Apparent Violation of the Fluctuation-Dissipation Theorem due to Dynamic Heterogeneity in a Model Glass-Forming Liquid

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Here we study the relation between the mobility and the translational diffusion in supercooled two-dimensional polydisperse colloidal liquids, using numerical simulations. We find an apparent violation of the Einstein-Smoluchowski (ES) relation $D = k_B T \mu$ (D: diffusion constant; μ: mobility; k_B: Boltzmann's constant; T: temperature). The violation is a direct consequence of the fact that it is difficult for a driven particle to enter a jammed region with high order due to its yield stress. The degree of this apparent ES violation is controlled solely by the characteristic size of slow jammed regions, ξ. Our finding implies that the characteristic time of this problem is not the structural relaxation time τ_α but the lifetime of dynamic heterogeneity, τ_ξ. A supercooled liquid can be regarded to be ergodic only over τ_ξ, which may be the slowest intrinsic time scale of the system.

When a liquid approaches its glass-transition temperature T_g upon cooling, the dynamics of the structural relaxation (α relaxation) not only drastically slow, but also become progressively more heterogeneous [1,2]. However, there is no indication of such heterogeneity in the static density correlation. Thus, it has been believed that dynamic heterogeneity can be seen only through dynamic variables such as trajectory patterns [3,4], the non-Gaussian parameter [3,5], bond-lifetime patterns [6], and multipoint dynamic susceptibilities [7,8]. However, Widmer-Cooper and Harrowell recently showed that heterogeneity in dynamics has a structural origin [9]. We also revealed that dynamic heterogeneity originates from medium-range crystalline order (MRCO) in two different types of two-dimensional (2D) glass-forming liquids [10,11] and a driven granular liquid (2DGL) [12].

In the temperature regions where super-Arrhenius enhancement of the structural relaxation time τ_α and the dynamic heterogeneity are observed, there appears another important feature: the violation of the Stokes-Einstein relation (SE violation), which is, for example, observed as translational-rotational decoupling [2]. Furthermore, it is known that in a nonergodic state, the Einstein-Smoluchowski (ES) relation is also violated [13–22]. The ES relation relates the diffusion constant D to the mobility μ as $D = k_B T_{\text{bath}} \mu$ for a particle put in a thermal bath (temperature T_{bath}) at equilibrium. For such a nonergodic system, the effective temperature defined as $T_{\text{eff}} = D/(k_B \mu)$ [16,22] is usually different from T. Thus, the ratio $T_{\text{eff}}/T_{\text{bath}}$ is used as a measure of the degree of the ES violation [14,15,17–21]. $T_{\text{eff}}/T_{\text{bath}} = 1$ in an ergodic liquid above T_g, as it should be. We note that the ES violation is also seen in other disordered systems such as spin glasses [23].

The ES violation is regarded as a manifestation of the breakdown of the fluctuation-dissipation theorem (FDT), a cornerstone of equilibrium statistical physics. The ES vio-

lation is associated with ergodicity breaking. Since a supercooled liquid is ergodic, the ES relation should hold. Contrary to this, we find its "apparent" violation in numerical simulations of a prototype model of glass-forming liquids, 2D polydisperse colloidal liquids (2DPC), where particles interact with a centrosymmetric repulsive potential. As mentioned above, we recently found in 2DPC [11] and 2DGL [12] that there is a one-to-one relationship between MRCO and dynamic heterogeneity and that the increase of τ_α is related to the growth of the characteristic size of MRCO, ξ. Here we study how dynamic heterogeneity (MRCO) affects the relation between D and μ and reveal a time scale over which the system can be regarded to be "ergodic."

A colloidal system has tremendously contributed to our understanding of the glass-transition phenomena [13]. In this system, increasing the volume fraction of colloids ϕ leads to the dynamical slowing down, implying the existence of a limiting density, ϕ_g, above which the system can no longer be equilibrated with its thermal bath on the experimental time scale and thus undergoes a glass transition. A number of studies on the ES and SE violation have been performed in repulsive colloidal glass-forming systems [13–15,18]. These systems have a significant merit in studying the ES and SE relation since there is no characteristic energy scale; thus, the thermal bath temperature T_{bath} can be kept constant, and ϕ is the only controlling parameter. Furthermore, 2D model systems have a great advantage over 3D systems as structural information may readily be accessed. This is why we use 2DPC [4] as a model.

We used a Brownian dynamics simulation. The particle motion is described by the following Langevin equation: $m_0 d\vec{v}^j/dt = \vec{F}_I^j - \zeta \vec{v}^j + \vec{F}_B^j$, where $\vec{v}^j$ is the velocity of j-th particle. m_0 and ζ are, respectively, mass and friction coefficient, both of which are set to be constant. $\vec{F}_I^j$ is the interparticle force acting on jth particle: $\vec{F}_I^j = -\sum_{k \neq j} \frac{\partial}{\partial \vec{r}_i} U_{jk}(|\vec{r}_{kj}|)$, where $\vec{r}_j$ represents the position of

jth particle and $\vec{r}_{kj} = \vec{r}_k - \vec{r}_j$. We employ the Weeks-Chandler-Andersen potential [24]: $U_{jk}(r) = 4\epsilon\{(\sigma_{jk}/r)^{12} - (\sigma_{jk}/r)^6 + 1/4\}$ for $r < 2^{1/6}\sigma_{jk}$, otherwise $U_{jk}(r) = 0$, where $\sigma_{jk} = (\sigma_j + \sigma_k)/2$ and σ_j represents the size of particle j.

We introduce the Gaussian distribution of particle size. Its standard deviation is regarded as polydispersity $\Delta = \sqrt{(\langle\sigma^2\rangle - \langle\sigma\rangle^2)}/\langle\sigma\rangle$, where $\langle x \rangle$ means the average of variable x_j among all the particles. The thermal noise $\vec{F}_B^j$ satisfies the following fluctuation-dissipation theorem: $\langle\vec{F}_B^j(t) \cdot \vec{F}_B^k(t')\rangle = 4\zeta k_B T_{\text{bath}}\delta_{jk}\delta(t - t')$. To measure the mobility of a particle, we drive a particle of the same size by an external force $\vec{F}_{\text{ex}}$. The motion of this tagged particle is described by $m_0 d\vec{v}/dt = \vec{F}_I - \zeta\vec{v} + \vec{F}_B + \vec{F}_{\text{ex}}$.

Hereafter, we scale the length and time by $\langle\sigma\rangle$ and $t_0 = 0.075 m_0/\zeta$, respectively. We simulate $N = 4096$ particles in a 2D square cell (L^2) under a periodic boundary condition. The volume fraction ϕ is defined as $\phi = \frac{1}{L^2} \times \sum_i^N \pi(\sigma_i/2)^2$. We solve the Langevin equation with an explicit Euler scheme with a time increment $\Delta t = 0.01 t_0$. For all simulations in this Letter, we set $k_B T_{\text{bath}}/\epsilon = 0.025$. Note that as shown in [11], for $\Delta \geq 9\%$, the system becomes glass at a high volume fraction, $\phi_g(\Delta = 9\%) \simeq 0.64$, without crystallization.

First we describe the motion of a tagged particle, which is driven by a constant force $\vec{F}_{\text{ex}} = F_{\text{ex}}\vec{f}$ at $t \geq 0$. Here $\vec{f}$ is the unit vector along the force direction: $\vec{f} = (1/\sqrt{2}, 1/\sqrt{2})$. Then the velocity of the particle increases and reaches the steady velocity $\langle v \rangle_{\text{st}}$. Figure 1(a) shows that the mean displacement of the tagged particle $\langle\Delta r(t)\rangle$ against the time scaled by τ_α, t/τ_α, for several values of F_{ex}. τ_α is estimated from the decay of the intermediate scattering function (ISF) $F(q_p, t) = \frac{1}{N}\sum_j \exp\{i\vec{q}_p \cdot (\vec{r}_j(t) - \vec{r}_j(0))\}$, where q_p corresponds to the wave number of the first peak of the structure factor and $i = \sqrt{-1}$. The α relaxation is more stretched for larger ϕ [11]. The long time decay of the ISF (α mode) is well fitted by a stretched exponential: $\exp\{-(t/\tau_\alpha)^\beta\}$, where β is the stretching parameter. $F(q_p, t)$ always decays to zero for the range of ϕ studied, indicating that our supercooled liquid is ergodic. We also confirm that $\langle\Delta r(t)\rangle$ is linear as a function of t in the long time region [Fig. 1(a)]. From the slope, the steady-state velocity $\langle v \rangle_{\text{st}}$ of the tagged particle is obtained as $\langle v \rangle_{\text{st}} = \lim_{t\to\infty}[\langle\Delta r(t)\rangle/t]$. Figure 1(b) plots the relationship between $\langle v \rangle_{\text{st}}$ and F_{ex}. For $\langle v \rangle_{\text{st}} \leq v_\xi$, $\langle v \rangle_{\text{st}}$ is proportional to F_{ex}. For $\langle v \rangle_{\text{st}} > v_\xi$, on the other hand, $\langle v \rangle_{\text{st}}$ is also proportional to F_{ex}, but with a different proportional constant. Here $v_\xi \equiv \xi/\tau_\xi$, which characterizes the critical velocity below which MRCO is "not" seen by the driven particle. Here τ_ξ is estimated from the decay of the time correlation of the Fourier component of the complex hexatic order parameter $\psi_6(q, t) \equiv \int d\vec{r} e^{i\vec{q}\cdot\vec{r}} \times \sum_{j=1}^N \psi_6^j(\vec{r}, t)\delta(\vec{r} - \vec{r}_j)$ (see below on the definition of ψ_6^j), $\langle\psi_6(q, 0)\psi_6(-q, t)\rangle$, at the wave number $q = 1/\xi$.
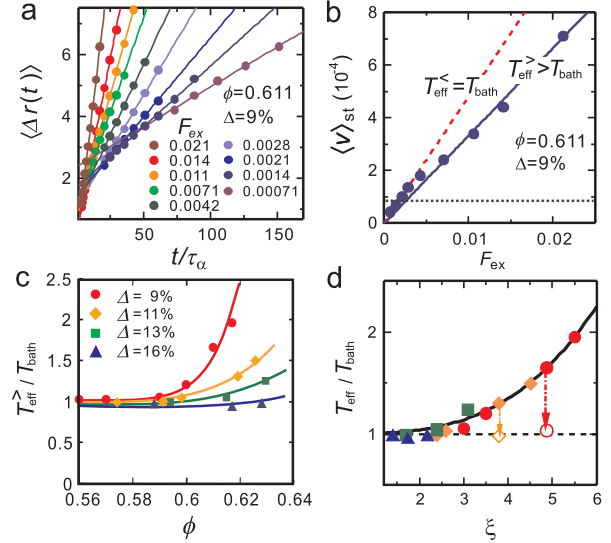

FIG. 1 (color online). (a) $\langle\Delta r(t)\rangle$ vs t/τ_α for several F_{ex}'s at $\phi = 0.611$ and $\Delta = 9\%$. Lines are linear fittings for large t regions. (b) $\langle v \rangle_{\text{st}}$ is plotted against F_{ex}. The dashed and solid lines are linear fittings for $\langle v \rangle_{\text{st}} < v_\xi$ and $\langle v \rangle_{\text{st}} > v_\xi$, respectively. The horizontal dotted line is $v_\xi = 0.9 \times 10^{-4}$. (c) ϕ-dependence of $T_{\text{eff}}^>/T_{\text{bath}}$ for $\Delta = 9\%$, 11%, 13%, and 16%. Curves are to guide the eye. (d) ξ-dependence of $T_{\text{eff}}/T_{\text{bath}}$. All data points for different ϕ's and Δ's can be plotted on a master curve (solid curve): $T_{\text{eff}}^>/T_{\text{bath}} - 1 \propto \xi^3$. The open circle and diamond are $T_{\text{eff}}^</T_{\text{bath}}$ for $\Delta = 9\%$ and $\phi = 0.611$ and for $\Delta = 11\%$ and $\phi = 0.619$, respectively.

The mobility can be estimated from the slope as $\mu = \langle v \rangle_{\text{st}}/F_{\text{ex}}$. Then, the effective temperature $T_{\text{eff}} = D/(k_B\mu)$ is estimated, using D calculated from $D = \lim_{t\to\infty}[\langle\Delta r^2(t)\rangle/(4t)]$. Figure 1(b) indicates that $T_{\text{eff}}^> > T_{\text{bath}}$ for $\langle v \rangle_{\text{st}} > v_\xi$, but $T_{\text{eff}}^< = T_{\text{bath}}$ for $\langle v \rangle_{\text{st}} \leq v_\xi$. This means that for the latter condition the driven particle feels a supercooled liquid is homogeneous and ergodic. Figure 1(c) shows the ϕ-dependence of $T_{\text{eff}}^>/T_{\text{bath}}$, at four different polydispersities Δ for $\langle v \rangle_{\text{st}} > v_\xi$. For smaller Δ, the ratio increases more rapidly with an increase in ϕ. We note that the system is ordered for $\Delta \leq 8\%$ [11,25,26]. How the behavior of $T_{\text{eff}}^>/T$ changes toward the critical Δ, which separates the ordered and disordered region, is an interesting problem, but it is beyond the scope of this Letter. The results unambiguously demonstrate the *apparent* ES violation for the high ϕ region for $\langle v \rangle_{\text{st}}/v_\xi > 1$.

Next we plot $T_{\text{eff}}/T_{\text{bath}}$ against ξ for various ϕ and Δ in Fig. 1(d). This suggests that the degree of the apparent ES violation, $T_{\text{eff}}^>/T_{\text{bath}}$, is controlled solely by ξ. This finding has a remarkable physical message: The degree of the apparent ES violation depends on ϕ and Δ only via their ξ-dependences. It does not depend on the fragility, which is controlled by Δ [11]. We find a simple empirical relation $T_{\text{eff}}^>/T_{\text{bath}} - 1 \propto \xi^3$ [see the solid curve in Fig. 1(d)], whose physical origin remains to be clarified. For $\langle v \rangle_{\text{st}} \leq v_\xi$, we have the relation $T_{\text{eff}}^< = T_{\text{bath}}$, namely, the ES relation holds for $\langle v \rangle_{\text{st}} \leq v_\xi$ [see the open symbols in

Fig. 1(d)]. This means that the relation $\langle v \rangle_{st} \le v_\xi$ is the necessary condition for retaining ergodicity.

Here we note that the observed behavior cannot be explained by the mobility distribution of particles due to the size polydispersity since the difference in the displacement during τ_α between particles larger and smaller than $\langle \sigma \rangle$ is only about 8%–9%, 10%–11%, 11%–12% for $\Delta = 9\%, 11\%, 16\%$, respectively. We also confirmed the absence of fractionation of particles in the lifetime of MRCO (even in our simulation time) [11,12].

To explore the relationship of the apparent ES violation with a spatiotemporal structure of a supercooled liquid, we characterize the local structure of a liquid as follows. We define a complex hexatic bond orientational order parameter as $\psi_6^j = \frac{1}{n_j} \sum_{m=1}^{n_j} e^{i6\theta_m^j}$, where n_j is the number of nearest neighbors of particle j. θ_m^j is the angle between $\vec{r}_{mj}$ and the x axis, where particle m is a neighbor of particle j. We regard particle m as a neighbor of particle j when $|\vec{r}_{mj}| < 1.5$. The value of $\Psi_6^j \equiv |\psi_6^j|$ is equal to 1 if all the particles sit on a hexagonal lattice, whereas becomes nearly 0 for a disordered structure. Since we are interested in the average local structure, which is not affected by thermal fluctuations, we calculated the time averaged Ψ_6^j over a period of τ_α as $\bar{\Psi}_6^j = \frac{1}{\tau_\alpha} \int_{t'}^{t'+\tau_\alpha} dt \Psi_6^j(t)$. We also calculated the correlation length of the hexatic order parameter, ξ [11].

Now we visualize the origin of the apparent ES violation. Figure 2 shows that the position of the tagged particle during $0 \le t \le 40\tau_\alpha$ for $\phi = 0.617$ and $\Delta = 9\%$, where the ES relation is violated [Fig. 1(c)]. In disordered regions, we see frequent hopping events reported in [19] (see Fig. 2, $t = 0$). When the tagged particle is in a rather disordered region, it moves linearly with time (from 0 to $24\tau_\alpha$). However, when it comes to an ordered (yellow, bright) region, it significantly slows down and almost stops moving (from $32\tau_\alpha$ to $40\tau_\alpha$). We can see a clear correlation between the local mobility $\mu_L = \langle \vec{v} \cdot \vec{f} \rangle / F_{ex}$ and the value of $\bar{\Psi}_6^j$ in front of the tagged particle $\bar{\Psi}_6 = \sum_{k=1}^{n_j} h_{jk} \bar{\Psi}_6^k / \sum_{k=1}^{n_j} h_{jk}$, where $h_{jk} = 1(0)$ if $\vec{r}_{jk} \cdot \vec{F}_{ex} \ge 0(<0)$. Figure 3 shows this correlation between $\bar{\Psi}_6$ and μ_L/D as a function of t/τ_α. Note that μ_L/D is proportional to the inverse of the local effective temperature $(T_{eff}^L)^{-1}$. In an equilibrium liquid state at low ϕ [Fig. 3(a)], $\bar{\Psi}_6$ and μ_L/D are more or less constant, and $\langle T_{eff}^L \rangle \cong T_{bath}$. In a supercooled liquid state at high ϕ [Fig. 3(b)], the ES relation is strongly violated. There is a clear negative correlation between $\bar{\Psi}_6$ and μ_L/D [Fig. 3(c)]. This indicates that higher order causes a lower mobility of the tagged particle, i.e., a higher T_{eff}^L. More precisely, the diffusion coefficient has more weight on more mobile particles compared to the mobility of a driven particle. This is because ordered regions have a yield stress so it is hard to drag a particle through them (Fig. 2). Thus, we can say that the apparent ES violation (i.e., $T_{eff}^> \cong$
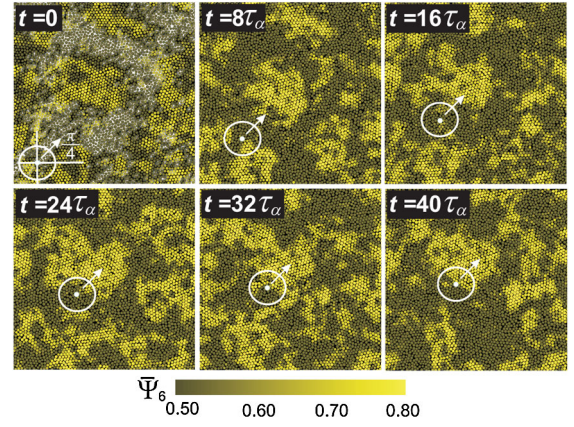

FIG. 2 (color online). The position of a tagged particle for $t = 0, 8\tau_\alpha, 16\tau_\alpha, 24\tau_\alpha, 32\tau_\alpha$, and $40\tau_\alpha$. Here $\phi = 0.617$, $\Delta = 9\%$ and $F_{ex} = 0.014$. The tagged particle is colored in white, whereas other particles are colored from dark yellow to light yellow, reflecting the value of $\bar{\Psi}_6$ (see the color bar). The whitish background in the image ($t = 0$) represents the extremely fast moving particles (hoppers [19]), whose local mean squared displacements $\langle \Delta r^2(10\tau_\alpha) \rangle > 2.5$. This threshold is the "hop" distance introduced in [19].

$\langle T_{eff}^L \rangle > T_{bath})$ originates from the intermittent motion of the driven particle linked to MRCO having size ξ and lifetime τ_ξ.

Next we consider the frequency dependence of the effective temperature to reveal the spatiotemporal nature of the apparent ES violation, employing a method used by Zangi and Kaufman [20]. We drive a tagged particle by applying an alternating external force $\vec{F}_{ex} = F_{ex} \vec{f} \cos\omega t$, where ω is the angular frequency. The ω dependence of the effective temperature is calculated from $k_B T_{eff}^>(\omega) = D(\omega)/\mu(\omega)$. We note that here we study a regime where the maximum velocity exceeds v_ξ. $D(\omega)$ is the Fourier transformed diffusion constant, which is calculated from the Green-Kubo relation $D(\omega) = \frac{1}{2} \int_0^\infty dt \langle \vec{v}(t) \cdot \vec{v}(0) \rangle e^{i\omega t}$. On the other hand, $\mu(\omega)$ is the Fourier transformed mobility, which is calculated from $\mu(\omega) = \langle v(\omega) \rangle / F_{ex}$, where $\langle v(\omega) \rangle = \int_0^\infty dt \langle \vec{v}(t) \cdot \vec{f} \rangle e^{i\omega t}$.
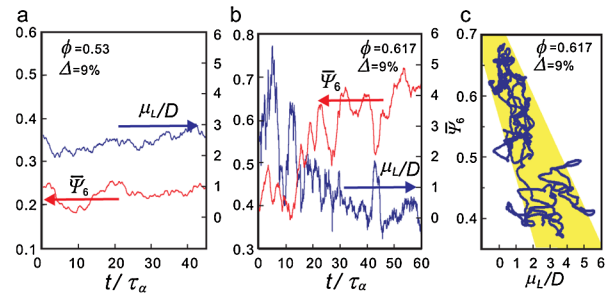

FIG. 3 (color online). Correlation between $\bar{\Psi}_6$ and μ_L/D as a function of t/τ_α. (a) $\Delta = 9\%$, $\phi = 0.530$, $F_{ex} = 0.007$. (b) $\Delta = 9\%$, $\phi = 0.617$, $F_{ex} = 0.014$. (c) Correlation map between $\bar{\Psi}_6$ and μ_L/D for (b).

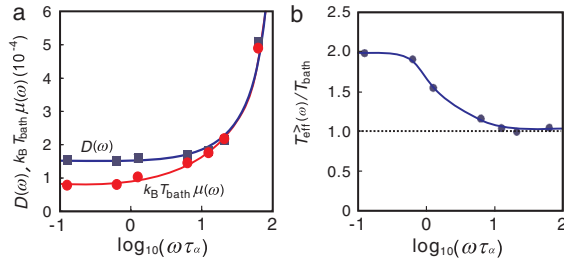FIG. 4 (color online). (a) ω dependences of $D(\omega)$ and $k_B T_{\text{bath}} \mu(\omega)$. (b) ω dependences of $T^>_{\text{eff}}(\omega)/T_{\text{bath}}$. $\phi = 0.617$ and $\Delta = 9\%$. The curves are to guide the eye. $T^>_{\text{eff}}(\omega)/T_{\text{bath}} = 1$ for $\omega \tau_\alpha \gg 1$, whereas $T^>_{\text{eff}}(\omega)/T_{\text{bath}}$ approaches the steady-state value [see Fig. 1(c)] for $\omega \tau_\alpha \ll 1$.

Figure 4(a) shows $D(\omega)$ and $k_B T_{\text{bath}} \mu(\omega)$ as a function of ω. The basic feature is similar to their experimentally observed behavior [17]. At high ω, $D(\omega) \cong k_B T_{\text{bath}} \mu(\omega)$. This is simply because during the time period of $2\pi/\omega$ the particle stays only in either an ordered or a disordered region. At low ω, on the other hand, $k_B T_{\text{bath}} \mu(\omega) < D(\omega)$, which leads to the apparent ES violation. Figure 4(b) shows the ratio $T^>_{\text{eff}}(\omega)/T_{\text{bath}}$ as a function of ω. $T^>_{\text{eff}}(\omega)/T_{\text{bath}}$ exceeds 1 for lower ω. The apparent ES violation occurs only for $\omega < 2\pi/\tau_\alpha$, i.e., only when the tagged particle experiences both highly ordered and disordered regions during $2\pi/\omega$.

This implies that a mode slower than τ_α should have an *exponential* relaxation. On noting that the dielectric spectroscopy picks up a slow mode with a large effective dipole moment, this may explain why the normal alcohols are so anomalous in exhibiting *exponential* relaxation with non-Arrhenius T dependence [27].

In summary, we conclude that the existence of dynamic heterogeneity, or critical-like transient structural ordering [11], is the common origin of slow dynamics, dynamic heterogeneity, and the apparent ES violation in our system. A supercooled liquid cannot be regarded to be ergodic in the time scale shorter than the lifetime of MRCO, τ_ξ. That is, the slowest relaxation time of the system is not τ_α, but τ_ξ, as experimentally confirmed (see, e.g., [2]). The influence of such an extra slow mode on glass-transition behavior has been a matter of discussion (see, e.g., [2,28]). We note that the existence of τ_ξ may have the following significant implications. (i) The ergodicity breaking may occur even above thermal T_g. The reason is that the ultra-slow mode may not affect the thermal signatures of glass transition, since the degrees of freedom related to "mesoscopic" MRCO are much less than the "microscopic" degrees of freedom associated with τ_α. In relation to this, it is worth mentioning that for a probe particle larger than ξ, which does not see any heterogeneity, there may be no ergodicity breaking. Such behavior was indeed reported by Ediger and his co-workers for the rotational motion of probe molecules in a glass-forming liquid (*o*-terphenyl) [29]. It is estimated that for this liquid the ergodicity

breaking may occur at about several K above T_g. (ii) Apparent ES violation may occur when a particle drag speed exceeds $\sim \xi/\tau_\xi$. (iii) Non-Newtonian rheology may appear when a shear rate exceeds $\sim 1/\tau_\xi$ [30]. We hope these will be checked experimentally in the future.

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