Shape of Dynamical Heterogeneities and Fractional Stokes-Einstein and Stokes-Einstein-Debye Relations in Quasi-Two-Dimensional Suspensions of Colloidal Ellipsoids

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We examine the influence of the shape of dynamical heterogeneities on the Stokes-Einstein (SE) and Stokes-Einstein-Debye (SED) relations in quasi-two-dimensional suspensions of colloidal ellipsoids. For ellipsoids with repulsive interactions, both SE and SED relations are violated at all area fractions. On approaching the glass transition, however, the extent to which this violation occurs changes beyond a crossover area fraction. Quite remarkably, we find that it is not just the presence of dynamical heterogeneities but their change in the shape from stringlike to compact that coincides with this crossover. On introducing a suitable short-range depletion attraction between the ellipsoids, associated with the lack of morphological evolution of dynamical heterogeneities, the extent to which the SE and SED relations are violated remains unchanged even for deep supercooling.

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While it is not possible to distinguish conventional liquids from supercooled ones using conventional static structural measures, a dynamical signature unique to the latter is the presence of spatial and temporal heterogeneities [1–5]. Regions of predominantly fast particles that contribute primarily to diffusivity, D, are spatially decoupled from the slow regions that govern the bulk viscosity η or, equivalently, the structural relaxation time τ_α [4,5]. A consequence of dynamical heterogeneities (DH) is the Stokes-Einstein (SE) relation $D^T = (k_BT/6\pi\eta a)$ [6], and/or the Stokes-Einstein-Debye (SED) relation $D^\theta = (k_BT/8\pi\eta a^3)$ [7], which are hallmarks of simple liquids, breakdown [4,5,8]. Here, the superscripts T, θ denote translational and rotational degrees of freedom (DOF), respectively, a is the particle radius, and k_BT is the thermal energy. The breakdown occurs at $T \sim 1.2T_g$, where T_g is the glass transition temperature. Below T_g, the SE relation has a fractional form, $D^T \propto {\tau_\alpha}^{-\xi}$ with $\xi < 1$. It has been shown recently that the extent of SE breakdown depends on spatial dimensionality—with weak or no breakdown ($\xi \sim 1$) until T_g in four dimensions, and the breakdown becoming progressively stronger ($\xi < 1$) with decreasing dimensionality [9,10]. Moreover, simulations predict that in two dimensions (2D), the SE relation is not valid ($\xi > 1$) even at high T [9,11]. However, with increasing supercooling a crossover in the exponent from $\xi > 1$ to $\xi < 1$ is observed [9,11]. Thus far, numerous studies have explored the connections between the extent of SE/SED breakdown and the standard quantifiers of DH, namely, the stretching exponent β, the non-Gaussian parameter $\alpha_2(t)$, and the four-point dynamic susceptibility χ_4 [4,9,12,13]. A key question, however, has remained unanswered. Do morphological changes in DH influence the breakdown of SE and/or SED relations? This question becomes all the more relevant in the context of random first-order transition (RFOT) theory, a prominent thermodynamic approach, which predicts a change in the morphology of DH from stringlike to compact on approaching the glass transition [14]. These predictions have been verified in recent experiments [15]. In fact, recent simulations have suggested that in three dimensions, although DH emerges at the onset temperature of slow dynamics T_o, the violation of the SE relation starts at the dynamical crossover temperature $T_s < T_o$ [16]. Interestingly, for $T < T_s$, $\chi_4 \propto {\xi_4}^3$, which indicates that DH are compact [16]. Here, ξ_4 is the dynamic correlation length. Furthermore, recent colloid experiments have shown that the shape of DH change from stringlike to compact on introducing attractive interactions [17], albeit its influence on the breakdown of the SE relation has not been explored. In fact, at present it is *even* unclear whether DH in the rotational DOF also shows morphological changes on approaching the glass transition, let alone its influence on the validity of the SED relation.

Before addressing the above questions, it is imperative to first highlight the lack of consensus between the two complementary approaches used to investigate the validity of the SED relation in supercooled liquids. Numerical studies, where D^θ is directly extracted from particle trajectories—the "Einstein method," find that the SED relation breakdown to the same extent as the SE ($D^\theta \propto {\tau_\alpha}^{-\chi}$ with $\chi < 1$) [18]. On the contrary, in studies that have access to the nth-order orientational relaxation

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time τ_n, only $n = 2$ can be accessed in molecular experiments, invoke the "Debye model" $D^\theta \propto (1/\tau_n)$, and find the SED relation to be valid even for deep supercooling ($(1/\tau_n) \propto \tau_\alpha^{-\chi}$ with $\chi = 1$) [2,19]. In supercooled liquids, the orientational correlators decay as stretched-exponentials leading to the failure of the Debye model. Simulations on hard dumbbells find that $1/\tau_2$, nevertheless, continues to scale linearly with τ_α, albeit D^θ extracted from the Einstein method shows a breakdown [20]. Recent colloid experiments that probed the dynamics of anisotropic tracers in a bath of smaller hard spheres, however, find that the SED relation remains valid even close to the glass transition, irrespective of the method used [21]. It is well known that the breakdown of the SED/SE relation depends on the size, shape, and roughness of the tracers with respect to the host [12,22]. It would therefore be worthwhile to investigate the SED and SE relations in an experimental model system where particle self-diffusivities, as opposed to tracer diffusivities, can be directly accessed.

Suspensions of micrometer-sized colloidal ellipsoids are an ideal test bed to probe translational and rotational dynamics in real-space and with single-particle resolution. In this Letter, we use previously acquired microscopy data [23] to investigate the SE and SED relations in quasi-two-dimensional suspensions of colloidal ellipsoids, aspect ratio $\alpha = 2.1$, with repulsive as well as attractive interactions. As seen in numerical studies in 2D for isotropic particles [9], we find that, for ellipsoids with purely repulsive interactions, the SE and SED relations are violated at all area fractions. Further, DH for both orientational and translational degrees of freedom become increasingly compact on approaching the glass transition [14]. While the Debye model fails irrespective of the nature of the inter-particle interactions, $1/\tau_n$ couples with τ_α for the repulsive case and decouples for the attractive case due to the onset of pseudonematic domains. Most importantly, we forge a link between the morphological evolution of DH and the crossover in the fractional SED and SE relations.

The experimental details are as described in Refs. [23,24]. First, we examined the validity of the SED relation, using the aforementioned approaches for ellipsoids with purely repulsive interactions. To ascertain if the Debye model can be used to estimate D^θ, we computed the nth-order orientational correlation function, $L_n(t) \equiv (1/N)\langle\sum_{k=1}^{N} \cos n[\Delta\theta_k(t)]\rangle$ [23,28] for $n = 2..5$ and for all area fractions, ϕ, investigated. Here, $\Delta\theta$ is the angular displacement of the kth ellipsoid, t is the lag time, and $\langle\ldots\rangle$ represents the time averaging. As seen in earlier experiments on colloidal ellipsoids ($\alpha = 6, 9$) [28], even for $\phi = 0.28$, the long-time decay of $L_n(t) = \exp[-(t/\tau_n)^\beta]$ was found to be a stretched-exponential ($\beta < 1$) [Fig. 1(a)]. On approaching the glass transition area fraction $\phi_g^\theta = 0.80$, and in accord with findings from experiments and simulations [12,13,20,23,28,29], β was found to

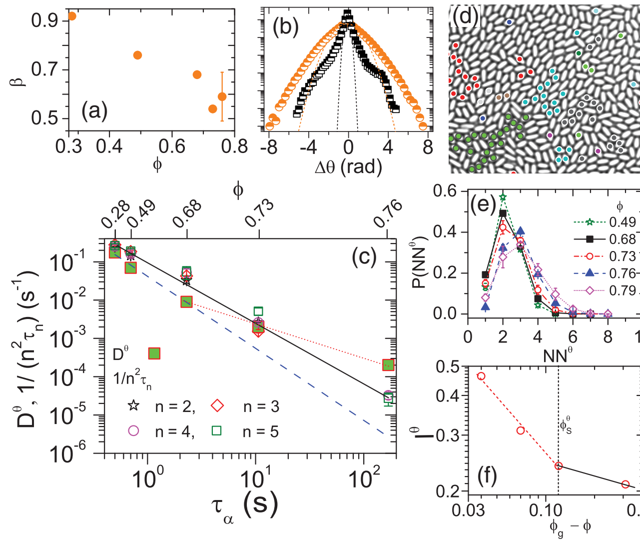

FIG. 1 (color online). (a) Variation of the stretching exponent β obtained from fits to $L_2(t)$, with ϕ. (b) Distribution of $\Delta\theta$, over t^* for $\phi = 0.49$ (half-filled circles) and $\phi = 0.76$ (half-filled squares). The dotted lines in (b) are Gaussian fits to $P(\Delta\theta)$. (c) Orientational diffusion coefficient D^θ and inverse of the nth-order orientational relaxation time $1/n^2\tau_n$ versus the structural relaxation time τ_α. The lines in (c) show $\tau_\alpha^{-1.2}$ (solid and dashed lines) and $\tau_\alpha^{-0.9}$ (dotted line) dependencies. (d) Clusters of the top 10% orientationally most-mobile particles for $\phi = 0.79$; the colors correspond to distinct clusters. (e) Distribution of orientationally fast nearest-neighbors for an orientationally fast particle $P(NN^\theta)$ for different ϕs. The experimental window at each ϕ was divided into four equal time intervals and the $P(NN^\theta)$ for various intervals were averaged to obtain the error bars in (e). (f) I^θ versus $(\phi_g - \phi)$. Here, $\phi_g = 0.80 \pm 0.01$ [23]. The black solid and red dashed line in (f) are guides to the eye. The vertical dashed line in (f) represents ϕ_s^θ beyond which $\chi < 1$, by Einstein formalism.

decrease [Fig. 1(a)]. This clearly signals a growing departure from the simple Debye type relaxation dynamics and is consistent with earlier observations of the increase in the size of DH in the rotational DOF on approaching ϕ_g [23]. The presence of DH is also reflected in the non-Gaussian nature of particle displacements evaluated over the cage rearrangement time t^* [Fig. 1(b)].

Next, following the Einstein method, we directly evaluated D^θ from the long-time diffusive region of the mean-squared angular displacements, $\langle\Delta\theta^2(t)\rangle = 2D^\theta t$ (see the Supplemental Material [24]). We were unable to calculate D^θ for $\phi > 0.76$, since $\langle\Delta\theta^2(t)\rangle$ does not reach the diffusive limit. Figure 1(c) shows $1/\tau_n$, for $n = 2..5$, and D^θ plotted against τ_α. τ_α at various ϕs was obtained from the decay of the self-intermediate scattering function $F_s(q,t) \equiv (1/N)\langle\sum_{k=1}^{N} \exp[i\mathbf{q}\cdot\Delta\mathbf{r}_k(t)]\rangle$ to $1/e$. Here, the wave vector q is chosen to correspond to the first peak of the pair-correlation function since for this particular choice, τ_α mimics the behavior of η [30]. Owing to the failure of the Debye model even at low ϕs, $1/n^2\tau_n$ and D^θ do not collapse, although they scale similarly with τ_α for

$\phi \leq 0.68$. At low ϕs, D^θ and $1/n^2\tau_n$ are found to scale as ${\tau_\alpha}^{-\chi}$, with $\chi > 1$ [Fig. 1(c)]. Although, the physical origins for these observations are lacking, our findings are consistent with previous studies [9,11]. Moreover, while a weak crossover in the fractional SED relation is observed via the Einstein formalism for $\phi > 0.68$, $1/n^2\tau_n$ for all n show complete collapse and stay coupled to τ_α [Fig. 1(c)]. These results are in agreement with recent simulations on hard dumbbells [20]. Further, analogous to τ_α, τ_n is also dominated by the dynamics of slow particles. Since for $\alpha = 2.1$ investigated here, rotational and translational DH are not spatially decoupled [23,31], we expect $1/\tau_n$ to stay coupled to τ_α.

We next set out to determine if there were any morphological changes in the DH and to explore its connection to the crossover in the fractional SED relation by the Einstein method. To identify DH, we picked the top 10% orientationally most-mobile particles over t^* and clustered them using a protocol followed earlier [23,28] [Fig. 1(d)]. We quantified the shapes of these clusters by finding the most probable number of orientationally fast nearest-neighbors for an orientationally fast particle, $P(NN^\theta)$ [15,17]. A narrow $P(NN^\theta)$ that is peaked at $NN^\theta = 2$ implies stringlike DH, while a broader distribution with $NN^\theta > 2$ signals the presence of more compact DH (see Supplemental Material [24]). Since small clusters will bias $P(NN^\theta)$, we only consider cluster sizes $N^\theta \geq 4$ to quantify their morphology. We find that DH for the orientational DOF become more compact with supercooling [Fig. 1(e)] [14,15]. Interestingly, the morphological changes in DH from stringlike to compact also coincides with the ϕ beyond which a crossover in the fractional SED relation is observed [Figs. 1(c) and 1(e)]. To further strengthen our observations, we define $I^\theta = \int_3^\infty P(NN^\theta) dNN^\theta$, where the limits of the integration ensure that the dominant contribution to I^θ is from compact clusters. Unlike the average cluster size $\langle N_c \rangle$, which diverges as a power law on approaching ϕ_g [23,28], I^θ versus $(\phi_g - \phi)$ shows a change in the slope that coincides with the change in the cluster morphology from stringlike to compact [Figs. 1(c)–1(f)].

Motivated by the above observations, the obvious next step was to examine the connections between the shape of DH in the translational DOF and the SE relation. Albeit the SE relation has been a subject of a large number of investigations [4,5,8], it is only recently that simulations have associated the breakdown of the SE relation with the morphological changes of DH [16]. Figure 2(a) shows the variation of D^T with τ_α for ellipsoids with purely repulsive interactions. Analogous to D^θ, D^T was extracted from the long-time slope of the mean squared displacements, $\langle \Delta r^2(t) \rangle = 4D^T t$ (see Supplemental Material [24]). For $\phi \leq 0.68$, $D^T \propto {\tau_\alpha}^{-\xi}$ and again $\xi > 1$ [Fig. 2(a)]. However, for $\phi > 0.68$, a crossover in the fractional SE relation is observed: $D^T \propto {\tau_\alpha}^{-\xi}$ with $\xi \approx 0.7$ [Fig. 2(a)] [9,11]. Following our earlier line of analysis, we identified

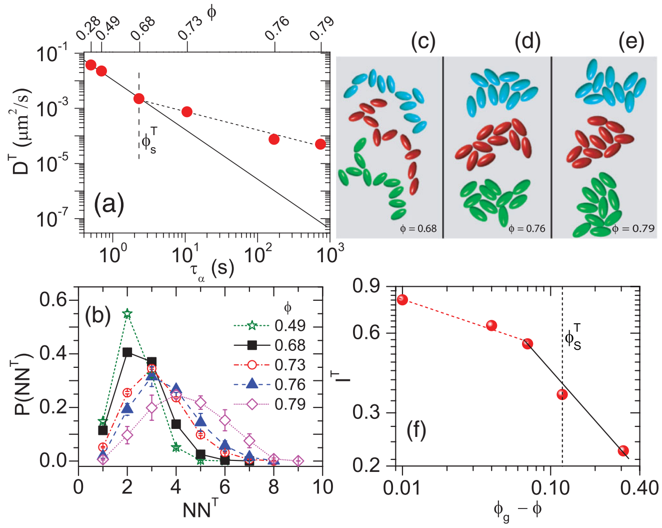

FIG. 2 (color online). (a) Translational diffusivity D^T versus the structural relaxation time τ_α. The lines in (a) show $\tau_\alpha^{-1.8}$ (solid) and $\tau_\alpha^{-0.7}$ (dotted line) dependencies. The vertical dashed line represents the dynamic crossover area fraction $\phi_s^T = 0.68$. (b) Most probable number of translationally fast nearest-neighbors for a translationally fast particle $P(NN^T)$ for different ϕs. Error bars in (b) were obtained as mentioned earlier [Fig. 1(b)]. Representative cluster morphologies for 10-particle clusters for (c) $\phi = 0.68$, (d) $\phi = 0.76$, and (e) $\phi = 0.79$. In (c)–(e), the colors correspond to distinct clusters. (f) I^T versus $(\phi_g - \phi)$. Here, $\phi_g = 0.80 \pm 0.01$ [23]. The black solid and red dashed line in (e) are guides to the eye. The vertical dashed line represents ϕ_s^T beyond which $\xi < 1$.

the most-probable number of translationally fast nearest-neighbors $P(NN^T)$ for a translationally fast particle. Across $\phi = 0.68$, the DH become more compact and $P(NN^T)$ becomes progressively broader with ϕ (Fig. 2b) (see Supplemental Material [24]). To show that the progressive broadening of $P(NN^T)$ is not a trivial outcome of growing $\langle N_c \rangle$ on approaching ϕ_g, we focused on clusters with a fixed size, $N = 10$ particles (see Supplemental Material [24]). Remarkably, Figs. 2(c)–2(e) show that the clusters indeed become more compact on approaching ϕ_g. This allowed us to identify $\phi = 0.68$ with the dynamical crossover area fraction ϕ_s^T. Interestingly, consistent with observations in the orientational DOF, I^T [$= \int_3^\infty P(NN^T) dNN^T$] versus $(\phi_g - \phi)$ shows two slopes with an apparent change in the trend occurring in the vicinity of ϕ_s^T [Fig. 2(f)]. These observations are in line with recent numerical predictions [16] and suggest that the crossover in the fractional SE and SED relation is accompanied by a change in shape of DH from stringlike to compact.

To bolster our claims, it would suffice to show that in the *absence* of changes in the shape of DH, χ and ξ do not show a change on approaching ϕ_g. To this end, we take recourse to the findings from molecular dynamics simulation on attractive hard sphere glasses where a reentrant behavior in the validity of the SE relation was observed [32]. While the

SE relation breakdown for the repulsive as well as the strong attraction case, the dynamics was found to be faster at intermediate attraction strengths with the SE relation remaining valid even for the deep supercooling [32]. This study, however, did not probe the connection between the validity of the SE relation and the nature of DH. In the context of ellipsoids, the introduction of small depletant molecules results in an anisotropic attraction that favors the lateral alignment of ellipsoids over to tip-to-tip ones [23]. Although MCT for hard ellipsoids predicts a single glass transition for both the rotational and translational DOF for $\alpha < 2.5$ [33], recent experiments have observed that depletion attraction enhances pseudonematic ordering at intermediate attraction strengths [23]. Consequently, the orientational glass transition was found to precede the translational one and reentrant glass dynamics was observed only in the translational DOF (see the Supplemental Material [24]. The dynamics for this system was observed to be fastest for an intermediate attraction strength of $\Delta U/k_BT = -1.16$, and allowed access to D^T, D^θ, and τ_n close to the glass transition. Moreover, the decay of $F_s(q,t)$ was found to be logarithmic close to ϕ_g^T and is indicative of its vicinity to the A_3 singularity (see the Supplemental Material [24]). β was once again found to decrease on approaching ϕ_g. In contrast to the repulsive case, the growth of pseudonematic domains with ϕ hinders the relaxation of lower order orientational correlators to a greater degree than the higher order ones. Thus, while $1/n^2\tau_n$ collapses at low ϕ for all n, they show marked deviations on approaching ϕ_g^θ [Fig. 3(a)]. Also, a recent study on the same system has observed that orientational and translational DH are spatially decoupled at this interaction strength [31] and we expect $1/\tau_n$ to progressively decouple from τ_α as well. This is indeed the case here with the decoupling of lower order orientational correlators being more pronounced [Fig. 3(a)]. By the Einstein method, $D^\theta \propto \tau_\alpha{}^{-\chi}$ with $\chi > 1$ [Fig. 3(a)], even close to ϕ_g^θ. Most remarkably, consistent with the absence of crossover in the fractional SED relation, while $P(NN^\theta)$ does not evolve with ϕ [Fig. 3(b)], I^θ versus $(\phi_g^\theta - \phi)$ shows no change in slope [Fig. 3(e)]. Further, for the SE relation, $D^T \propto \tau_\alpha{}^{-\xi}$ with $\xi = 1$, even for deep supercooling [Fig. 3(c)]. Lending further strength to our findings and in stark contrast to our earlier observations [Fig. 2(b)], $P(NN^T)$ does not show any appreciable change with increasing ϕ [Fig. 3(d)]. Moreover, I^T mimics the behavior of I^θ on approaching ϕ_g^T [Fig. 3(e)].

Our observations that the change in the shape of DH coincides with the crossover in fractional SE and SED relations is further substantiated by results for $\Delta U/k_BT = -0.44$. Here, we observe that a crossover in the fractional SE relation at $\phi_s^T \sim 0.73$ is accompanied by the change in the shape of translational DH from stringlike to compact (see Supplemental Material [24]). However, for orientational DOF the shape of DH continues to remain

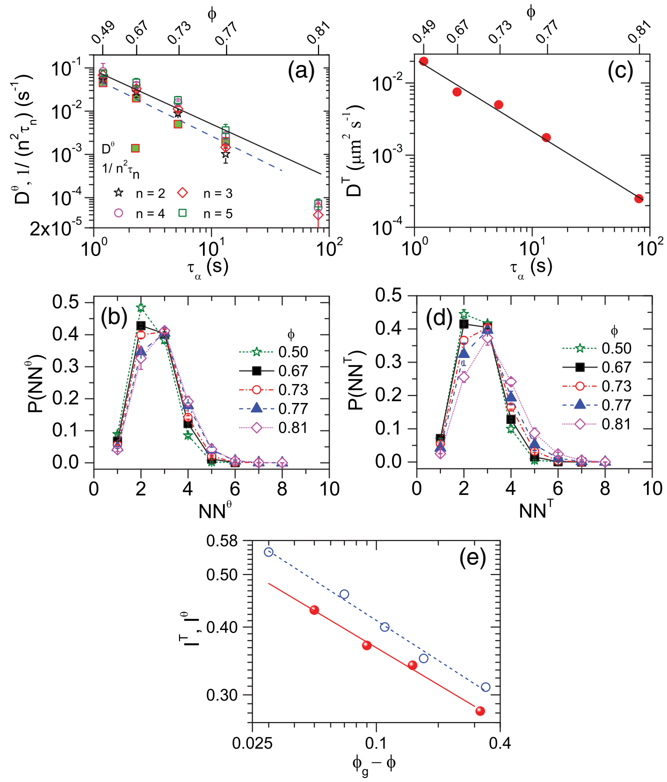

FIG. 3 (color online). (a) Orientational diffusion coefficient D^θ and inverse of the nth-order orientational relaxation time, $1/n^2\tau_n$ versus the structural relaxation time τ_α. The lines in (a) show $\tau_\alpha^{-1.3}$ dependencies. (b) Most probable number of orientationally fast nearest-neighbors for a orientationally fast particle $P(NN^\theta)$ for different ϕs. (c) Translational diffusivity D^T versus τ_α. The solid line in (c) shows $\tau_\alpha{}^{-1}$ dependency. (d) Most probable number of translationally fast nearest-neighbors for a translationally fast particle $P(NN^T)$ for different ϕs. Error bars in (b) and (d) as mentioned earlier [Fig. 1(b)]. (e) I^θ (solid circle) and I^T (hollow circle) versus $(\phi_g - \phi)$. Here, $\phi_g^\theta = 0.82 \pm 0.01$ and $\phi_g^T = 0.84 \pm 0.01$ [23]. The solid and dashed line in (e) are guides to the eye.

stringlike and no crossover is observed in the fractional SED relation within the range of ϕs studied. At higher attraction strengths ($(\Delta U/k_BT) < -1.16$), owing to slow dynamics for $\phi > 0.72$, $\langle \Delta\theta^2(t)\rangle$ and $\langle \Delta r^2(t)\rangle$ did not approach the diffusive limit within the experimental duration and, consequently, we were unable to extract $D^{T,\theta}$. We find that for $\phi \leq 0.72$, no crossover in the fractional SE and SED relations for $\Delta U/k_BT = -1.47$ (see Supplemental Material [24]) and $\Delta U/k_BT = -1.95$ (data not shown) was observed and as expected $P(NN^{T,\theta})$ do not evolve with ϕ.

Taken together, our study has helped establish a link between the morphological evolution of DH and crossover in the fractional SE and SED relations. Our findings show that, albeit DH are present at $\phi < \phi_s^{\theta,T} \sim 0.68$ in both the translational and orientational DOF, it is the change in the shape from stringlike to compact that coincides with the observed crossover. These results are in agreement with recent simulations in three dimensions [16]. Consistent with predictions of RFOT theory [14,15], DH indeed become more compact on approaching the glass transition. While for ellipsoids with purely repulsive interactions, a crossover in the fractional SE and SED relation (Einstein method) is observed beyond ϕ_s, $1/\tau_n$ stays coupled to τ_α. For suitable strengths of short-ranged attractive interaction, the glass melted and allowed us to access the translational and orientational dynamics even for deep supercooling. Although earlier studies, on the same system, have provided clear evidence for the presence of DH [23], these heterogeneities continue to remain stringlike and, consequently, there is no change in exponent in the SE and SED relation. These observations further provide the first experimental confirmation of the validity of the SE relation along the A_3 singularity, a scenario that has remained untested even in supercooled liquids of attractive hard spheres.

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