Slow dynamics coupled with cluster formation in ultrasoft-potential glasses

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We numerically investigate slow dynamics of a binary mixture of ultrasoft particles interacting with the generalized Hertzian potential. If the softness parameter, α, is small, the particles at high densities start penetrating each other, form clusters, and eventually undergo the glass transition. We find multiple cluster-glass phases characterized by different number of particles per cluster, whose boundary lines are sharply separated by the cluster size. Anomalous logarithmic slow relaxation of the density correlation functions is observed in the vicinity of these glass-glass phase boundaries, which hints the existence of the higher-order dynamical singularities predicted by the mode-coupling theory. Deeply in the cluster glass phases, it is found that the dynamics of a single particle is decoupled from that of the collective fluctuations.

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I. INTRODUCTION

The ultrasoft potentials are pairwise isotropic and repulsive interactions whose value remains finite even if the two particles fully overlap each other.¹,² The Gaussian, harmonic, and Hertzian potentials are typical examples. The ultrasoft potential systems are known to exhibit very rich and complex thermodynamic and dynamic behaviors at high densities, which are never observed in systems with sharp short-ranged repulsions such as the hard-sphere and Lennard-Jones potentials. As originally proposed by Likos et al. based on a mean-field analysis, the ultrasoft potential systems are categorized crudely into two types, i.e., the $Q^+$ and $Q^-$ classes, depending on the shape of the interparticle potential $v(r)$, or more precisely, the shape of its Fourier transformation $\tilde{v}(k)$. The $Q^+$ class is a system with a positive-definite $\tilde{v}(k)$, where $\tilde{v}(k) > 0$ for all wavenumbers $k$. The Gaussian-core model (GCM) and Hertzian potential system belong to this class.² The most salient feature of the systems in this class is the reentrant melting. The system which crystallized at moderate densities at a fixed temperature melts again as the density is increased. If one plots the binodal, or melting temperature, $T(\rho)$, of the fluid-solid phase boundary as a function of the density ($\rho$), or the pressure ($p$), it first steeply increases with the density like a standard molecular systems but it reaches a reentrant peak and becomes a decreasing function. At high densities beyond this peak, many systems exhibit multiple solid phases, each of which is characterized by distinct crystalline structures.³–⁸ On the other hand, the $Q^-$ class systems are characterized by $\tilde{v}(k)$ which can take negative values at finite $k$’s. A representative example is the generalized exponential model (GEM) defined by $v(r) = \epsilon \exp[-(r/\sigma)^n]$ with $n > 2$, where $\epsilon$ and $\sigma$ are the energy and length scales, respectively. In the $Q^-$ class systems, the reentrant transition is either suppressed or absent and instead the particles can overlap each other and form clusters consisting of multiple particles bonding together at high densities.³,⁹–¹⁴ The melting line becomes a monotonic function of the density in the high density limit. The density determines the number of particles in a cluster at low temperatures, where very rich multiple crystalline phases characterized by different cluster sizes are observed.¹⁵,¹⁶ Peculiar dynamics such as fast intercluster ballistic hopping of particles has also been reported.¹⁷–¹⁹ The ultrasoft potential systems are not just idealized theoretical models but they can be seen in many realistic macromolecular systems, such as star polymers and dendrimers.² and even in some quantum systems such as the vortices of Type 1.5 superconductors.²⁰–²³ Indeed some model macromolecules have been demonstrated to form clusters at high densities by simulations.²⁴–²⁶

The ultrasoft potential systems have also been studied in the context of the glass and jamming transitions. Binary and polydisperse systems of the harmonic and Hertzian potential systems have been pet models to study both jamming and glass transitions.²⁷–³⁰ The glass transitions of these systems in the vicinity of the jamming transition point have been extensively investigated, and the glass transition line $T_g(\rho)$ of this $Q^+$ systems were found to show the reentrant behaviors at high densities. Some anomalies of the jamming/glass transitions associated with the large particle overlap at high densities are also reported. The GCM is another $Q^+$ class glass former. In contrast to typical glass formers, it was demonstrated that the monatomic GCM undergoes the glass transition at extremely high densities and its dynamical asymptotic behaviors agree unprecedentedly well with the mode-coupling theory (MCT).³⁴–³⁷

Compared to the $Q^+$ class, the glass transition of $Q^-$ class systems is largely unexplored.⁹,³⁸–⁴⁰ Numerical study of the glass transition has been first reported for GEM with $n = 4$, a typical $Q^-$ system, where the particles are clumped to form clusters and these clusters exhibit the glassy slow dynamics at low tempera-

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The system showed a singular relaxation dynamics in the boundary of the multiple glass phases characterized by semi-discontinuously as the density increases. The phase number of particles per cluster increases one by one per temperatures and high densities. It was demonstrated that the GHP model is an ideal test bench to study the polyamorphism of complex fluids and, possibly, help understanding the putative liquid-liquid transition underlying at lower temperatures. The paper is organized as follows. We first introduce the numerical model and explain the method in Section II. The glass phase diagram, the iso-relaxation-time lines as a function of T and ρ, for the models with different α’s and the static properties are discussed in Section III. We investigate dynamical properties in detail in Section IV and we conclude in Section V.

II. MODEL AND METHODS

We investigate a three-dimensional 50:50 binary mixture of large (L) and small (S) spherical particles interacting with the GHP potential defined by Eq. (1). For the binary mixture, we replace the radius σ with σ_{ab} = (σ_a + σ_b)/2, where σ_a is the particle diameter of the a (∈ L, S) component. The size ratio of the particles, σ_L/σ_S, is set to 1.4 and the mass of the particles is set to m for both components. As argued in the previous section, this model belongs to the Q^± class when α < 2. There is an argument that if the second derivative of the potential at origin \( v''(r = 0) \) is not negative, the system belongs to the Q^± class but this is not the case for GHP since \( v''(0) \) is always positive even for \( \alpha \geq 2 \).

We run the molecular dynamics simulation for the systems with \( \alpha = 1.5, 1.7, 2.0, \) and 2.5. We set \( \sigma_S, m, 10^{-4} \epsilon/k_B \) with the Boltzmann constant \( k_B \), and \( \sqrt{m\sigma_S^2/\epsilon} \), as the units of the length, mass, temperature, and time, respectively. The simulations are performed in the \( NVE \) ensemble with the velocity Verlet algorithm over a wide range of temperatures T and densities \( \rho = N/V \) with the number N of the particles and the volume V of the simulation box\(^{41}\). We mainly study the system of N = 1000. We also run simulations for different N at several temperatures and densities and confirmed that no appreciable finite size effect for our results was observed. The time step in our simulations is 0.002 for the systems with \( \alpha = 1.5 \) and 1.7 and 0.02 for \( \alpha = 2 \) and 2.5. The time step for \( \alpha < 2 \) is set to be much smaller than that for \( \alpha \geq 2 \) to avoid energy drift in our simulation time windows. The system was equilibrated at a high temperature (\( T = 200 \)) at first. We subsequently...
cooled the system to lower temperatures by normalizing velocities of particles every 5000 steps over $10^4$ or $10^5$ time units for the lowest temperatures we investigate. In order to equilibrate the system after the annealing, every run was performed over $20\tau$ at least. Here $\tau$ is the structural relaxation time defined as the time at which the intermediate scattering function is equal to 0.1. We assured that no aging was observed after the equilibration run.

III. GLASS PHASE DIAGRAM AND STATIC PROPERTIES

A. One component systems

Before investigating the glass transition of the binary GHP, we briefly summarize our simulation results for the one component GHP with $\alpha = 1.5$ which is well below the $Q^k$ criteria of $\alpha = 2$. We run the simulation long enough to assure that the potential energy becomes constant and the system is well equilibrated. The snapshots of the observed crystalline structures are shown in Figure 2. Contrary to our anticipation, none of the solid phase observed in the simulation boxes is the cluster crystals even at densities as high as $\rho = 2.6$ and 4.0. Instead, for both densities, we observe the quasi-hexagonal crystal phase where the particles form the two dimensional hexagonal layers laminated in the vertical direction of the layers. This structure is unchanged at higher densities ($\rho = 4.0$) but the hexagonal layers are undulated along the direction parallel to the layers. The absence of the cluster phases is consistent with the previous study for the two dimensional system, in which series of exotic crystalline phases were obtained over a wide range of densities but no cluster phase was observed. The hexagonal phases which we observed are akin to the lane phase observed in the two dimensional counterpart. More elaborate free energy assessment using the thermodynamic integration is necessary in order to determine the accurate and full thermodynamic phase diagram of the crystalline structures but it is beyond the scope of this present study.

B. Glass Phase Diagram

Let us go back to the binary system and study the glass transition of GHP. We first draw the glass phase diagram for the large component, $\Phi_L(k,t)$, defined by

$$\Phi_L(k,t) = \frac{\langle \rho_L(k,t)\rho_L(-k,0) \rangle}{\langle |\rho_L(k,0)|^2 \rangle}, \quad (3)$$

where $\rho_L(k,t) = \sum_{j \in \{ L \}} \exp[i\vec{k} \cdot \vec{r}_j(t)]$ is the density fluctuations of the large component in the Fourier space, $\{ L \}$ in the summation denotes the set of particles of the large component, $\vec{r}_j(t)$ is the position of the $j$-th particle. We define $\tau$ by $\Phi_L(k = 6.0, \tau = 0.1)$. Here, the wavenumber $k = 6.0$ is chosen to be close to the position of the nearest neighbor peak of the static structure factor $S_{LL}(k)$ for the large component (see Eq. (5) below). As we shall discuss below, $\tau$ for the correlation functions for the small component or for their self-part are different at high densities and small $\alpha$’s. However, it does not qualitatively affect the overall shape of the phase diagram shown here. We defined the empirical glass transition temperature $T_g$ as the point at which $\tau$ reaches $10^3$. We run the simulation for a range of densities, $0.5 \leq \rho \leq 3.0$. The glass transition lines thus obtained are shown in Figure 3 for $\alpha = 1.5, 1.7, 2.0,$ and 2.5. They are the iso-$\tau$-lines whose shape can shift up and down depending on the definition of $T_g$ but the overall shapes are unchanged. For $\alpha = 2.5$, $T_g(\rho)$ has the maximum peak around $\rho \approx 1.2$ before it gradually decreases at higher densities. Above $\rho \approx 1.6$, the system is found to nucleate to form the fcc crystal and no glassy behavior is observed. This reentrance behavior is consistent with the Likos criteria for the $Q^+$ class systems. Similar behavior is reported for the polydisperse system with the same potential. Asides that the polydisperse system did not crystallizes at high densities, $T_g(\rho)$ agree with that for the binary system almost quantitatively, hinting that the result is insensitive to the size dispersity of particles. The result for $\alpha = 2.0$ is also qualitatively similar; $T_g(\rho)$ increases, reaches the maximal peak, and then gradually decreases. A cusp is ob-
served slightly above the reentrant peak, around $\rho = 1.4$, which may be a precursor of a new glass phase but we did not observe any qualitative structural changes there (not shown). We again could not access higher densities above $\rho \approx 2.4$ as demixing and nucleation intervene the glassy slow dynamics. Interestingly, the position of the peak is close to the phase boundary of the fcc and bcc crystals of the one-component counterpart. Overall shape of $T_g(\rho)$ for $\alpha = 2.5$ and 2.0, including the positions of the reentrant peaks, are similar to the fluid-crystal bimodal lines for the one-component systems, although the latter lie at higher temperatures. As $\alpha$ is lowered below 2, the overall trends of $T_g(\rho)$ start changing qualitatively. For $\alpha = 1.7$, $T_g(\rho)$ is enhanced and two minima of $T_g(\rho)$ are clearly observed around $\rho \approx 1.2$ and 2.0. For $\alpha = 1.5$, the deeper minima appear at $\rho \approx 1.1$ and 1.8 and, furthermore, $T_g(\rho)$ increases at higher densities, instead of decreasing as observed for systems with $\alpha > 2$, which is consistent with the mean-field prediction for the $Q^2$ class fluids and the results for other cluster-forming systems. The presence of the distinct minima observed for $\alpha < 2$ is a clear sign that there exist multiple glass phases. In the following, we mainly focus on the system with $\alpha = 1.5$ and discuss thoroughly about static, thermodynamic, and dynamic properties of the system in the vicinity of $T_g(\rho)$.

C. Static structures

We investigate static properties of systems with $\alpha = 1.5$ and compare with those of $\alpha = 2.0$ in the vicinity of $T_g(\rho)$ shown in Fig. 3 for several densities. We evaluate the partial radial distribution functions $g_{ab}(r)$ ($a, b \in L, S$) defined by

$$g_{ab}(r) = \frac{V}{4\pi r^2 N_a N_b} \sum_{i \in \{a\}} \sum_{j \in \{b\}} \langle \delta(r - |\vec{r}_i - \vec{r}_j|) \rangle$$

(4)

and their Fourier transformations, the partial static structure factors $S_{ab}(k)$ ($a, b \in L, S$) defined by

$$S_{ab}(k) = \frac{1}{\sqrt{N_a N_b}} \langle p_a(k) p_b^*(k) \rangle$$

(5)

We show $g_{ab}(r)$, $S_{ab}(k)$, and several snapshots of the systems for $\alpha = 2.0$ in Fig. 4 and for $\alpha = 1.5$ in Fig. 5, respectively. First look at Fig. 4 for $\alpha = 2.0$. In Fig. 4 (a), one observes that, when the density is small, $g_{LL}(r)$ is
qualitatively similar to those of simple liquids and characterized by a sharp nearest-neighbor peak at \( r \approx \sigma_{ab} \) followed by oscillatory tail. As the density increases (see \( \rho = 1.2 \) and 1.4), the nearest-neighbor peak shifts to smaller \( r \) and the peak width broadens, which is a reflection that the particles are squashed and start overlapping. At \( \rho \geq 1.6 \), the nearest-neighbor peak of \( g_{LL}(r) \) splits into two. The separation between the two peaks gradually increases as the density increases and the peak at smaller \( r \) moves to and stops at \( r \approx 0.7 = \sigma_L/2 \), whereas the peak at larger \( r \) moves back to \( r \approx \sigma_L \) at the highest density, \( \rho = 2.4 \). Similar behaviors were reported for the same systems with the pressure control simulation at a finite temperature\(^32\) and at \( T = 0 \)\(^33\). Note that the position of the small-\( r \) peak does not move after it reaches around \( \sigma_L/2 \) at high densities. We checked that the peak position does not change appreciably as the temperature is lowered at a fixed density. The split of the peaks of \( g_{LL}(r) \) is a consequence of the particles’ overlap but the fact that the two peaks are located at \( r = \sigma_L/2 \) and \( \sigma_L \) suggests that the particles are overlapped with their neighbors but do not form clusters. If they were clusters, the inter-particle distance corresponding to the large \( r \) peak position should be separated more than twice of the intra-particle distance corresponding to the small \( r \) peak position. This observation is reflected in \( S_{LL}(k) \) in Fig. 4 (d). It exhibits the growth of the second peak, which corresponds to the additional peak at smaller \( r \) in \( g_{LL}(r) \) at higher densities. We also note that the small and large particles of the system at the highest density of \( \rho = 2.4 \) partly demix as seen in Fig. 4 (i). This is reflected in mild growth of \( S_{LL}(k) \) at small \( k \)’s. In this density, we do not observe the glassy slow dynamics anyway. Likewise, \( g_{SS}(r) \) in Fig. 4 (b) shows that the position of the peak shift to lower \( r \) and its width widens as the density increases. However, the trend is weaker than that observed in \( g_{LL}(r) \). We observe the onset of the split of the first peak only at the highest density of \( \rho \approx 2.4 \). It is interesting that the similar trend is observed for \( g_{LS}(r) \) [see Figure 4 (c)]. \( S_{SS}(k) \) and \( S_{LS}(k) \) in Fig. 4 (e) and (f) reflect the properties of \( g_{SS}(r) \) and \( g_{LS}(r) \). Note that the increase of \( S_{SS}(k) \) at \( k \rightarrow 0 \) is more dramatic than \( S_{LL}(k) \), suggesting that demixing is predominantly driven by small particles. The existence of the demixing or the phase separation of binary ultrasoft-potential systems at high densities was predicted by a mean-field analysis and using the hypernetted-chain closure\(^43–45\).

Figure 5 is the results for \( \alpha = 1.5 \) at \( T_g(\rho) \). At the lowest density of \( \rho = 0.675 \), all \( g_{ab}(r) \) and \( S_{ab}(k) \) are similar to those for \( \alpha = 2.0 \). As the density increases, anomalies first appear in \( g_{LL}(r) \). The nearest-neighbor peak broaden and its tail stretches to smaller \( r \). Its position barely changes whereas the height substantially lowers. At \( \rho \approx 1.1 \), where \( T_g(\rho) \) has the first minimum [see Figure 3], another peak appears at \( r \approx 0.4 \). Increasing the density further, the small-\( r \) peak grows but its position slightly moves to smaller \( r \) and eventually stops at \( r \approx 0.2 \). Furthermore, the minimum between the small-\( r \)

\[ g_{LL}(r) \]

\[ S_{LL}(k) \]

\[ g_{SS}(r) \]

\[ S_{SS}(k) \]

\[ g_{LS}(r) \]

\[ S_{LS}(k) \]

\[ \alpha = 1.5 \]

\[ \alpha = 2.0 \]

\[ \alpha = 3.0 \]

\[ \rho = 1.3 \]

\[ \rho = 2.0 \]

\[ \rho = 3.0 \]

Figure 5. (a)–(c) Partial radial distribution functions for \( \alpha = 1.5 \). (a) \( g_{LL}(r) \), (b) \( g_{SS}(r) \), and (c) \( g_{LS}(r) \) at \( T_g(\rho) \) for \( \rho = 0.675, 1.0, 1.1, 1.2, 1.7, 1.9, \) and 2.2 from bottom to top. The alternate solid and dashed lines are shifted vertically by 1 for clarity. (d)–(f): the corresponding partial static structure factors. (g)–(i): the snapshots of the equilibrated systems at \( \rho = 1.3 \) at \( T = 98 \), (f) \( \rho = 2.0 \) at \( T = 86 \), and \( \rho = 3.0 \) at \( T = 135 \). The particle sizes are not drawn to scale but reduced by 30%. The insets are their close-ups highlighting dimer-, trimer-, and tetramer-shaped clusters of the large particles.
and the nearest-neighbor peaks deepens. This is a clear sign of the cluster formation. The presence of the small-$r$ peak, or the cluster peak, at $r < \sigma_L/2$ and a deep minimum $(g_{LL}(r) \approx 0)$ between the two peaks mean that a pair of particles is well separated from other pairs. This is in stark contrast from the case for $\alpha = 2.0$ [Fig. 4 (a)] for which the position of the cluster peak is located at larger $r \approx \sigma_L/2$ and the depth of the minimum between the two peaks remains finite, implying that the inter-particles distances of a fraction of particles are shortened because they are pressured but particles are not coagulated yet. Figure 5 (g) is the snapshot of the system at $\rho = 1.3$. One can clearly observe dimer-shaped clusters of the large particles at $\rho \gtrsim 1.1$. The position of the cluster peak corresponds to the bond length of a dimer. As the density increases further, the large particles form the trimers [Fig. 5 (h)] and tetramer [Fig. 5 (i)]. These observations are also reflected in the shape of the static structure factor. $S_{LL}(k)$’s for $\alpha = 2.0$ in Fig. 4 (d) demonstrates that the second peak at higher $k$’s continuously grows as a direct consequence that more particles prefer to interacts with shorter distance, whereas the shape of $S_{LL}(k)$’s for $\alpha = 1.5$ [Fig. 5 (d)] is qualitatively unchanged, which suggests that clusters formed by particles with the short bond length are separated by $\sigma_L$ from their neighbors.

Similar cluster formation is also observed for small particles but at higher densities as seen in Fig. 5 (b) and (e). The cluster peak of $g_{SS}(r)$ shows up at $\rho \approx 1.9$ which is close to the second minimum of $T_\rho(\rho)$ (Fig. 3). This peak also grows as the density increases and is located at less than $\sigma_S/2$ like for the large particles. However, its height is lower and the minimum between the cluster peak and the nearest-neighbor peak is higher than those for the large particles. These features suggest that the the clusters of the small particles are more unstable and the size of the clusters fluctuates. Contrary to $g_{LL}(r)$ and $g_{SS}(r)$, no cluster peak is observed in $g_{LS}(r)$ for all densities we studied as shown in Fig. 5 (c). This means that the cluster formation always takes place between the particles of the same size. The large particles do not pair with the small ones. This was observed also in a binary mixture of GEM. Distinct from the cluster phases of GEM is the shape of the clusters. For GEM, particles in one cluster are completely overlapped with each other and the averaged bond length is 0 with broad fluctuations. This is natural because the shape of the GEM potential is flat at $r = 0$, so that the particles can sit on top of each other with no energetic penalty. On the other hand, the potential of GHP with $\alpha < 2$ remains repulsive up to $r = 0$ and the particles bond together at a finite distance determined by the characteristic length encoded in $\tilde{v}(k)$.

Finally, in Figure 6, the temperature dependence of $g_{LL}(r)$ for $\alpha = 1.5$ for a fixed density ($\rho = 2.0$) is shown. At high temperatures $T = 200$, $g_{LL}(r)$ show no sharp peak and almost flat even at $r < \sigma_L$, meaning that the particles can easily penetrate each other. We can see a precursor of the cluster peak at $r \approx 0.4$. As the temperature is lowered, both the cluster and nearest neighbor peaks grow and sharpen but the growth of the cluster peak is more pronounced than the nearest neighbor peak. The minimum between the peaks concomitantly decreases. This result shows that the cluster formation is crossover and no sharp phase transition from the fluid phase to a “cluster-fluid” phase exists, which is also the case for the binary mixture of GEM.

### D. Cluster sizes

We investigate the properties of clusters formed in the system with $\alpha = 1.5$ in detail. As discussed in the previous subsection, the cluster formation is evident from the shape of $g_{LL}(r)$ and $g_{SS}(r)$. In order to evaluate the number of particles contained in one cluster, one has to integrate $g_{aa}(r)$ over a cut-off distance $r_c$.

We define $r_c$ to be a center of the minimum of $g_{aa}(r)$ between the cluster
and nearest neighbor peaks. Since all clustering systems develop clear minima and their positions are almost independent of temperatures and densities, we fix \( r_{c,LL}, r_{c,SS}, \) and \( r_{c,LS} \) to be 0.7, 0.6, and 0.65, respectively and use these values for all densities and temperatures. Hereafter, we consider the number of particles per cluster for the large \((n_L)\) and small \((n_S)\) particles near \(T_g(\rho)\). The average numbers of \(n_L\) and \(n_S\) are shown together with \(T_g(\rho)\) in Fig. 7. At low densities, both \(n_L\) and \(n_S\) are unity and no cluster is formed. As the density increases, \(n_L\) increases by one. This stepwise increase takes place at \(\rho \approx 1.1\) where \(T_g(\rho)\) shows the first minimum and the cluster peak of \(g_{LL}(r)\) starts growing (Fig. 5 (a)). As the density increases further, \(n_L\) increases one by one and the system enters from the dimer \((n_L = 2)\) to trimer \((n_L = 3)\), and to the tetramer \((n_L = 4)\) phases. The density where a stepwise increase is observed synchronizes with the minimum of \(T_g(\rho)\). On the other hand, clustering of the small particles starts at higher densities. The dimer phase \((n_S = 2)\) appears exactly at the density where the large particles enter the trimer phase and the increase to \(n_S = 3\) takes place at \(\rho \approx 2.6\) where the large particles become tetramers, although the increase of \(n_S\) is less sharp. The multiple cluster phases with relatively sharp phase boundary shown in Fig. 7, however, are already seen at relatively high temperatures. In other words, the cluster formation is not triggered by the glass transition nor vice versa. In Figure 8 (a), we show the temperature dependence of the fraction of the large particles forming a cluster of the size \(n_L\) at \(\rho = 2.0\) where the large particles are in the trimer phase. At very high temperatures, the system consists of the mixture of clusters of various sizes from \(n_L = 1\) to \(n_L = 5\) but as the temperature is lowered, the system is gradually dominated by the trimer and eventually the system is almost completely occupied by trimers at \(T_g(\rho) \approx 98\). Temperature dependence of the average of the number of the cluster \(\overline{n_L}\) also confirm that there is no sharp transition from the monomer phase to the trimer phase (Fig. 8 (b)). The gradual but monotonic reduction of the error bars shown in this figure at lower temperatures is a clear sign that the emergence of \(n_L = 3\) phase is a crossover. Clusters of small particles show similar trend except that the variances are larger than the large particles (not shown).

The stepwise increase of the cluster size with density, whose edges tend to sharpen as the temperature is lowered, hints that the crossover between the different cluster phases becomes thermodynamic transition as the temperature is lowered, i.e., there might exist the liquid-liquid phase transition hidden at a low temperature which is not accessible due to inhibitedly slow glassy dynamics. This transition may be a liquid version of the first-order transition between the multiple crystalline phases which has been reported for the monatomic GEM at high densities and low temperatures. As it is often the case of the studies of the polyamorphism and associated liquid-liquid phase transition, the precursor of the transition can be seen as the Widom line of the isothermal compressibility at higher temperatures. We estimate the isothermal compressibility \(K_T\) defined by

\[
K_T = \left\{ \rho \left( \frac{\partial P}{\partial \rho} \right)_T \right\}^{-1}
\]

by evaluating the pressure \(P\) for various densities at fixed temperatures around the first minima of \(T_g(\rho)\), where the monomer-dimer phase boundary is observed for the large particles. The density dependence of isothermal compressibility \(K_T\) is shown in Figure 9. At high temperatures, \(K_T\) is a monotonically decreasing function of the density. As the temperature is lowered, \(K_T\) develops a peak at \(\rho \approx 1.05\). Although the temperatures which we explored are still too high to be conclusive, this trend is similar to what has been observed for prospective liquid-liquid phase transitions for other systems.

Finally, we assess the static properties of configurations of the clusters. We compute the partial radial distribution function \(g^{LL}_r(\rho)\) of clusters’ center of mass. Figure 10 is \(g^{LL}_r(\rho)\) for \(\alpha = 1.5\) in the trimer phase at \(\rho = 2.0\) at several temperatures near \(T_g(\rho)\). It is single-peaked near \(r \approx \sigma_L\) which corresponds to the nearest neighbor distance between the trimers and the peak monotonically increases as the temperature is lowered. Similar trends are observed at other densities and for \(g^{SS}(r)\). This means that slow dynamics of the cluster fluids near its glass
transition is caused by cage formation of clusters much the same way as the cage formation of atoms or molecules causes the glass transition of simple liquids.

IV. DYNAMICS

In this section, we discuss slow dynamics near \( T_g(\rho) \) of clustered fluids by analyzing the intermediate scattering functions. We specifically focus on the collective and self part of the scattering functions for the same species. The collective part is written explicitly as

\[
\Phi_a(k, t) = \frac{1}{S_{aa}(k)} \left\langle \frac{1}{N_a} \sum_{i \in \{a\}} e^{i\mathbf{k} \cdot \left( \mathbf{r}_i(t) - \mathbf{r}_i(0) \right)} \right\rangle.
\]

and the self part is

\[
\Phi_{s,a}(k, t) = \left\langle \frac{1}{N_a} \sum_{j \in \{a\}} e^{i\mathbf{k} \cdot \left( \mathbf{r}_j(t) - \mathbf{r}_j(0) \right)} \right\rangle.
\]

A. Density dependence

We first display \( \Phi_L(k, t) \), \( \Phi_{s,L}(k, t) \), \( \Phi_S(k, t) \), and \( \Phi_{s,S}(k, t) \) for a wide range of densities for \( \alpha = 1.5 \) for which the rich cluster phases are observed. Figure 11 (a)–(f) are the collective parts for the large and small particles, \( \Phi_L(k, t) \) and \( \Phi_S(k, t) \) and (g)–(l) are the self parts, \( \Phi_{s,L}(k, t) \) and \( \Phi_{s,S}(k, t) \) for various temperatures and for selected densities, \( \rho = 0.675, 1.1, 1.4, 1.8, 1.9, \) and \( 3.0 \). For all figures, \( k \) is chosen to be \( k = 6.0 \) for large and \( k = 8.0 \) for small particles, which are close to the first peak of \( S_{aa}(k) \) [see Fig. 5]. At low densities, \( \rho = 0.675 \), around which \( T_g(\rho) \) increases with density, both collective and self correlation functions for large and small particles exhibit typical slow dynamics of canonical supercooled fluids, i.e., the two-step relaxation characterized by a well-developed plateau followed by the stretched exponential relaxation as shown in Figs. 11 (a) and (g). Furthermore, the time-temperature superposition holds as for standard glass formers (not shown)\(^{51} \). At \( \rho = 1.1 \), where \( T_g(\rho) \) has a minimum and the large particles start clustering, the plateaus of \( \Phi_L(k, t) \) and \( \Phi_{s,L}(k, t) \) shown in Figs. 11 (b) and (h) disappear and the relaxation qualitatively changes. Almost linear decays in the semi-log plot in time means that the relaxation is logarithmic. The detail of this anomalous relaxation is discussed in the next subsection. On the other hand, \( \Phi_S(k, t) \) and \( \Phi_{s,S}(k, t) \) for small particles still show two-step relaxations. At \( \rho = 1.4 \), we find that both \( \Phi_L(k, t) \) and \( \Phi_{s,L}(k, t) \) retrieve the two-step relaxation as shown in Figs. 11 (c) and (i). At \( \rho = 1.9 \), where \( T_g(\rho) \) shows the second minimum and the small particles also start clustering to form dimers, \( \Phi_L(k, t) \) remains qualitatively unchanged, but the dynamics of \( \Phi_S(k, t) \) and \( \Phi_{s,S}(k, t) \) become singular, showing the logarithmic decay instead of two-step relaxation. Furthermore, \( \Phi_{s,L}(k, t) \) also shows the logarithmic decay. This suggests a decoupling of the collective and self dynamics at this density for the large particles [see Figs. 11 (e) and (k)]. At the highest density \( \rho = 3.0 \), one observes that both \( \Phi_L(k, t) \) and \( \Phi_S(k, t) \) retrieves the two-step relaxation again but two distinct changes are observed for their self parts, \( \Phi_{s,L}(k, t) \) and \( \Phi_{s,S}(k, t) \). First, the self part for the large particles \( \Phi_{s,L}(k, t) \) retrieves the two-step relaxation but its relaxation time is substantially shorter than its collective part. Secondly, the self part for the small particles \( \Phi_{s,S}(k, t) \) does not show the two-step relaxation nor logarithmic relaxation and the relaxation is much faster than other correlation functions. This facilitated relaxation of small particles and decoupling both from its collective dynamics and those of large particles are reminiscent of the dynamical anomaly observed in the binary mixture of the...
shows the temperature dependence of the relaxation time \( \tau \) that can be lucidly seen in the temperature. Mixed dynamics of type A and B is observed when two competing arresting mechanisms, such as gelation and glass transitions, are at play. This qualitative change from the two-step relaxation to the single-step relaxation is also similar to the transition from the so-called Type B to Type A dynamics. Type A and Type B dynamics are the two distinct glassy slow dynamics originally predicted by the mode-coupling theory (MCT). The former refers to a single step relaxation with continuous growth of the height of \( \Phi_\alpha(k, \tau) \) whereas the latter refers to a two-step relaxation with discontinuous jump of the plateau height of \( \Phi_\alpha(k, \tau) \) near the glass transition temperature. Mixed dynamics of type A and B is often observed when two competing arresting mechanisms, such as gelation and glass transitions, are at play.

Decoupling of the self and collective relaxation and the large and small particles can be lucidly seen in the temperature dependence of the relaxation time \( \tau \). Figure 12 shows the temperature dependence of \( \tau \) for \( \alpha = 1.5 \), \( \rho = 0.675 \), 1.1, 1.4, 1.8, 1.9, and 3.0 at several temperatures (see legend). The collective parts for the large and small particles, \( \Phi_L(k, t) \) and \( \Phi_S(k, t) \), and the self parts, \( \Phi_{s,L}(k, t) \) and \( \Phi_{s,S}(k, t) \). The solid and dashed lines are for the large and small particles, respectively. The wave number \( k \) is chosen to be 6.0 for the large and 8.0 for the small particles.

Particles with disparate size ratio\(^{52,53} \). This qualitative change from the two-step relaxation to the single-step relaxation is also similar to the transition from the so-called Type B to Type A dynamics. Type A and Type B dynamics are the two distinct glassy slow dynamics originally predicted by the mode-coupling theory (MCT)\(^{54} \). The former refers to a single step relaxation with continuous growth of the height of \( \Phi_\alpha(k, \tau) \) whereas the latter refers to a two-step relaxation with discontinuous jump of the plateau height of \( \Phi_\alpha(k, \tau) \) near the glass transition temperature. Mixed dynamics of type A and B is often observed when two competing arresting mechanisms, such as gelation and glass transitions, are at play\(^ {55} \).

Decoupling of the self and collective relaxation and the large and small particles can be lucidly seen in the temperature dependence of the relaxation time \( \tau \). Figure 12 shows the temperature dependence of \( \tau \) for \( \rho = 0.675 \) and 2.0 for the non-clustering system with \( \alpha = 2.0 \) (Fig. 12 (a)–(b)) and for several densities for the clustering system with \( \alpha = 1.5 \) (Figs. 12 (c)–(f)). All \( \tau \)'s for \( \Phi_L(k, t) \), \( \Phi_S(k, t) \), \( \Phi_{s,L}(k, t) \), and \( \Phi_{s,S}(k, t) \) are plotted. It is well established that all relaxation times for both collective and self and for different components behave similarly for conventional glass models such as the Lennard-Jones and hard sphere mixtures\(^ {54} \). This is indeed the case for \( \alpha = 2.0 \) as shown in Fig. 12 (a). Aside that \( \tau \) for the small particles is slightly smaller, their temperature dependence are identical. Agreement is even better at high densities for \( \rho = 2.0 \) (Fig. 12 (b)). For \( \alpha = 1.5 \), \( \tau \) at the low density \( \rho = 0.675 \) is almost identical with those for \( \alpha = 2.0 \) (Fig. 12 (c)). Interestingly, even at the density \( \rho = 1.1 \) where the anomalous logarithmic decay is observed for \( \Phi_L(k, t) \) and \( \Phi_{s,L}(k, t) \), \( \tau \)'s for all correlation functions are similar except for small deviation of \( \tau \) for \( \Phi_{s,L}(k, t) \) at the lowest temperature. The situation changes at higher densities. At \( \rho = 2.0 \), the four \( \tau \)'s deviate from each other (Fig. 12 (e)). \( \tau \)'s for the collective parts tend to be larger than those of the self parts. Especially, \( \tau \) for \( \Phi_{s,S}(k, t) \) is substantially smaller and its temperature dependence is weaker than other \( \tau \)'s. This trend is more enhanced at higher density, \( \rho = 3.0 \) (Fig. 12 (f)). These observations are consistent with overall trend demonstrated in Fig. 11 and strongly indicates decoupling of dynamics between the self and collective fluctuations and between small and large particles. Dynamics of the self part of small particles is the fastest and its relaxation is very different from the typical glassy dynamics.

### B. Relaxations of the center of mass correlations

We investigate microscopic origins of differences of dynamics between the collective and self correlations and
between the small and large particles. Similar decoupling of glassy dynamics has been also reported for a binary mixture of GEM near the glass transition temperature, according to which the faster relaxation of the self part is due to intercluster hopping of particles. The facilitation of the relaxation due to hopping is even more spectacular for the cluster crystals of a monatomic GEM system, where the particles hop over 10 nearest neighbors distances in a single hopping event.

We first introduce the collective intermediate scattering function for the clusters, defined by the center of mass of clusters instead of particles as

\[ \Phi^c_{\alpha}(k,t) = \left\langle \frac{\rho^c_{\alpha}(k,t)\rho^c_{\alpha}(-k,0)}{|\rho^c_{\alpha}(k,0)|^2} \right\rangle, \quad (9) \]

where \( \rho^c_{\alpha}(k,t) = \sum_{j\in\Omega^c_{\alpha}} \exp[i\vec{k} \cdot \vec{r}_{ij}(t)] \). \( \Omega^c_{\alpha} \) denotes the set of indices for the clusters of the component \( \alpha \) and \( \vec{r}_{ij} \) is the position of the center of mass of the \( j \)-th cluster. The self part \( \Phi^c_{s,a}(k,t) \) is defined in the same way.

Note that the self part is calculated only during the time interval in which a particle resides in a single cluster. Figure 13 shows \( \Phi^c_L(k,t) \) and \( \Phi^c_S(k,t) \) for \( \alpha = 1.5 \) at \( \rho = 2.0 \), at which the system is in the trimer phase. \( \Phi^c_L(k,t) \) and \( \Phi^c_S(k,t) \) are also shown in the figure for comparison. At high temperatures (100 \( \lesssim T \lesssim 120 \)), \( \Phi^c_L(k,t) \) decays faster than \( \Phi^c_S(k,t) \) in short times, while it merges to \( \Phi^c_L(k,t) \) at long times. This faster relaxation can be understood as the instability of clusters at the high temperatures as demonstrated in Figs. 6 and 8, where \( g_{LL}(r) \) exhibits a low and broad peak. The positions of the center of mass of the clusters are easily changed by annihilation or rearrangement by thermal fluctuations. At long time, however, \( \Phi^c_{s,a}(k,t) \) almost collapses to \( \Phi^c_L(k,t) \) for all temperatures. This result eloquently demonstrates that the collective slow dynamics of \( \Phi^c_L(k,t) \) is governed by slow dynamics of clusters each of which behaves like a rigid molecule. Similar behavior is observed for the small particles. However, \( \Phi^c_{s,a}(k,t) \) decays slightly faster than \( \Phi^c_S(k,t) \). This is speculated as the consequences that the clusters of small particles are more unstable than the larger ones as evidenced as a lower and broader peak of \( g_{SS}(r) \) [see Figs. 6 and 8]. From these observations, we conclude that glassy slow dynamics of both large and small collective fluctuations are governed not by individual particles but by the clusters.

Next, let us compare the self and collective dynamics. Substantial difference of the shapes of the collective and self correlation functions and their relaxation times discussed in the previous subsection suggests that there exists another relaxation mechanism in the self-correlation functions to facilitate dynamics. To clarify this point, we introduce another function called the single particle correlation function without hopping defined by

\[ \tilde{\Phi}_{s,a}(k,t) = \left\langle \frac{1}{N_{a}(t)} \sum_{j\in\tilde{a}(t)} e^{ik\cdot(r_{ij}(t)-r_{ij}(0))} \right\rangle, \quad (10) \]

where \( \tilde{a}(t) \) denotes a set of particles of the \( a \)-th component which belong to the same clusters in a time window \( (0,t) \). We expect this function to detect particles which have not left the cluster during this time window. This function is introduced in order to assess the contribution of the intercluster particle hopping during the relaxation. In Figure 13, we show the results at a large density and at a low temperature, where the characteristics of the two functions are most clearly seen. We observe several interesting features, in particular, for the large particles. First, the self-part of the center-of-mass correlator \( \Phi^c_{s,L}(k,t) \) agrees very well with \( \Phi^c_L(k,t) \) and \( \Phi^c_{s,L}(k,t) \) from the short to intermediate time windows where the plateau is well developed, before it departs from the plateau. Relaxation of \( \Phi^c_{s,L}(k,t) \) is slower than those of \( \Phi^c_L(k,t) \) and
The intermediate scattering functions defined in several ways (see text) for the system with $\alpha = 1.5$ at $\rho = 2.0$ and several temperatures. (a) The lines is $\Phi_c^L(k, t)$ for large particles defined by Eq. (9) and the dots is $\Phi_L(k, t)$. The corresponding functions for the small clusters and particles. The several intermediate scattering functions of the (c) large and (d) small particles for the system at $T = 85$. $\Phi_c^L(k, t)$ and $\Phi_{s,L}(k, t)$ are defined by Eqs. (9) and (10). $\Phi_{s,L}(k, t)$ is the corresponding self part defined in the same way as Eq. (9).

$\Phi_c^L(k, t)$. Eventually $\Phi_{s,L}^c(k, t)$ abruptly relaxes to zero with jerky oscillations, which is due to dissociation and annihilation of clusters at long times. This result demonstrates that the self dynamics and the collective dynamics of clusters are similar as it is the case for canonical simple glass formers. In other words, the difference between the collective $\Phi_L(k, t)$ and the self $\Phi_{s,L}(k, t)$ is attributed to the dynamics of the individual particles inside each clusters and the inter-cluster hopping of the particles. The effects of the intra-cluster dynamics and the inter-cluster hopping are distinguished by comparing $\Phi_{s,L}(k, t)$ and $\Phi_{s,L}(k, t)$ in Fig. 13 (c). The two functions display the same behavior in the $\beta$-relaxation regime, while $\Phi_{s,L}(k, t)$ shows clearer plateau than $\Phi_{s,L}(k, t)$ and its slow relaxation is similar to $\Phi_L(k, t)$. This fact demonstrates that the intra-cluster dynamics, detected by both functions, causes the low plateau height and is the primary reason for the different shape of $\Phi_L(k, t)$ in the short-time window. Fig. 13 (c) also shows that the hopping is responsible for the faster relaxation of $\Phi_{s,L}(k, t)$ than $\Phi_L(k, t)$. On the other hand, the dynamics of the small particles shown in Fig. 13 (d) is more complicated than that of the large ones. The single-particle correlation function without hopping $\Phi_{s,S}(k, t)$ has a higher plateau than $\Phi_{s,L}(k, t)$ and the self part of the center-of-mass correlator $\Phi_{c,S}(k, t)$ also displays a higher plateau than the collective $\Phi_S(k, t)$ and its single-particle counterpart $\Phi_S(k, t)$. Since both $\Phi_{c,S}(k, t)$ and $\Phi_{s,S}(k, t)$ do not contain the particles which hop to other clusters, one concludes that the inter-cluster exchange of the particles is one of the reasons for the faster relaxation of $\Phi_{s,L}(k, t)$. However, the departure of $\Phi_{s,S}(k, t)$ from $\Phi_S(k, t)$ and $\Phi_S(k, t)$ starts before that of $\Phi_{s,S}(k, t)$ from $\Phi_S(k, t)$. This hints that a different type of dynamics may also exist and affect the relaxation of small particles.

### C. Higher order singularities

The most outstanding dynamical property of the GHP glass is the logarithmic relaxation appearing at densities where $T_g(\rho)$ exhibits minima and the particles start forming clusters. As shown in Fig. 11 (b), this anomalous relaxation is most clearly seen at $\rho = 1.1$ where the large particles start forming the dimer. The plateau of $\Phi_L(k, t)$ disappears and the relaxation becomes logarithmic, whereas $\Phi_S(k, t)$ still show the two-step relaxation. The logarithmic relaxation has been originally predicted by MCT as a signal of the so-called higher-order $(A_3$ or $A_4$) singularity around the end point of the MCT (dynamical) transition line. Subsequent simulations and experimental studies demonstrated the logarithmic relaxation in various systems, such as short-ranged attractive colloids, star polymers, soft colloidal particles, square-shoulder potential fluids, polymer blends, binary mixtures of particles with disparate size ratio, proteins, and tRNA. This higher-order singularity tends to appear when the two competing glassy dynamics coexist in the system. For the attractive glasses, the glass transition caused by hard-sphere-like repulsion competes with the glass transition caused by bonding of particles due to sticky short-ranged attraction. For binary systems with the disparate size ratio, the two glassy dynamics characterized by disparate time-scales compete. In our system, the coexistence of the two glass phases,
the monomer glass and dimer glass is expected to be the origin of the logarithmic singularity. At the lowest temperature in our system the logarithmic relaxation persisted over four decades and this is observed for both collective and self parts of the correlation functions. To verify that the observed behavior is genuinely due to the higher-order singularity, we fit the data for $\Phi_L(k,t)$ with the MCT asymptotic function:

$$\Phi_L(k,t) \sim f_k - H_k^{(1)} \ln(t/t_0) + H_k^{(2)} \ln^2(t/t_0),$$

where $f_k$, $H_k^{(1)}$, and $H_k^{(2)}$ are the critical non-ergodicity parameters, the critical amplitudes of the first, and second orders, respectively. The time scale $t_0$ is determined by the plateau height. We here neglect higher order terms, $\ln^3(t/t_0)$ and $\ln^4(t/t_0)$, which can be the same order of magnitude as the term $\ln^2(t/t_0)$ but is predicted to vanish in the case of the $\alpha_4$ singularity. $f_k$, $H_k^{(1)}$, and $H_k^{(2)}$ calculated for $\rho = 1.1$ are plotted as functions of $k$ in Figs. 14 (a)–(c). We determined $t_0$ in such a way that $f_k = 6.0 \simeq 0.7$. The curves of $f_k$ for different temperatures collapse on a single function as shown in Fig. 14 (a). In Figure 14 (b), we plot $H_k^{(1)}$ scaled with a $k$-independent and $T$-dependent function $B(T)$. This result demonstrates that $H_k^{(1)}$ is self-similar in $k$ and can be decomposed as $H_k^{(1)} = h_k B(T)$. This is consistent with the prediction of MCT which claims that $B(T)$ is independent of $k$.

The concave-to-convex crossover as $k$ increases shown in Fig. 15 shows $H_k^{(2)}$. We find that $H_k^{(2)}$ is negative for small $k$ and positive for large $k$, and it vanishes at $k \approx 6.0$ which is close to the first peak of the static structure factor for the large particles. If $\Phi_L(k,t)$ is purely logarithmic, $\Phi_L(k,t)$ is a straight linear function of $\ln(t/t_0)$. The deviation from a logarithmic function is found at small and large $k$. Although our result shares similarity with other systems known to exhibit the singular dynamics, the wavevector at which $H_k^{(2)} \approx 0$ is much larger than those of other systems. In our systems, this wavevector is close to $k \approx 2\pi/\sigma_L$, implying that the microscopic length scale is at play in our model and that the mechanism behind the singularity is different from other systems. Another difference is that the singular dynamics is most clearly observed for the large particles. For other systems, such as the binary mixture with disparate size ratio, the singular dynamics is observed for small particles.

In Figures 14 (d)–(f), the density dependence of $f_k$, $H_k^{(1)}$, and $H_k^{(2)}$ is shown. One finds no qualitative difference of these parameters slightly below ($\rho = 1.0$) and above ($\rho = 1.2$) the critical point, although the parameters for $\rho = 1.2$ are slightly smaller. This is in stark contrast with the case of the short-range attractive colloids for which $f_k$ discontinuously changes in the vicinity of the singular point. Notice, however, that the latter
is a generic feature of the dynamical singularity but it is
due to the intervention of the attractive glass transition
caused by strong bonds of the colloidal particles. According
to the original formulation of MCT, the higher order
dynamical singularity is not necessarily accompanied by
the discontinuous changes in the critical parameters.

As the density increases and reaches the second mini-
num of $T_g(\rho)$ at $\rho \approx 1.8$, where the large particles form
trimers and the small particles form dimer, the loga-
ritmic relaxation is observed for the self part of the large
particles, $\Phi_{s,L}(k, t)$, and for the collective and self parts
of the small particles, $\Phi_S(k, t)$ and $\Phi_{s,S}(k, t)$, as shown
in Figs. 11 (e), (j), and (k). $\Phi_L(k, t)$ remains to be a
two-step relaxation function. At the third minimum at
$\rho \approx 2.5$, where the number of particles per cluster in-
creases further, we have not found any logarithmic relax-
ation any more. Although the higher-order singularities
are most clearly seen at the phase boundary from the
monomer to dimer phases, it is unclear whether they are
completely absent at higher densities or they are simply
masked by other complicated relaxation mechanism such
as intercluster hopping.

V. CONCLUSION

In this paper, we have presented detailed numerical
results for structural and dynamical properties of the
binary generalized Hertzian potential (GHP) fluids super-
cooled near the glass transition temperatures. We
especially focused on the interplay of glassy slow dynam-
ics with cluster formation at high densities. The multiple
maxima and minima observed in $T_g(\rho)$ synchronizes with
the growth of the cluster sizes. The cluster size $n$ shows
stepwise increases at every minimum of $T_g(\rho)$. Contrary
to the conventional glass formers, each of collective and
self parts of the intermediate scattering functions for the
large and small particles exhibits a distinct dynamics at
high densities. The collective part is dominated by dy-
namics of the clusters’ center of mass, whereas the self
part is influenced sensitively by hopping and intra-cluster
fluctuations. The terminal relaxations for both the col-
lective and self parts are influenced by the life time of the
clusters. Most significant in our studies is the loga-
rithmic relaxation observed most clearly at the phase
boundaries separating the monomer and dimer glasses
shown as the minima of $T_g(\rho)$. At the first minimum
of $T_g(\rho)$, only the large particles exhibits the logarith-
mic relaxation, and the singularity of the small particles
is observed at the second minimum. The singular dy-
namics we observed agrees well with the prediction of the
mode-coupling theory.\(^{51,59}\) However, the singularity
were not clearly observed at higher densities where the
size of clusters are larger, which may be hidden due to the
complex intra- and inter-cluster dynamics. The stepwise
change of $n$ as a function of density and the fact that this
change becomes sharper as the temperature is decreased
suggest the putative thermodynamic liquid-liquid transi-
tion between the different cluster phases at an even lower
temperature. We also observed that the isothermal com-
pressibility develops a peak in the vicinity of the density
at which the first clustering is observed. The temperature
range over which we have investigated is too high to draw
any solid conclusion about the liquid-liquid phase transi-
tion. Further and independent investigation is required.
However, we envisage that the (thermodynamics + dy-
namic) phase diagram near the first glass-glass transition
(from the monomer to dimer glass phases) would look like
Fig. 16. As sketched in this figure, we speculate that the
liquid-liquid phase binodal line lies down at the low tem-
perature region and would look similar to the solid-solid
binodal found for the cluster crystal of the monatomic
Generalized Exponential Model (GEM) [see Fig. 1 of
Ref.\(^{15}\)]. On the other hand, the MCT dynamical transi-
tion line would look like the two dashed lines $T_{MCT}(\rho)$’s
in this figure. We expect that at the intersection (more
precisely at the close vicinity of the intersection) of the
two lines rests the $A_3$ or $A_4$ singular point. Note that
this is not a proof, but it is known in many systems that
the higher order singularities are observed in the vicinity
of the intersection or termination point where the two
glass lines meet.\(^{51}\) Also plotted in this figure are the loci
of the maxima of the compressibility and the minima of the
iso-$\tau$ lines ($T_g(\rho)$). This is still a preliminary result
but it suggests that the two loci meet at a prospective
liquid-liquid critical point at a low temperature. We still

![Figure 16. A schematic phase diagram near the glass-glass transition around $\rho \approx 1.1$. The black solid line is the glass-
transition line, $T_g(\rho)$, defined as the iso-$\tau$ line with $\tau = 10^3$. The gray solid lines are the iso-$\tau$ lines for different $\tau$ (see legend). The broken green and cyan lines are the speculated MCT critical temperatures $T_{MCT}$ for the monomer and dimer
glasses, respectively. The $A_3$ or $A_4$ singular point (star) lies at the end point of one or both of the two lines. The blue
pentagons and red diamonds are the loci of the maxima of the compressibility and the minima of the iso-$\tau$ lines obtained by
our simulations, respectively. These two loci are extrapolated to lower temperatures where they may meet at the putative
liquid-liquid critical point which is given by the terminal point of the coexistence region drawn as the dark blue shaded area.](image-url)
do not know whether the observed higher order dynamical singularity is generically connected to the underlying liquid-liquid thermodynamic transition. The glass-glass dynamic crossover (such as the fragile-strong crossover) above the liquid-liquid critical point has been discussed in the past but, to the best of our knowledge, the dynamical singularity has never been discussed in the context of the liquid-liquid phase transition. It would be worthwhile to study whether this dynamical anomaly is universally linked to thermodynamic anomaly.

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