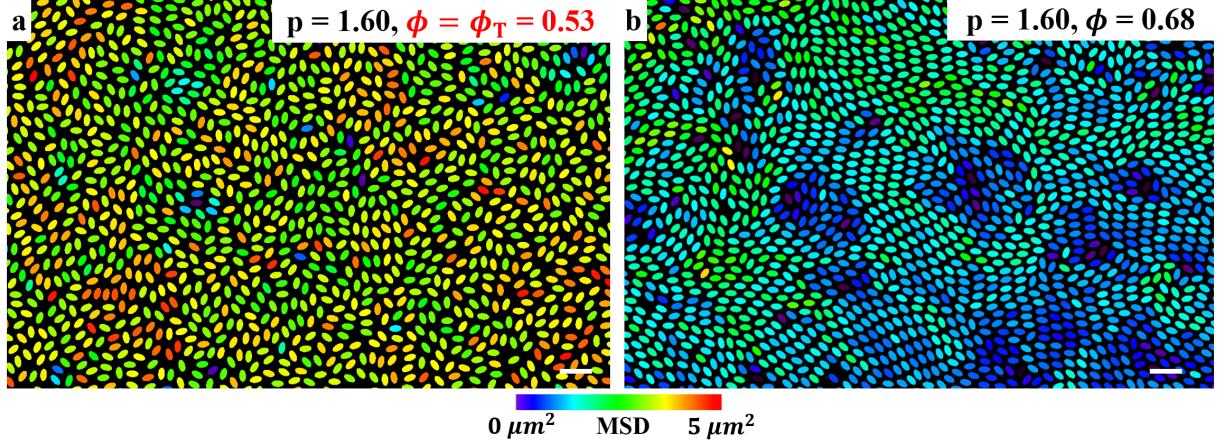
systems (Supplementary Figs. 6a, 7a). DH did not occur until the area fractions were more than 10% higher than ϕ_T (Supplementary Figs. 6b-d, 7b). Therefore, the DH played no role in the turning of $D^T - s_2^T$ scaling for either binary spheres or $p = 1.60$ ellipsoids.

An immediate consequence of DH is the breakdown of the Stokes-Einstein (SE) relation $D^T = k_B T / 6\pi\eta a$ [11], which has been proven to be a hallmark of simple liquids [12, 13]. The superscript T denotes the translational degree of freedom, a is the particle radius, and $k_B T$ is the thermal energy. Because the viscosity η is always proportional to the relaxation time τ_α of the system, it is expected that D^T is proportional to τ_α^{-1} if the dynamics of the system is homogeneous. It was reported from both a simulation [12] and a colloidal experiment [13] that onset of DH was directly associated with the breakdown of the SE relation.

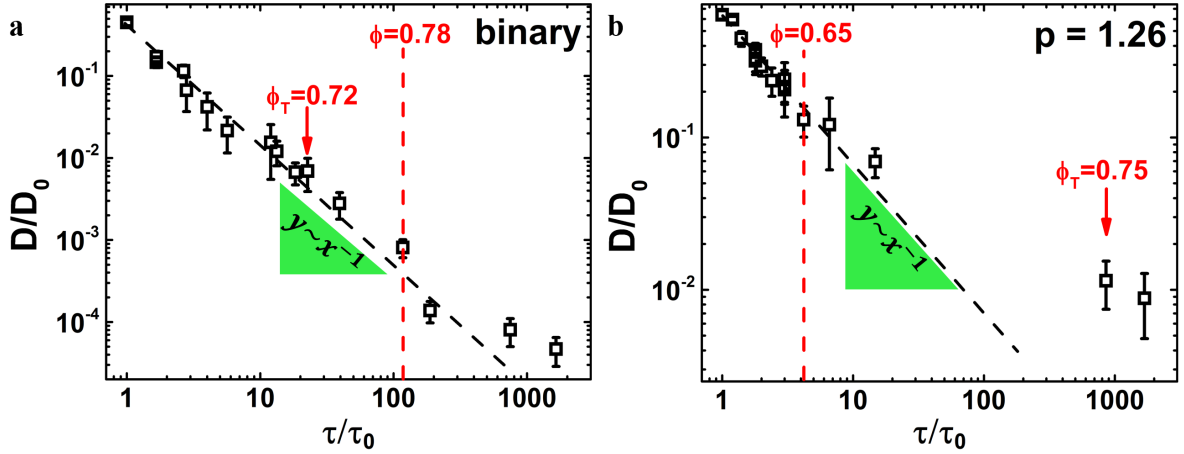


Supplementary Fig. 6: Dynamical heterogeneity of binary spheres under **a** $\phi = \phi_T = 0.72$, **b** $\phi = 0.78$, **c** $\phi = 0.83$, and **d** $\phi = 0.88$. The color represents the value of the mean square displacement of a particle during 500 s. The scale bar is 10 μm .

To clarify the relation between onset of DH and the $D^T - s_2^T$ turning point, we investigated the SE relation in our glass-forming liquids; the results of binary spheres and $p = 1.26$ ellipsoids are presented in Supplementary Fig. 8. In accordance with the real space analysis (Supplementary Figs. 5, 6), we found that ϕ_T was smaller than the breakdown point of the SE relation for binary spheres (Supplementary Fig. 8a) and larger for $p = 1.26$ ellipsoids (Supplementary Fig. 8b). Through the same method, we found that for the other six ellipsoid systems, each ϕ_T was far lower than the breakdown point of the SE relation, or equivalently, the onset of DH. For direct comparison with Fig. 3, the raw images corresponding to the breakdown point of the SE relation are presented in Supplementary Fig. 9. Unambiguously, ϕ_T and ϕ_{DH} differed substantially from each other.

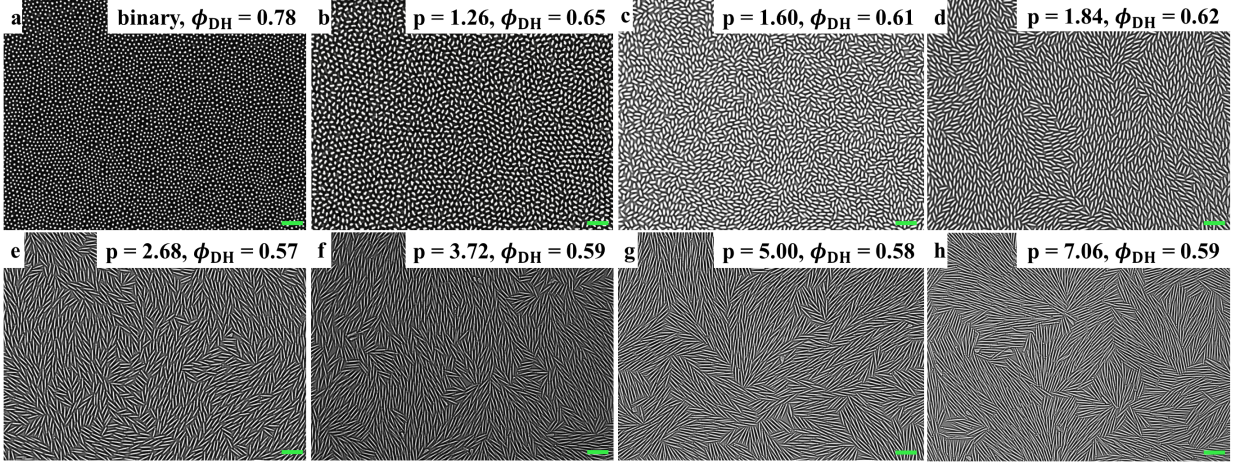


Supplementary Fig. 7: Dynamical heterogeneity of $p = 1.60$ ellipsoids under **a** $\phi = \phi_T = 0.53$ and **b** $\phi = 0.68$. The color represents the value of the mean square displacement of a particle during 500 s. The scale bar is 10 μm .



Supplementary Fig. 8: Rescaled self-diffusion coefficient D/D_0 as a function of rescaled relaxation time $\tau_\alpha/\tau_\alpha^0$ for **a** binary spheres and **b** $p = 1.26$ ellipsoids. The dashed lines are fits of the data at low ϕ to the equation $y \sim x^{-1}$. The red arrows indicate the data point corresponding to the turning of $D^T - s_2^T$ scaling, ϕ_T . The vertical dashed lines indicate the onset of DH.

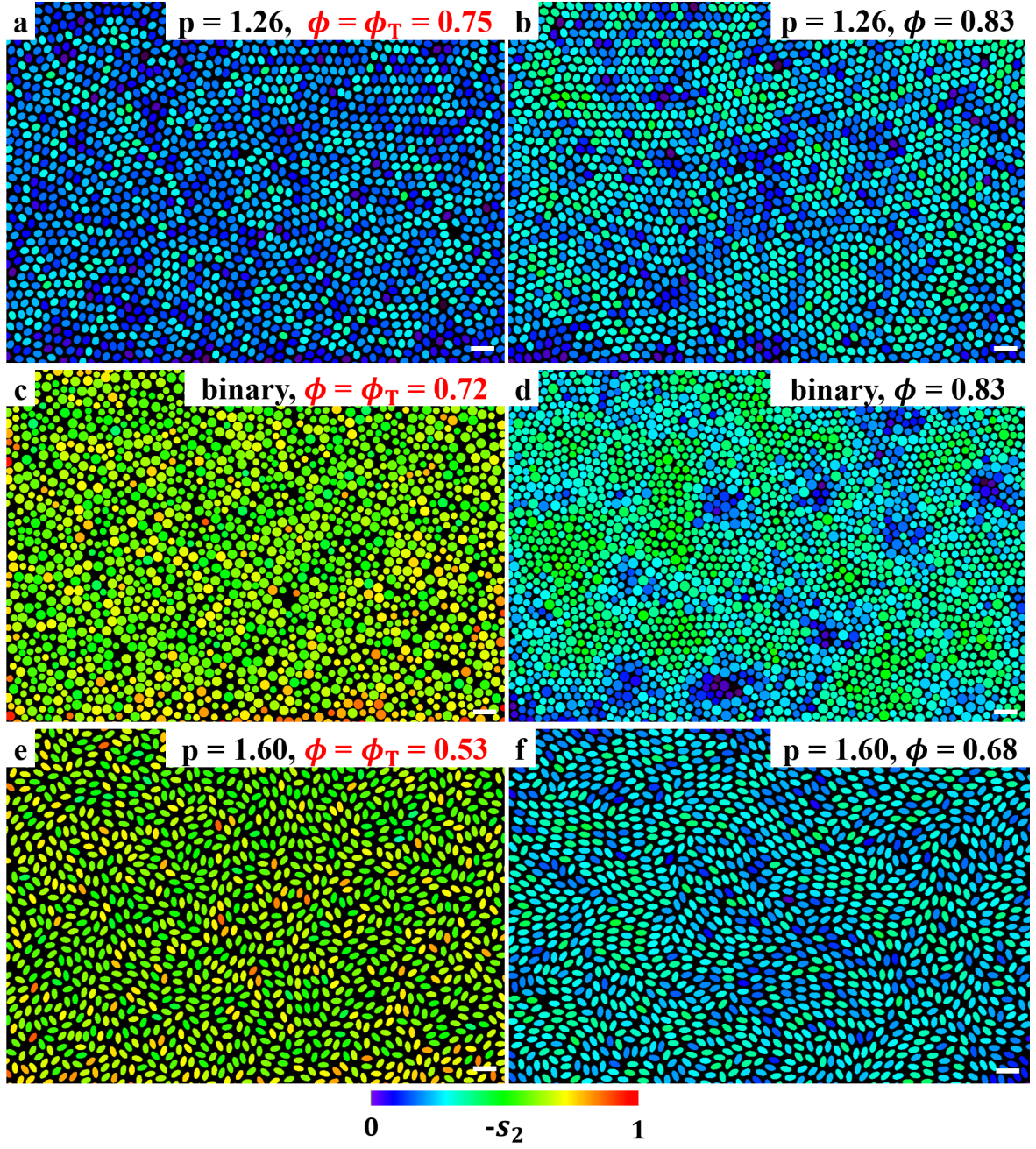
We further tested the spatial distribution of s_2^T for binary spheres and $p = 1.26$ and $p = 1.60$ ellipsoids. The distributions became highly heterogeneous at high values of ϕ (Supplementary Fig. 10); and in a manner similar to the case of DH, the s_2^T heterogeneity



Supplementary Fig. 9: Raw images at the breakdown points of the Stokes-Einstein relation. The area fractions (ϕ_{DH}) corresponding to the breakdown points are specified in each figure. The scale bar is $5 \mu\text{m}$.

(SH) was irrelevant to the $D^T - s_2^T$ turning because the distribution of s_2^T was still homogeneous at ϕ_T (Supplementary Fig. 10a, c, e). In accordance with previous observations [7, 14, 15], although the correlation between structural heterogeneity and DH existed over ϕ , their spatial correlation was weak in our experiments.

The analysis regarding DH and SH further strengthens the argument in the main text that DH is irrelevant to the turning of $D^T - s_2^T$ scaling. Majority of glass-forming liquids remained completely homogeneous in both dynamics and structure at ϕ_T . For the exception, $p = 1.26$ ellipsoids, both DH and SH were established before ϕ_T . As discussed in the main text, the slowing down of kinetics, in our observation, is directly controlled by the inherent structure of the system. A deep understanding of the turning thus requires a detailed description of the Φ -scape.

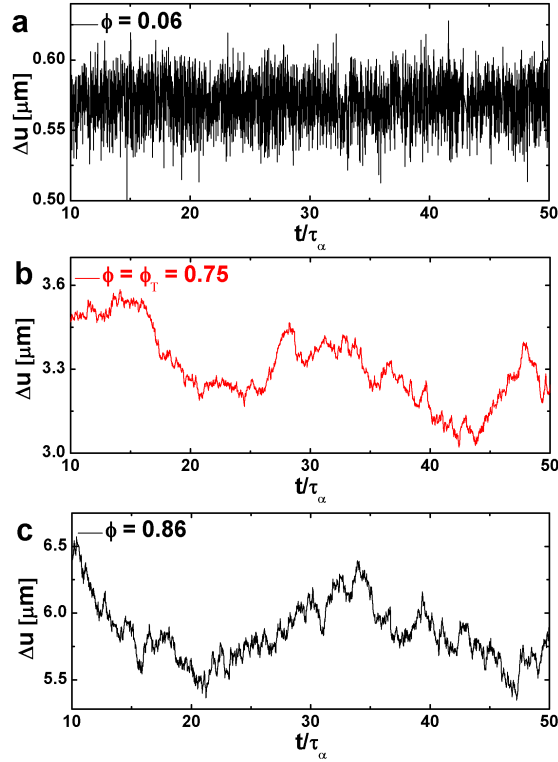


Supplementary Fig. 10: SH of **a**, **b** $p = 1.26$ ellipsoids, **c**, **d** binary spheres, and **e**, **f** $p = 1.60$ ellipsoids. The color represents the value of the excess entropy of a particle. The scale bar is $10 \mu\text{m}$.

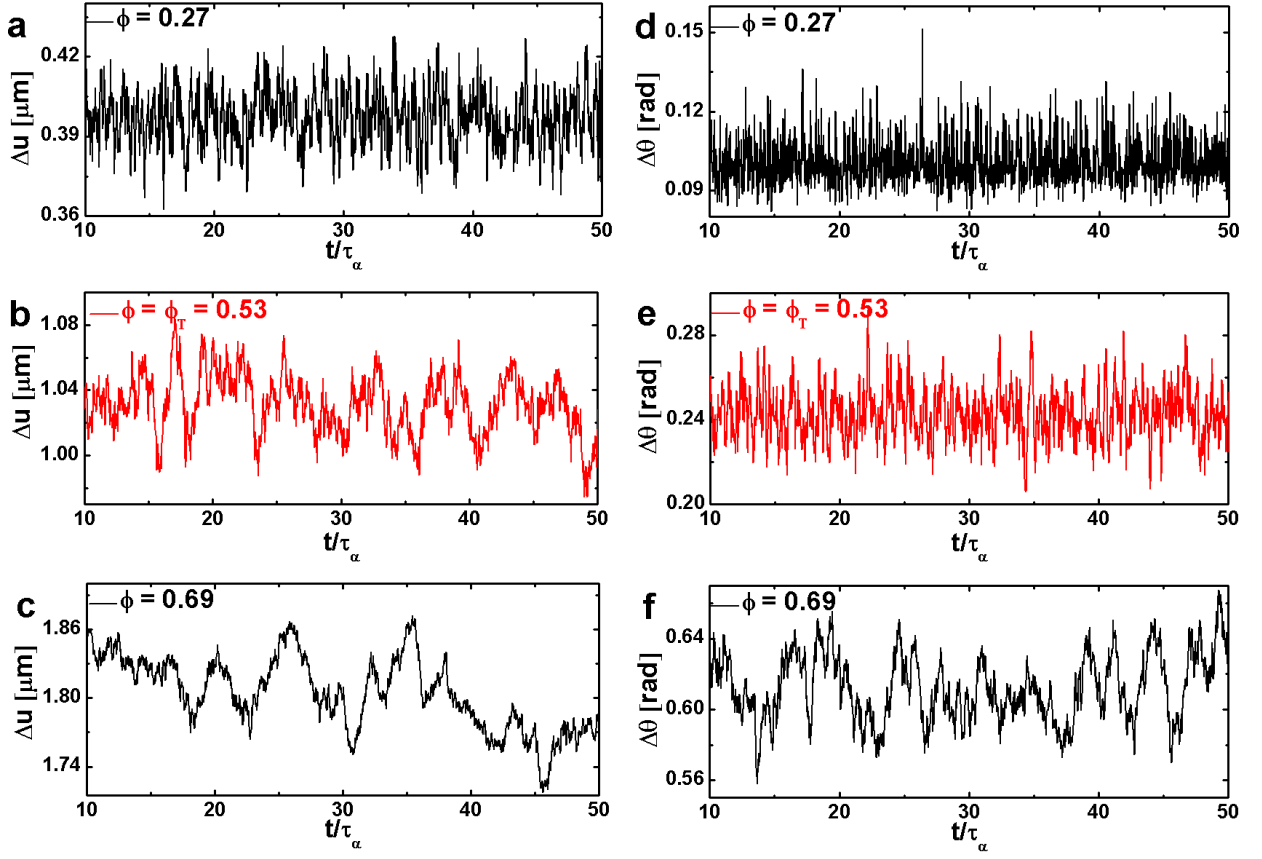
Supplementary Note 3: Φ -scape topography

In the main text, we report that the topography of the Φ -scape in translational motion

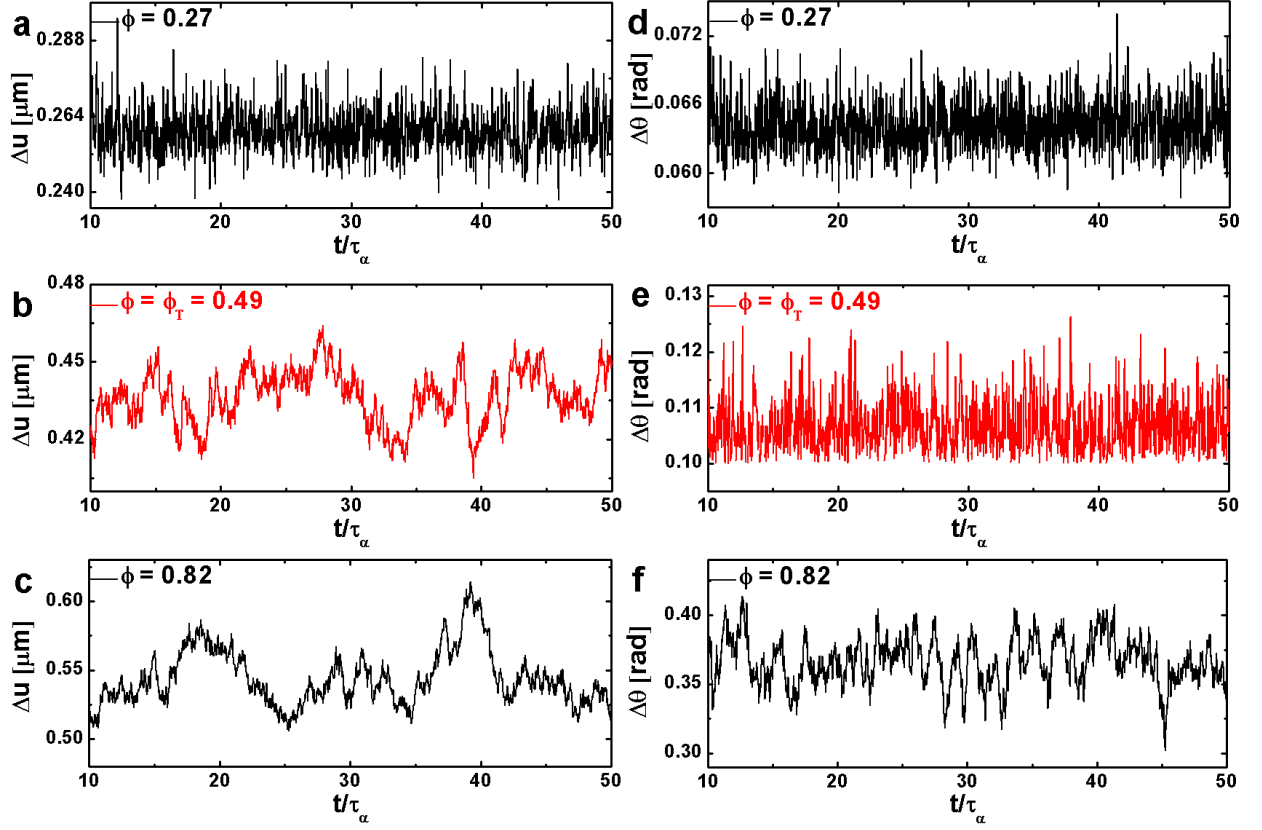
started to become rugged in the vicinity of ϕ_T for both $p = 5.00$ ellipsoids (Fig. 5a-c) and binary systems (Fig. 5g-i) whereas it remained smooth in rotational motion (Fig. 5d-f) for $p = 5.00$ ellipsoids. Based on this observation, it was concluded that the turning of $D^T - s_2^T$ scaling was caused by a change in the Φ -scape topography for translational motion. Here, we provide the translational and rotational Φ -scape topographies in mobility representation for all other ellipsoids (Supplementary Figs. 11-16). Without exception, the $D^T - s_2^T$ plot turned when the Φ -scape became rugged in translational motion. For rotational motion, no larger-scaled structures or basins were observed in the Φ -scape until area fractions were close to ϕ_g , which was consistent with the absence of turnings in the $D^\theta - s_2^\theta$ plots.



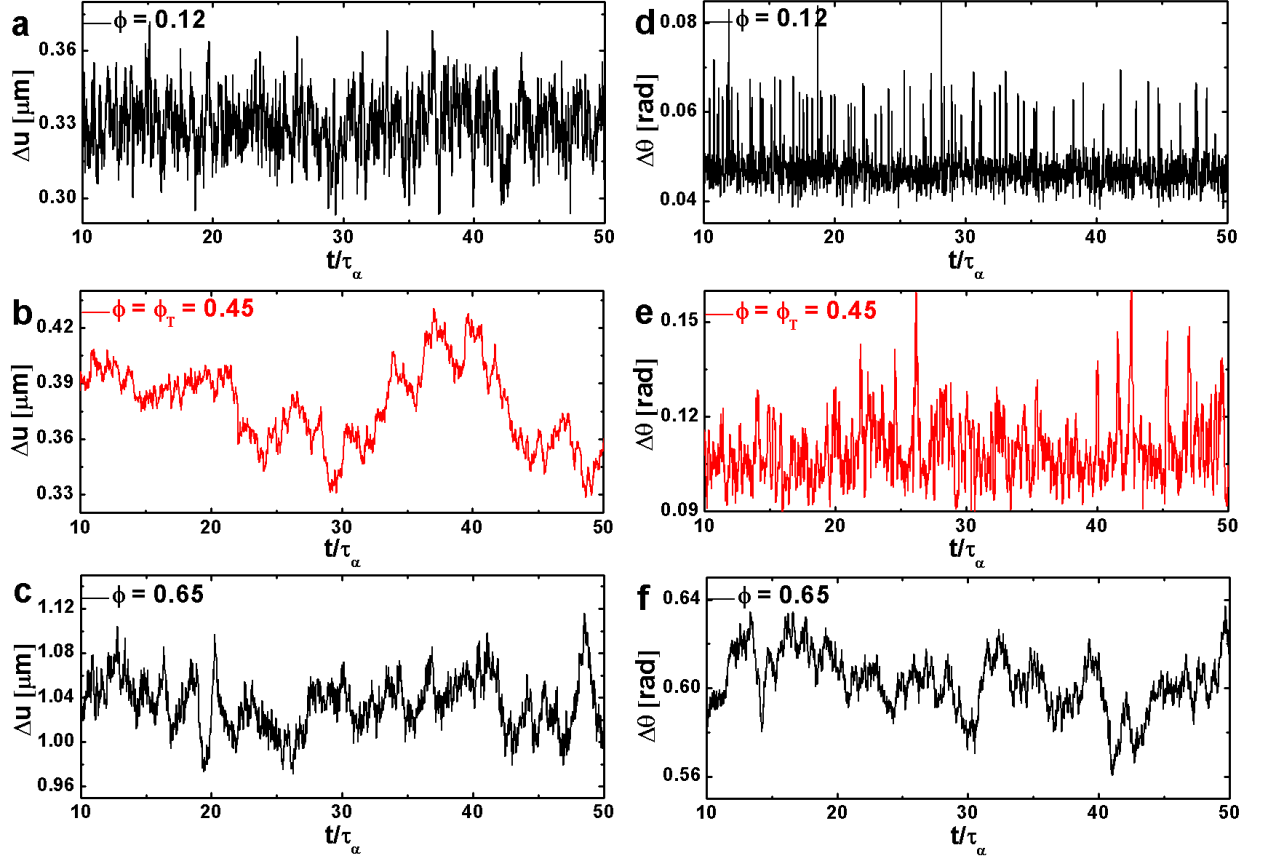
Supplementary Fig. 11: Topography of the Φ -scape in representation of particle mobility for $p = 1.26$ ellipsoid system. We chose **a**, $\phi = 0.06$, **b**, $\phi = \phi_T = 0.75$, and **c**, $\phi = 0.86$ samples and calculated the time evolution of their displacement, $\Delta u(t)$, during the relaxation time τ_α . τ_α was defined as the time at which the dynamical structure factor in Fig. 1a had decayed to $1/e$. The mobility in rotational motion is missing because, for $p = 1.26$ ellipsoid, the determination of particles' orientation was inaccurate when they slightly deviated from xy-plane.



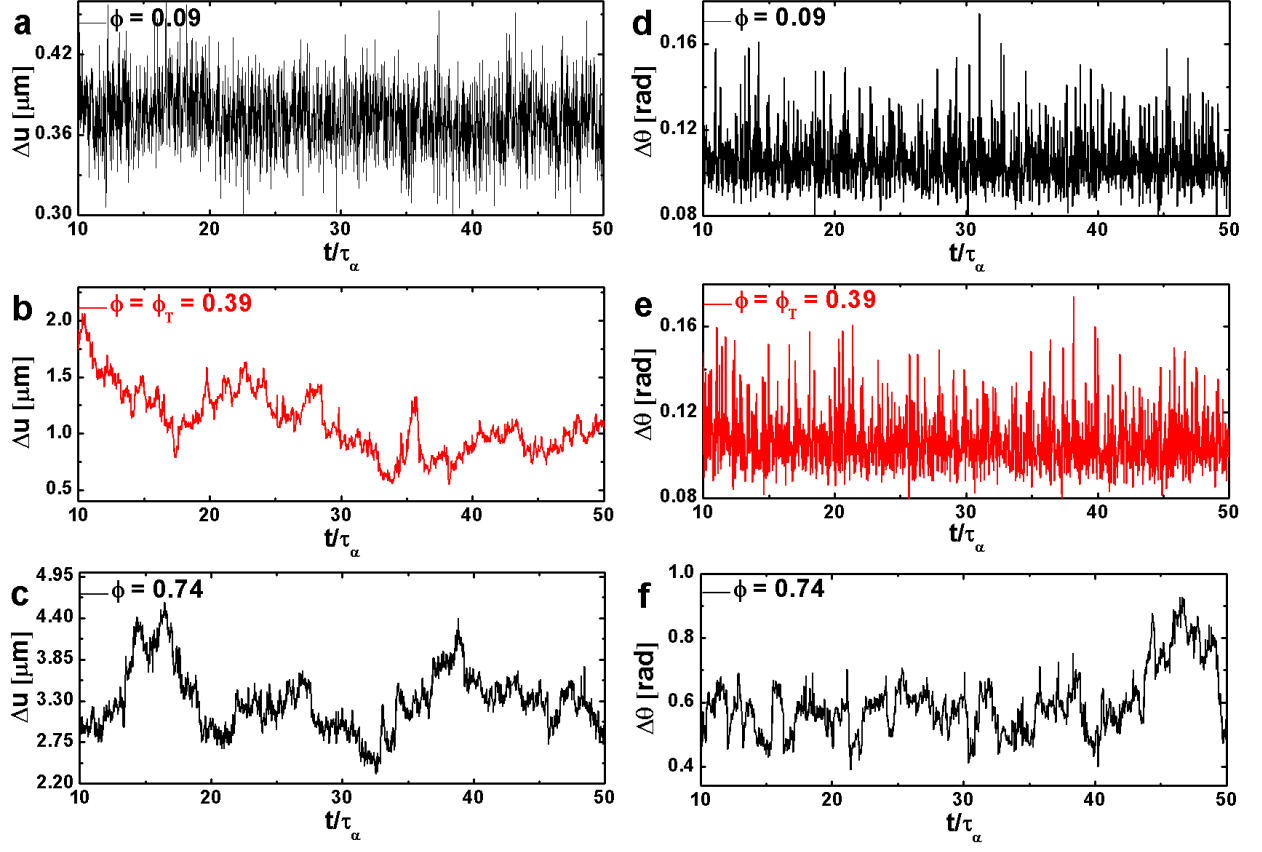
Supplementary Fig. 12: Topography of the Φ -scape in representation of particle mobility for $p = 1.60$ ellipsoid system. We chose **a**, $\phi = 0.27$, **b**, $\phi = \phi_T = 0.53$, and **c**, $\phi = 0.69$ samples and calculated the time evolution of their displacement, $\Delta u(t)$, during the relaxation time τ_α . **d-f**, The rotational mobility $\Delta\theta(t)$ under the same ϕ . τ_α was defined as the time at which the dynamical structure factor in Fig. 1a had decayed to $1/e$.



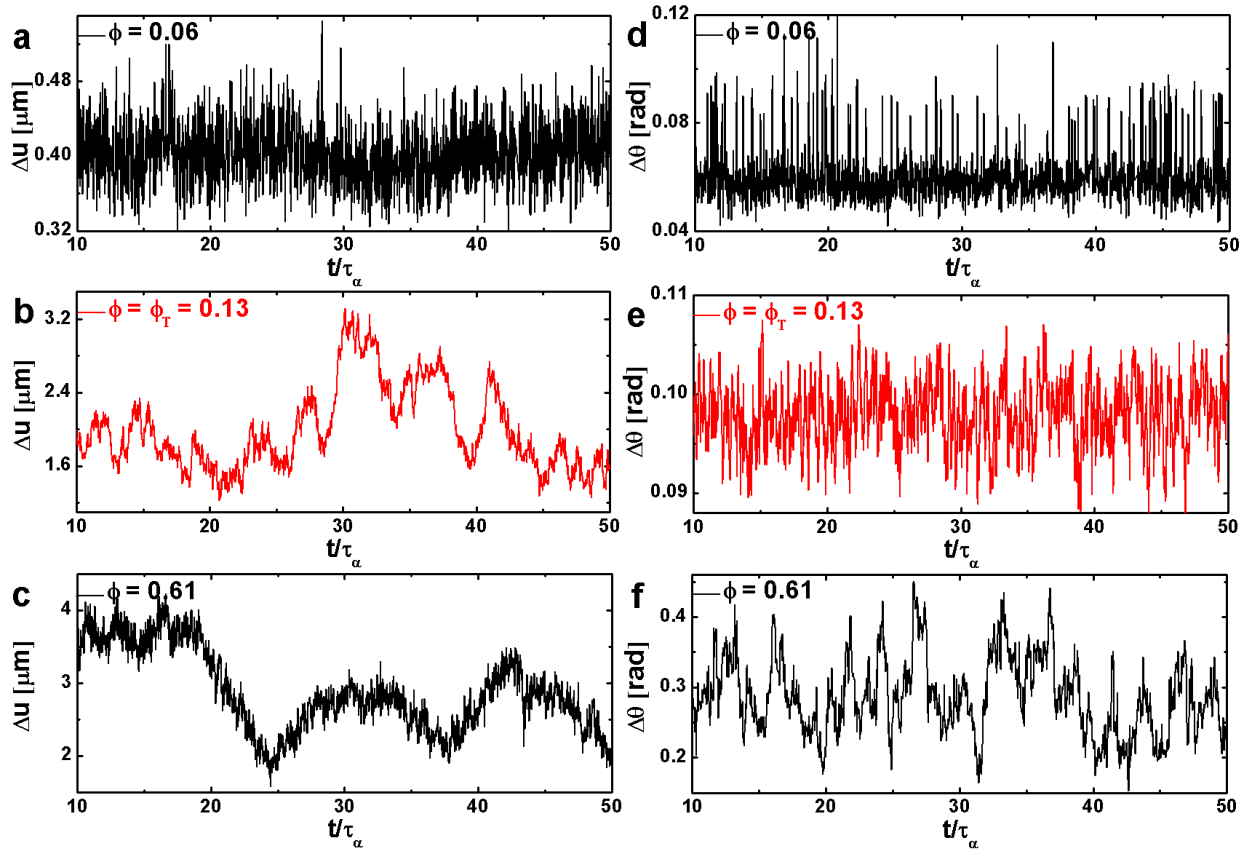
Supplementary Fig. 13: Topography of the Φ -scape in representation of particle mobility for $p = 1.84$ ellipsoid system. We chose **a**, $\phi = 0.27$, **b**, $\phi = \phi_T = 0.49$, and **c**, $\phi = 0.82$ samples and calculated the time evolution of their displacement, $\Delta u(t)$, during the relaxation time τ_α . **d-f**, The rotational mobility $\Delta\theta(t)$ under same ϕ . τ_α was defined as the time when the dynamical structure factor in Fig. 1a had decayed to $1/e$.



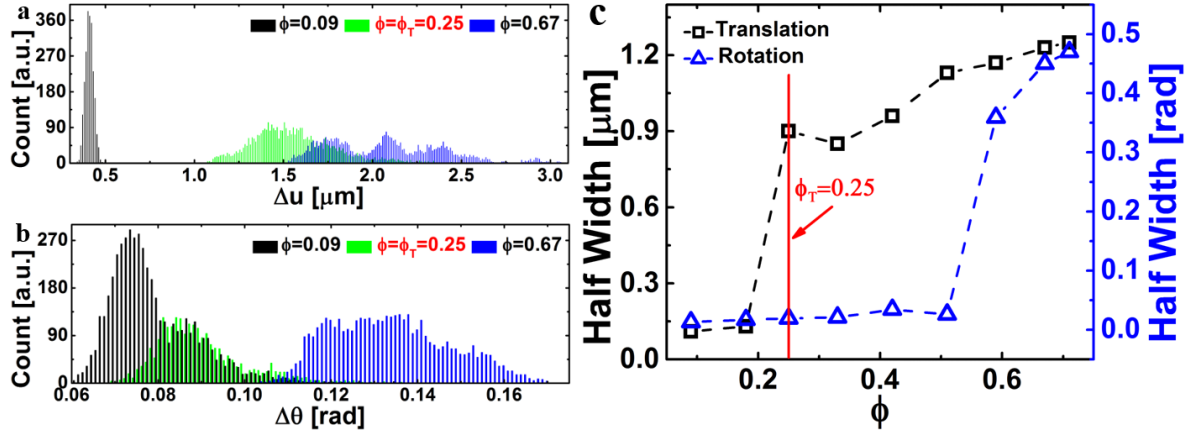
Supplementary Fig. 14: Topography of the Φ -scape in representation of particle mobility for $p = 2.68$ ellipsoid system. We chose **a**, $\phi = 0.12$, **b**, $\phi = \phi_T = 0.45$, and **c**, $\phi = 0.65$ samples and calculated the time evolution of their displacement, $\Delta u(t)$, during the relaxation time τ_α . **d-f**, The rotational mobility $\Delta\theta(t)$ under same ϕ . τ_α was defined as the time when the dynamical structure factor in Fig. 1a had decayed to $1/e$.



Supplementary Fig. 15: Topography of the Φ -scape in representation of particle mobility for $p = 3.72$ ellipsoid system. We chose **a**, $\phi = 0.09$, **b**, $\phi = \phi_T = 0.39$, and **c**, $\phi = 0.74$ samples and calculated the time evolution of their displacement, $\Delta u(t)$, during the relaxation time τ_α . **d-f**, The rotational mobility $\Delta\theta(t)$ under same ϕ . τ_α was defined as the time when the dynamical structure factor in Fig. 1a had decayed to $1/e$.



Supplementary Fig. 16: Topography of the Φ -scape in representation of particle mobility for $p = 7.06$ ellipsoid system. We chose **a**, $\phi = 0.06$, **b**, $\phi = \phi_T = 0.13$, and **c**, $\phi = 0.61$ samples and calculated the time evolution of their displacement, $\Delta u(t)$, during the relaxation time τ_α . **d-f**, The rotational mobility $\Delta\theta(t)$ under same ϕ . τ_α was defined as the time when the dynamical structure factor in Fig. 1a had decayed to $1/e$.

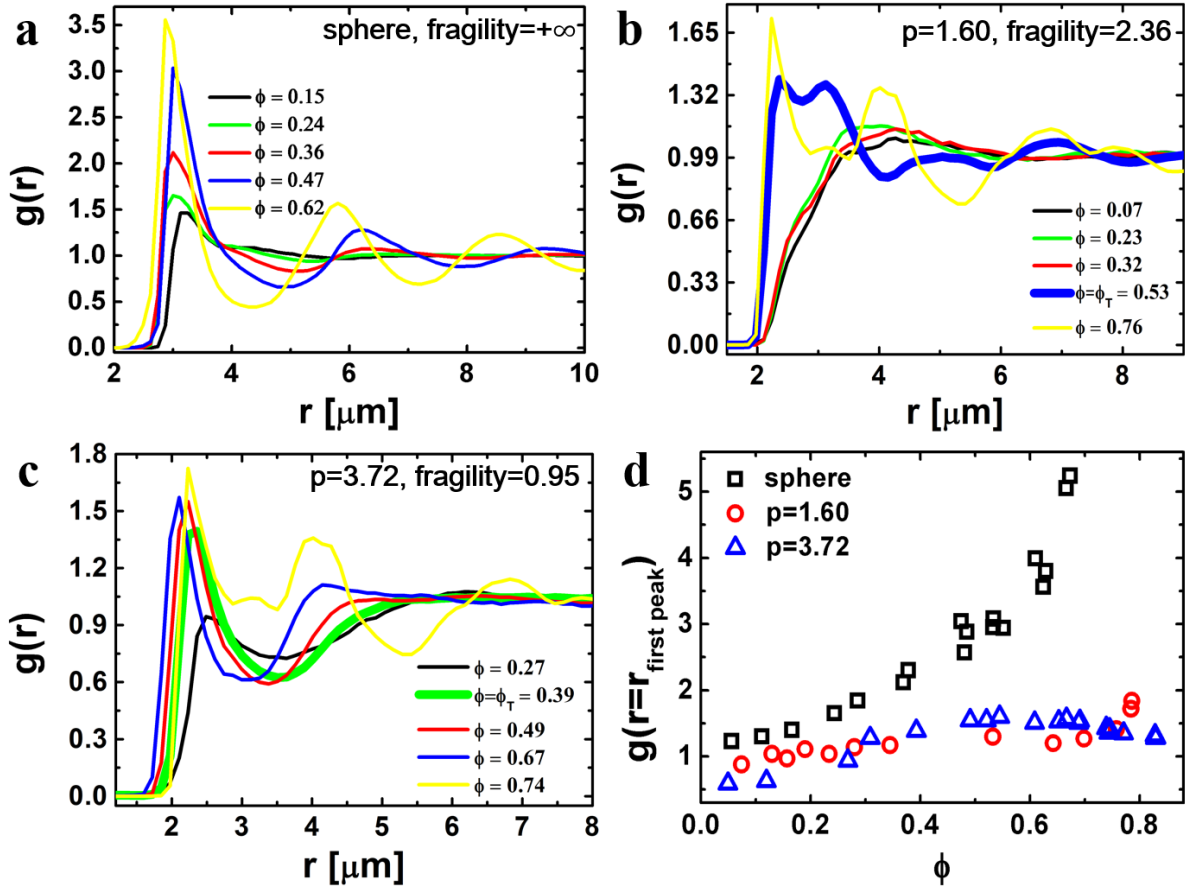


Supplementary Fig. 17: The probability distribution of the mobility in **a** translational and **b** rotational degrees of freedom for $p = 5.00$ ellipsoid system; corresponding to Fig. 5a-f in the main text. **c**, the half width of the distribution in **a**, **b** as a function of ϕ .

To be more quantitative, we calculated the probability distribution function (PDF) of mobility and the half width of it as a function of ϕ (Supplementary Fig. 17). For translational motion (Fig. 5a-c and Supplementary Fig. 17a), the PDF at ϕ_T was significantly broadened and shifted to much larger mean value; while for rotational motion (Fig. 5d-f and Supplementary Fig. 17b), the PDF at ϕ_T was still the form of the low density sample. The sudden jump of half width (Supplementary Fig. 17c) defined a new point, at which the FEL became rugged. As clearly shown in Supplementary Fig. 17c, this point matched well with ϕ_T for translational motion while it was much larger than ϕ_T in rotational motion. These observations strengthen our conclusion in the main text that rugged FEL had deep connection with the turning we observed; and thus strongly influenced the kinetic pathway towards glass transition.

Supplementary Note 4: More discussion on the relaxation

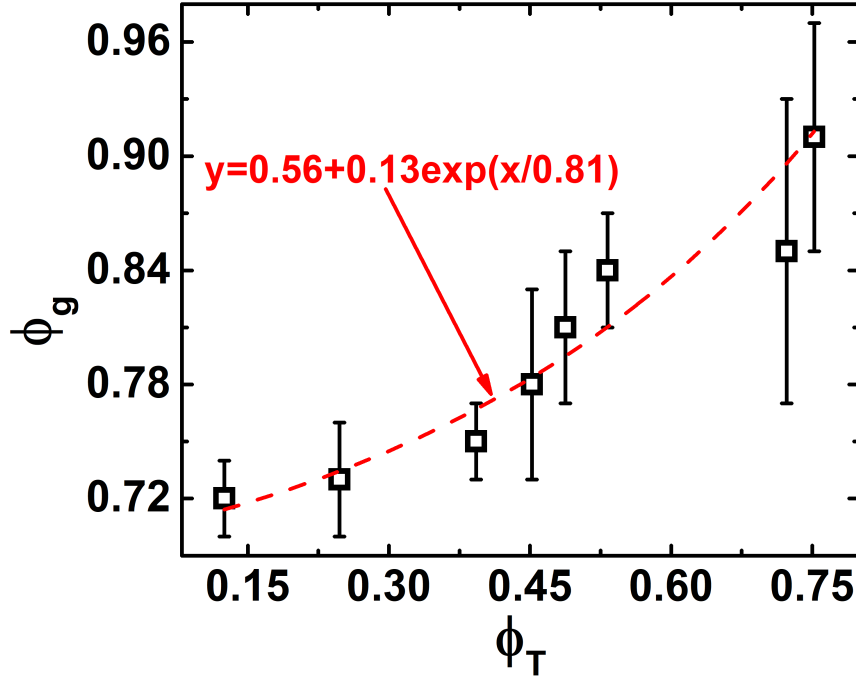
The distinction between strong and fragile liquids can be vividly appreciated from their structures, because liquid structure reacts to cooling in a manner that is dependent on the liquid's fragility. For a strong liquid, cooling can not alter the structure considerably [16]. As a result, the radial distribution functions of a strong liquid at high ϕ remained similar to that at low ϕ (Supplementary Fig. 18c); this differed from the case of fragile liquids



Supplementary Fig. 18: Radial distribution function $g(r)$ for **a** sphere, **b** $p = 1.60$ ellipsoid, and **c** $p = 3.72$ ellipsoid systems. **d**, first peak value of $g(r)$ as a function of ϕ . The bold curves in **b**, **c** represent $g(r)$ at ϕ_T .

(Supplementary Fig. 18a, b). The evolution of the first $g(r)$ peak value (Supplementary Fig. 18d) quantitatively demonstrates this difference. For the strong liquid, containing $p = 3.72$ ellipsoids, the fragility of which was smaller than 1, the value of $g(r = r_{\text{first peak}})$ even slightly decreased with ϕ in the high-density region. For spherical system, $g(r = r_{\text{first peak}})$ increased dramatically as ϕ approached ϕ_m . Note that after the melting point, $\phi_m (< \phi_g)$, the system crystalised and the relaxation time jumped to infinity. Therefore, we can conclude that the structure of a c-path liquid is much more sensitive to the cooling process than that of a g-path liquid.

We found that ϕ_g and ϕ_T had a one-to-one relationship in the form of stretched expo-



Supplementary Fig. 19: ϕ_g as a function of ϕ_T . The error was the standard deviation of the fitted ϕ , at which the relation time diverged.

nential (Supplementary Fig. 19). This indicated that ϕ_g somehow scaled with ϕ_T . Since previous simulation showed ϕ_g also scaled with the jamming packing fraction (ϕ_J) [17, 18], it's reasonable to expect that the turning also has some relation with the jamming transition. Therefore, the connection among behaviours at various time and length scales, i.e. liquid, glass and jammed states, raised to be an interesting open question.

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