

Fragility of two-dimensional binary soft disk suspensions with large size ratios

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We simulate a binary soft disk system in two dimensions, and investigate how the dynamics slow as the area fraction is increased toward the glass transition. The “fragility” quantifies how sensitively the relaxation time scale depends on the area fraction, and the fragility strongly depends on the composition of the mixture. We confirm prior results for mixtures of particles with similar sizes, where the ability to form small crystalline regions correlates with fragility. However, for mixtures with particle size ratios above 1.4, we find fragility is not correlated with structural ordering, but rather with the spatial character of heterogeneous dynamics.

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Many liquids form glasses if they are cooled rapidly, and glassy materials have technological applications such as optical fibers and plastic materials [1, 2, 3]. However, the origin of the glass transition is still unclear. Upon approaching the glass transition, the structural relaxation time (τ_α) increases by several orders of magnitude without a corresponding growing static correlation length. The rate of this increase of τ_α is called “fragility” and depends on the material [1, 2, 3]. For “fragile” glass-formers, τ_α steeply increases for a small decrease in temperature, while for “strong” glass-formers, a similar increase of τ_α requires a larger decrease in temperature. The relaxation time is related to the viscosity, and thus the fragility is an important factor when processing glass-forming materials. Typically it is desirable to mold a glass-forming material with the viscosity held within a certain range; for fragile materials, this may correspond to a restrictively narrow range of temperature. Fragility also correlates with other properties of glass-forming materials [2]. For example, many fragile liquids exhibit dynamical heterogeneity, where different regions have different local relaxation rates [4]. Furthermore, fragility is connected with liquid-liquid transitions, another unsolved phenomenon. For example, in triphenyl phosphite, the fragility changes during the transformation from one liquid to another [5].

Fragility has been experimentally investigated in many liquids, but a clear understanding is hindered by the complexity of real materials. Numerical simulations with simple intermolecular interactions enable study of factors controlling fragility [6, 7, 8, 9]. Some simulations show that liquids become less fragile when the polydispersity increases (or a larger size ratio for binary mixtures is used) [7, 8, 9]. In 2D systems, it is observed that small regions with hexagonal order can form which correspond with larger values of τ_α , and thus increasing the polydispersity frustrates formation of these ordered regions and diminishes the fragility [7].

However, prior work focused on binary mixtures with size ratios close to 1, or with moderately small polydispersity. For larger size ratios, it is not as obvious that

local ordering is a useful concept. Furthermore, binary mixtures with large size ratios have complex phase diagrams [10] and have new features such as an effective depletion interaction between large particles [11]. It is plausible that the glass transition in large size ratio binary systems may be quite different from that of small size ratio systems. In this manuscript, we study the fragility of binary soft disk mixtures with various size ratios and area fraction ratios. We show that local structural arrangements are not significant for large size ratio systems. Instead, our data suggest that the large particles act as confining walls for the smaller particles, and that confinement effects increase the fragility of such systems by suppressing dynamical heterogeneity.

We perform Brownian dynamics simulations for binary mixtures composed of soft disk components L and S which correspond to large and small particles. The particles interact via the purely repulsive Weeks-Chandler-Andersen potential [12]; $U_{ij}=4\epsilon[(\sigma_{ij}/r)^{12}-(\sigma_{ij}/r)^6+1/4]$ for $r < 2^{1/6}\sigma_{ij}$, otherwise $U_{ij}=0$, where $\sigma_{ij}=(\sigma_i+\sigma_j)/2$ and $i, j \in \{L, S\}$. We fix $k_B T/\epsilon=0.04$, so the total area fraction ϕ is our control parameter to approach the glass transition. The mass ratio is $m_L/m_S=(\sigma_L/\sigma_S)^2$ and the length is normalized by σ_S . The total number of particles is $N=N_L+N_S=1024$ (or 4096) where N_L and N_S are the number of large and small species, respectively. We simulate the dynamics at size ratios $\sigma_L/\sigma_S=1.2, 1.25, 1.5, 1.75, 2, 2.5$ and 3 and area fraction ratios $\phi_L/\phi_S=N_L\sigma_L^2/N_S\sigma_S^2=0.5, 0.75, 1, 1.5$ and 2; these states are indicated by the circles in Fig. 1(a).

We obtain the relaxation time τ_α from the self-part of the intermediate scattering function for all particles, which is given by $F(k, t)=\frac{1}{N}\sum_j\langle\exp i\vec{k}\cdot[\vec{r}_j(t)-\vec{r}_j(0)]\rangle$, where \vec{r}_j is the position vector of particle j , $\langle\rangle$ indicates a time average and \vec{k} is the wave vector. τ_α is determined when $F(k_p, \tau_\alpha)=1/e$ where k_p corresponds to the wave number of the first peak of the structure factor. The ϕ dependence of τ_α is well fitted by Vogel-Fulcher (VF) function substituting ϕ for $1/T$: $\tau_\alpha=\tau_0\exp[D\phi/(\phi_0-\phi)]$, where D is the fragility index and ϕ_0 is the area fraction of the ideal glass transition [see Fig. 2(a)] [2]. Fragile

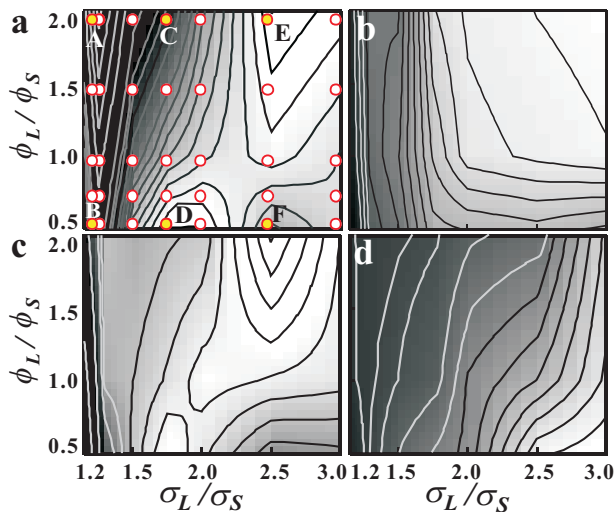


FIG. 1: (Color online.) The contour plot of (a) fragility index D , (b) the growth rate of hexagonal order $\partial\langle\psi_6\rangle/\partial\phi$, (c) the growth rate of dynamical correlation length $\partial\xi/\partial\phi$ and (d) the dynamical correlation around a large particle Θ in a plane of $(\sigma_L/\sigma_S, \phi_L/\phi_S)$. All those figures except (a) are obtained at $\phi=0.66$. The color in each panel is brighter when each value is small, thus, the brighter regions correspond to (a) fragile liquids, (b) low growth of hexagonal order, (c) low growth of dynamical correlation length and (d) minimal correlations of motion between a large particle and its neighbors. The circles in (a) are the simulated points and specific states A–F are labeled.

liquids have smaller values of D . For example, $D \sim 4$ for triphenyl phosphite which is one of the most fragile liquids, while for the less fragile liquid butyronitrile, $D \sim 30$ [13]. For our simulations, $0.4 \lesssim D \lesssim 1.0$, smaller than the molecular liquids.

Figure 1(a) shows the contour plot of D in a $(\sigma_L/\sigma_S, \phi_L/\phi_S)$ plane. The circles indicate the states simulated. This figure shows that the fragility is not a monotonic function of the size ratio or the area fraction ratio. For example, for $\phi_L/\phi_S = 2.0$, the fragility has values $D = 1.05, 0.82, 0.45$ for states A, C, and E, but then increases slightly to 0.49 for the state to the right of E. Likewise, for $\phi_L/\phi_S = 0.5$, the fragility behaves non-monotonically with increasing size ratio: $D = 0.64, 0.48, 0.77$ for states B, D, and F. Comparing states A and B, or C and D, suggests that increasing the number of large particles increases the fragility index D , but comparing states E and F disproves this trend.

Prior work shows two-dimensional systems can form small hexagonally ordered regions where particles move slower. More fragile liquids are observed to have large growth rates of the size of these regions with respect to ϕ [7, 8, 9]. To check this we study the ϕ dependence of hexagonal order for our samples. We use the local hexatic order parameter $\psi_6^j = \frac{1}{n_j} \left| \sum_{m=1}^{n_j} e^{i6\theta_m^j} \right|$ where n_j is the number of nearest neighbors for particle j and

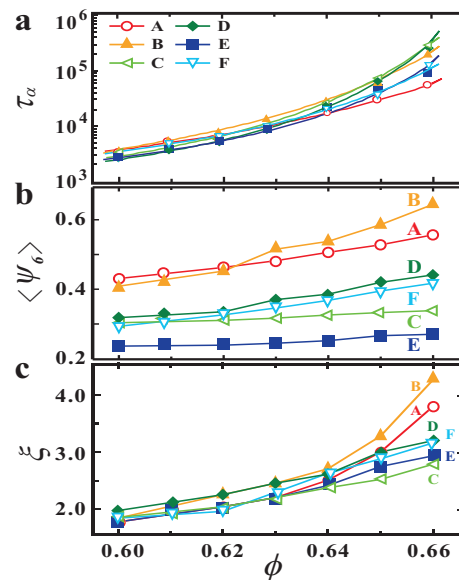


FIG. 2: (Color online.) ϕ dependence of (a) relaxation time τ_α , (b) hexagonal ordering $\langle\psi_6\rangle$ and (c) dynamic correlation length ξ at states A, B, C, D, E and F indicated in Fig. 1(a). The solid lines in (a) is a fitting line with the VF function at each state. Filled and open symbols correspond to fragile liquids and less fragile liquids, respectively.

θ_m^j is the angle of the relative vector $\vec{r}_m - \vec{r}_j$ with respect to the x axis. $\psi_6^j=1$ means that a hexagonal arrangement is formed around particle j , while $\psi_6^j=0$ corresponds to a non-hexagonal arrangement. We then consider $\langle\psi_6\rangle$, the time and particle average of ψ_6^j . We compare the ϕ dependence of $\langle\psi_6\rangle$ with that of τ_α [Fig. 2(a) and (b)]. States A and B have a small size ratio, $\sigma_L/\sigma_S = 1.2$, and here both τ_α and $\langle\psi_6\rangle$ increase dramatically as ϕ increases, suggesting they are indeed related as seen in prior work. However, for states C and E, the systems slow without significant hexagonal ordering.

Next, we compare fragility with the growth rate of hexagonal ordering $\partial\langle\psi_6\rangle/\partial\phi$. This derivative is computed as $\partial\langle\psi_6\rangle/\partial\phi = [\langle\psi_6(\phi)\rangle - \langle\psi_6(\phi - \Delta\phi)\rangle]/\Delta\phi$ where we choose $\Delta\phi = 0.01$. Figure 1(b) shows the contour plot of $\partial\langle\psi_6\rangle/\partial\phi$ at $\phi = 0.66$ in a plane of $(\sigma_L/\sigma_S, \phi_L/\phi_S)$. The growth of hexagonal order is small at large σ_L/σ_S and ϕ_L/ϕ_S (upper right region). This behavior is expected since hexagonal ordering should be frustrated with increasing σ_L/σ_S . Figure 3(a) shows D as a function of $\partial\langle\psi_6\rangle/\partial\phi$. We observe two distinct behaviors. For small size ratio systems ($\sigma_L/\sigma_S < 1.4$, triangles), more fragile liquids (smaller D) have a larger dependence of hexagonal order on ϕ , in agreement with prior work [7]. In contrast, large size ratio systems ($\sigma_L/\sigma_S > 1.4$, circles) show much less correlation between the growth of hexagonal order and the fragility index.

For large size ratio systems, we see little hexagonal structure on average [curves E and F in Fig. 2(b)], but

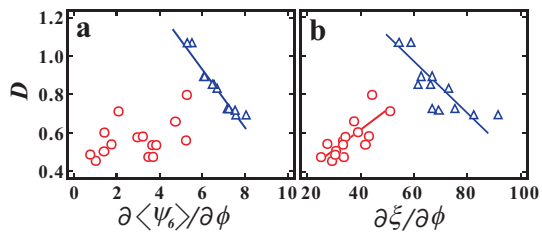


FIG. 3: (Color online.) The fragility index D as a function of (a) $\partial\langle\psi_6\rangle/\partial\phi$ and (b) $\partial\xi/\partial\phi$ at $\phi=0.66$. The triangles correspond to small size ratio systems ($\sigma_L/\sigma_S < 1.4$) and the circles correspond to large ones (> 1.4). The lines are added as a guide to the eye.

this does not preclude the possibility that locally there may be hexagonal ordering which influences the dynamics. To check this, we compare the local mobility with local structure. We compute $\Delta r_j^2(\Delta t)$ which is the squared displacement of particle j , using the time scale $\Delta t = \Delta t^*$ when the peak height of the non-Gaussian parameter is maximum [14]. Figure 4(a) shows a snapshot of the system in state B at $\phi=0.66$ with the darker colors indicating particles with larger values of Δr_j^2 , and Fig. 4(b) shows the same snapshot coloring the particles by their value of ψ_6^j . The circled region in Fig. 4(a,b) shows that mobile regions correspond to regions with less ordering. Furthermore, we calculate the Pearson correlation coefficient $C(\Delta r_j^2, \psi_6^j)$, finding $C = -0.13$, supporting the idea that mobility is slightly anticorrelated with hexagonal ordering. In contrast, Figs. 4(c,d) show Δr_j^2 and ψ_6^j for state E, with a much larger size ratio, and here there is no correspondence ($C = 0.01$). Overall, for the large size ratio samples ($\sigma_L/\sigma_S > 1.4$), we never observe any ordered structures at any area fraction. However, we cannot rule out the possibility that there is subtle ordering that might be present and influencing the dynamics.

Cooperative motion of groups of particles is a common phenomenon as the glass transition is approached [4, 14, 15, 16, 17], and this behavior is thought to be more common in fragile glasses. To look for this connection in our sample, we need to characterize the cooperative motion such as that suggested by the darker clusters in Fig. 4(a,c). We compute a correlation function $S(R) = \langle \Delta \vec{r}_i \cdot \Delta \vec{r}_j \rangle / \langle |\Delta \vec{r}|^2 \rangle$, where R is the distance between particles i and j , and $\Delta \vec{r}_i$ is the displacement of particle i at $\Delta t = \Delta t^*$ [17]. We find that $S(R)$ shows exponential decay with R , which was previously observed in experiments [14] and simulations [17]. This exponential decay yields a decay length ξ , which we plot in Fig. 2(c) as a function of ϕ for our six representative states.

Figure 2(c) shows little relationship between the magnitude of ξ and the fragility, so we focus on the growth rate of ξ , $\partial\xi/\partial\phi$. This is sensible since the fragility index D relates to the ϕ -dependence of τ_α . We calculate the derivative $\partial\xi/\partial\phi$ as $[\xi(\phi) - \xi(\phi - \Delta\phi)]/\Delta\phi$ where we chose

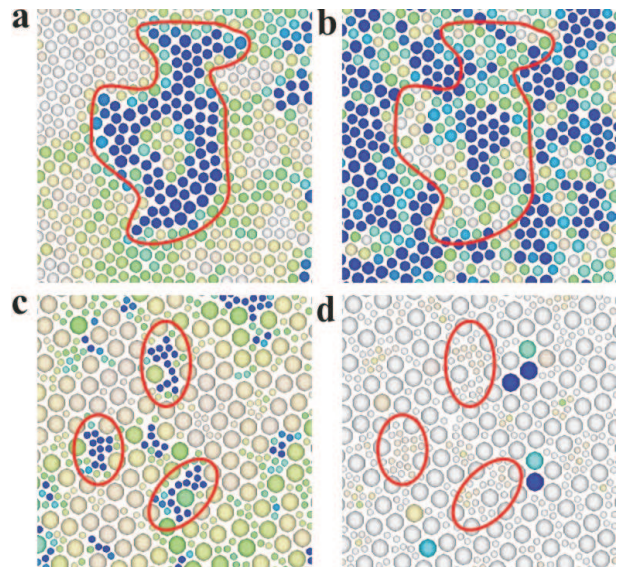


FIG. 4: (Color online.) (a) and (b) are snapshots of the system at state B, $\phi = 0.66$; (c) and (d) are at state E, $\phi = 0.66$. The simulation box is four times as large as those snapshots in each side. In (a) and (c), particles are colored based on mobility Δr_j^2 , with darker colors indicating more mobile particles. The darkest color corresponds to $\Delta r_j^2 = 0.25\sigma_s^2$. In (b) and (d), particles are colored based on the hexagonal order parameter ψ_6^j , with the darkest color corresponding to $\psi_6^j = 0.8$. The outlined regions are guides to the eye.

$\Delta\phi = 0.01$. Figure 1(c) shows the contour plot of $\partial\xi/\partial\phi$ in a $(\sigma_L/\sigma_S, \phi_L/\phi_S)$ plane. This plot has a rough qualitative similarity to the fragility [Fig. 1(a)]. Figure 3(b) more directly shows that D is related to $\partial\xi/\partial\phi$, with distinct behaviors for the small and large size ratio systems. In small size ratio cases (triangles), fragile liquids have larger increase of ξ with respect to ϕ and it is natural that the increase of τ_α is related to this [14, 16]. In contrast, the opposite relationship is seen for the large size ratio states (circles). The most fragile states (small D) correspond to those where ξ grows least as the glass transition is approached.

To understand this unusual relation between ξ and fragility in large size ratio systems, we consider dynamical differences between the two particle species. Figure 5(a) shows the mean square displacement $\langle \Delta r^2 \rangle$ of large and small species for state E at $\phi = 0.66$. The large particles are significantly slower than the small particles. We next consider how the motion of small and large particles are coupled. To quantify this, we compute the correlation between the directions of motion of a large particle and its neighboring particles as $\Theta = \langle \frac{1}{n_i} \sum_i \cos \theta_{ij} \rangle$ where j indicates a large particle, i are the nearest neighbor particles, n_i is the number of these neighbors, θ_{ij} is the angle between $\Delta \vec{r}_i$ and $\Delta \vec{r}_j$, $\Delta \vec{r}_j$ is the displacement of j particle at $\Delta t = \Delta t^*$, and the angle brackets indicate a time average and an average over all large particles j .

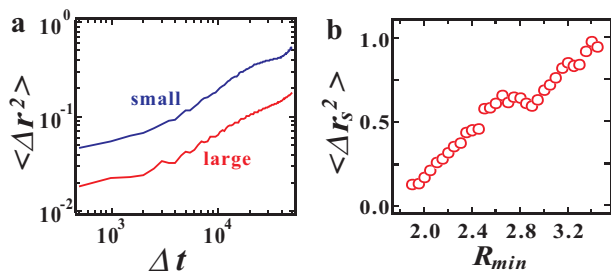


FIG. 5: (Color online.) (a) The mean square displacement $\langle \Delta r^2 \rangle$. The motion of large particles is slower than that of small particles. (b) The square displacement of small particles $\langle \Delta r_s^2 \rangle$ as a function of the distance from nearest large particle, R_{min} . Both (a) and (b) are obtained from state E at $\phi=0.66$.

$\Theta = 1$ indicates that particles around a large particle move with the same direction as the large particle on this time scale, while $\Theta = 0$ means that their movements are random. Figure 1(d) shows the contour plot of Θ in the plane of $(\sigma_L/\sigma_S, \phi_L/\phi_S)$. Θ ranges from 0.7 (upper left corner) to 0.4 (lower right corner). Cooperativity decreases as the size ratio increases, and as the number of large particles decreases.

If large particles move slower [Fig. 5(a)] and small particles move independently of the large ones [Fig. 1(d)], this suggests that the large particles act as slow-moving walls within the large size ratio systems. The small particles are effectively trapped in pores between the large particles [see Fig. 4(c)]. In confined geometries, τ_α can dramatically change compared to an unconfined system at the same temperature and density [18, 19, 20]. Confined systems with free surfaces typically have smaller values of τ_α , while those with rigid walls have larger values of τ_α . Our data suggest the latter situation is relevant for our large size ratio systems.

To test this, we measure the mobility of small particles as a function of their distance R_{min} from the nearest large particle, shown in Fig. 5(b). This plot indicates that the mobility of small particles is dramatically decreased near the large particles [21]. When glass-formers are confined, there are two main effects: a finite size effect, which can slow the particle motion; and a surface effect, which slows particle motion near rough surfaces [18]. Our data cannot distinguish between these two effects, but both are consistent with Fig. 5(b).

Thus, we suggest the fragility of large size ratio systems may be connected to the “strength” of confinement effects. Less fragile liquids may have more mobile walls, such as state C with a large value of Θ . Or, less fragile liquids may have larger spacings between the large particles, such as state F, with a relatively small value of ϕ_L/ϕ_S . In contrast, the more fragile states D and E have small values of Θ and smaller distances between large particles. These systems are in the ultra-confined limit,

where the spacing between large particles is of order ξ or even smaller, thus limiting $\partial\xi/\partial\phi$. If particles need to move in groups of size ξ , but groups of this size cannot form, this would suggest particle motion is more difficult and thus explain the increase in τ_α . We note the opposite influence of confinement on fragility has been seen in simulations of polymer thin films, but this was likely due to a free surface boundary condition [22]. Those simulations found enhanced mobility near the free surface, in contrast to our reduced mobility seen in Fig. 5(b).

In summary, we have investigated the fragility of binary particle mixtures with size ratios between 1.2 and 3.0. The fragility of small size ratio systems ($\sigma_L/\sigma_S < 1.4$) is related to the growth of ordered regions [6, 7, 8, 9]. However, the large size ratio systems do not show this relation. Both types of systems have fragilities which are related to the growth of a dynamical length scale ξ , although the sign of this correlation is opposite for the small and large size ratio systems. The data are suggestive that in the large size ratio systems, the large particles act as quasi-immobile walls which confine the small particles and slow the dynamics overall. This suggests that the fragility of materials could be enhanced by adding a small concentration of a larger species.

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