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Dynamic scaling for anomalous transport in supercooled liquids

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The anomalous mesoscopic transport in supercooled liquids was investigated using three-dimensional molecular dynamics simulation. We show that the dynamic correlation length, ξ, can be identified as a crossover length between the microscopic and macroscopic transports. We also find that in highly supercooled states, where a clear stress plateau is observed in the stress autocorrelation, cooperative transport, in both the (longitudinal) density diffusion and the (transverse) viscous relaxation, can be characterized by the single length scale, ξ. The present identification of the dynamic correlation length has an advantage over other characterization methods in that it directly interprets the anomalous hydrodynamic transport in terms of the growing length scale. In the context of the present study, we provide a simple explanation for the long-standing problem of the breakdown of the Stokes-Einstein relation.

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As the glass transition point T_g is approached in a supercooled liquid, the structural relaxation dramatically slows and the viscosity steeply increases. The origin of this viscous slowdown is the central issue in glass physics [1–3]. During the last two decades, the concept of dynamic heterogeneity (DH) has been extensively explored in both experimental and simulation studies [4–7]. It is now well established that in glassy liquids, slow structural relaxation accompanies a spatially heterogeneous and correlated particle rearrangement whose characteristic size grows as the system approaches T_g. Usually, the growing length scales associated with DH are characterized by the correlation length of the mobility field, which is measured by the multipoint (in most studies, four-point) density correlation function. This characterization method has been systematically developed and is now considered to be the standard method for quantifying DH (see recent reviews [5–7] and references therein). However, despite the great success in describing the statistical properties of spatiotemporally fluctuating particle dynamics and its cooperative kinetic features in supercooled liquids, the link between DH and anomalous hydrodynamic transport, such as the divergence of the viscosity or of the structural relaxation time, remains unidentified. One of the difficulties in using this approach is an ambiguity in relating the hydrodynamic transport coefficients with the correlation function of the mobility field.

Another important growing length scale that is directly related to the transport can be characterized by the crossover behavior of transport coefficients; one of the most studied phenomena is the crossover from Fickian to non-Fickian diffusion of a tagged particle [8–10]. The crossover length scale can be directly determined from the wave number (k)–dependent relaxation rate of the incoherent (self-) intermediate scattering function, which behaves as $\sim D_s k^2$ and $\sim 1/\tau_\alpha$ for $k\ell^* \ll 1$ and $k\ell^* \gg 1$, respectively [8,9], where D_s is the self-diffusion coefficient, τ_α is the α-relaxation time, and thus the crossover length scale to Fickian particle diffusion is given by $\ell^* \cong \sqrt{D_s \tau_\alpha}$. Notice that in Lennard-Jones systems ℓ^* is found to be comparable to the characteristic size of DH [8]. A similar wave-number dependence of the relaxation rate of a tracer molecule was observed in self-diffusion experiments of supercooled tris-naphthylbenzene [11]. Measurements of the self-diffusion coefficient near T_g are found to be significantly larger than the value predicted from the Stokes-Einstein (SE) relation [12–14]. This breakdown of the SE relation is believed to be a consequence of the cooperative effect associated with DH [4–9].

Recently, similar crossover phenomena in viscous transport and viscoelasticity have been reported [15–18]. With a decrease in k, the k-dependent viscosity, $\eta(k)$, increases from a microscopic viscosity to a macroscopic viscosity, at which point a distinct crossover occurs at a length ξ, which is comparable to the characteristic size of DH [16]. The marked k dependence in $\eta(k)$ is essential to connect transport properties between different length scales [16,17]. Furthermore, by analyzing the k-dependent complex shear modulus, we found that the shear stress is dominated by velocity fluctuations over distances of $\sim\xi$ and times of $\sim\tau_\alpha$, which indicates the shear-stress relaxation and response take place nonlocally not only in time but also in space [17].

These crossover phenomena in the transport strongly indicate that a long-lived correlated structure associated with DH is the essential origin of anomalous transport. It is worth mentioning that in most soft matters (or complex liquids), slow structural relaxation arises as a direct consequence of the existence of a mesoscopic cooperative structure [19,20]. This results in the marked wave-number dependence of the hydrodynamic transport coefficients, where the crossover length from microscopic to macroscopic transport directly measures the cooperative length scale (for example, see Refs. [20–25]). It is interesting and of great importance to investigate whether this physical description is still valid for supercooled liquids.

In this Rapid Communication, we provide concrete evidence that the dynamic scaling holds more generally, where dynamic correlation length, ξ, can be identified as a crossover length between microscopic and macroscopic hydrodynamic transport through the use of a three-dimensional molecular dynamics simulation. Additionally, in the context of the present study, we can provide a simple explanation of the long-standing mystery behind the breakdown of the SE relation.

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We used a three-dimensional model of glass-forming liquids [26–28], which is a mixture of two types of particles, 1 and 2, with $N_1 = N_2 = 20000$. The particles interact through the soft-core potentials $U_{ab}(r) = \epsilon(d_{ab}/r)^{12}$ with $d_{ab} = (d_a + d_b)/2$, where r is the distance between two particles, d_a is the particle size, and $a,b = 1,2$. The mass and size ratios are $m_2/m_1 = 2$ and $d_2/d_1 = 1.2$, respectively. The particle number density was fixed at a value of $N/V = 0.8/d_1^3$, where $N = N_1 + N_2$, and V is the system volume. Space and time were measured in units of d_1 and $\tau_0 = (m_1 d_1^2/\epsilon)^{1/2}$, respectively. The linear dimension of the system was $L = 36.84$. The temperature, T, and the viscosity, η, were measured in units of ϵ/k_B, where k_B is the Boltzmann constant, and $\epsilon\tau_0/d_1^3$. The simulations were performed using velocity Verlet algorithms, in the *NVE* ensemble [29]. The present model has been thoroughly studied by many authors and found to exhibit almost all characteristic and common features of supercooled liquids [26–28].

First, let us define the dynamic correlation length as a crossover length in the wave-number-dependent shear viscosity $\eta(k)$. The detailed method for computing $\eta(k)$ and ξ, as well as the physical meanings of the k dependence of $\eta(k)$, have already been presented in Refs. [16,17], and thus we only show the results. In Fig. 1(a), we show the k-dependent shear viscosity $\eta(k)$, which is essentially the same plot as that shown in Refs. [16,17] but includes additional information. It is evident that with decreasing k, $\eta(k)$ increases from a microscopic viscosity to a macroscopic viscosity and that a distinct crossover occurs at a length ξ. In (b), we show the scaled viscosity $\eta(k)/\eta$ as a function of the scaled wave number $k\xi$ in highly supercooled states ($T \lesssim 0.306$), in which a clear plateau appears in the shear stress autocorrelation [17]. $\eta(k)/\eta$ almost lies on a single master curve, and thus, the viscous transport in highly supercooled states can be characterized only by ξ.

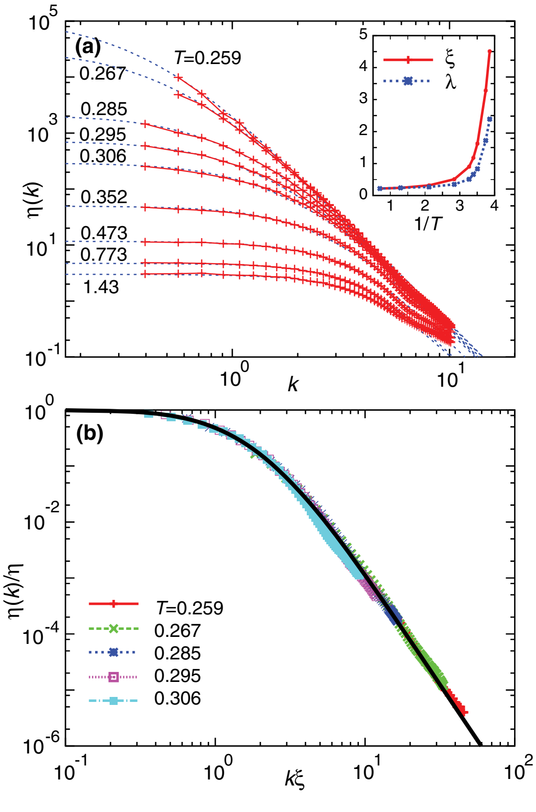

FIG. 1. (Color online) (a) The k-dependent viscosity $\eta(k)/\eta(k = 0)$ as a function of k, for both the supercooled and normal liquid states (red solid curves). The blue dashed curves represent the empirical fitting function $\eta/[1 + (k\xi)^2 + (k\lambda)^4]$, where η is the macroscopic ($k = 0$) viscosity determined by the Green-Kubo formula and ξ and λ are the fitting parameters. The inset shows the temperature dependence of ξ (red solid curve) and λ (blue dashed curve). ξ is the correlation length of the nonlocal viscous response. (b) The scaled viscosity $\eta(k)/\eta$ as a function of the scaled wave number $k\xi$ in highly supercooled states ($T \lesssim 0.306$), which almost lies on a single master curve (thick black solid curve) given by $1/[1 + (k\xi)^2 + 0.289(k\xi)^4]$.

Next, we evaluate whether the dynamic correlation length ξ in the viscous transport gives that in the collective density diffusion. In Fig. 2(a), the k-dependent relaxation time of the density fluctuations $\tau_\rho(k)$ is plotted for both the supercooled and the normal liquid states [30]. Here, $\tau_\rho(k)$ is calculated by fitting the longer time behavior of the coherent scattering function to a stretched exponential function $A_k \exp\{-[t/\tau_\rho(k)]^{B_k}\}$, where A_k and B_k are the k-dependent coefficient and exponent, respectively. We perform the fitting for $t \gtrsim \tau_\alpha$. In this Rapid

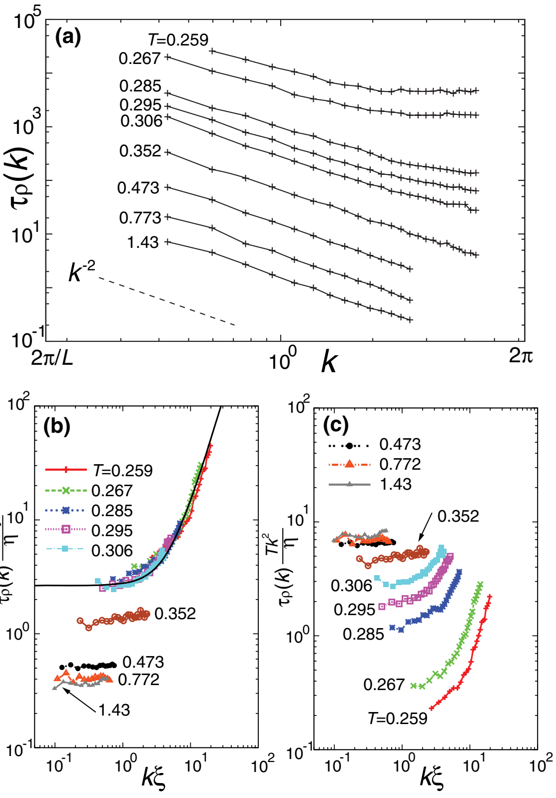

FIG. 2. (Color online) (a) The k-dependent relaxation time of the density fluctuations $\tau_\rho(k)$, for various temperatures. In the long wavelength regime, the diffusive behavior [$\tau_\rho(k) \propto k^{-2}$] can be observed over the entire temperature range. In the diffusive regime $B_k \cong 1$. We plot $\tau_\rho(k)$ scaled by $\eta/Tk^2\xi^2$ and η/Tk^2 as a function of the scaled wave number $k\xi$ in panels (b) and (c), respectively. In panel (b), $\tau_\rho(k) \times (Tk^2\xi^2/\eta)$ in highly supercooled states ($T \lesssim 0.306$) falls on a single master curve (thick black solid curve) given by $2.6 + 0.13(k\xi)^2$.

Communication, τ_α is defined as the relaxation time of the macroscopic ($k = 0$) shear stress autocorrelation that was obtained in the previous study [17]. We can see that the density fluctuations show the diffusive behavior [$\tau_\rho(k) \propto k^{-2}$] in the long wavelength regimes over the entire temperature range.

The slowly relaxing density fluctuations, which we hereafter refer to as $\hat{\rho}$, obey the diffusion equation, $\partial\hat{\rho}/\partial t \cong D_{\mathrm{c}}\nabla^2\hat{\rho}$, where D_{c} is the collective diffusion coefficient [32]. We assume that in highly supercooled states, at lower wave numbers ($k\xi \ll 1$) and frequencies ($\omega\tau_\alpha \ll 1$), the density diffusion should directly reflect the cooperative effect with the characteristic correlation length ξ. Based on this assumption, D_{c} in the supercooled state can be estimated as follows. The restoring force associated with the density fluctuations is given by $-(1/K_0)\nabla(\hat{\rho}/\hat{\rho}_0)$, where K_0 is the compressibility in the long wavelength regime. The friction coefficient (per unit volume) is given by $\zeta \sim \eta\xi^{-2}$ from Stokes law [33]. Therefore, we obtain

$$D_{\mathrm{c}} \cong \frac{1}{K_0}\frac{1}{\eta\xi^{-2}} \sim \frac{\xi^2}{\tau_\alpha}, \tag{1}$$

where we make use of the Maxwell relation $\eta \cong G_0\tau_\alpha$, and the relation $K_0G_0 \sim 1$ is assumed. Here, G_0 is the plateau shear modulus.

Notice that Eq. (1) is similar to the definition of the crossover length that was introduced in the self-diffusion studies in Refs. [8,9]. However, the present argument further indicates that Eq. (1) is an expression of the self-diffusion of the correlated structure associated with DH with the size ξ in the medium with the macroscopic viscosity $\eta \propto \tau_\alpha$ (see also the discussion below). In other words, in supercooled states, the SE relation is violated at the particle level but should be restored at the mesoscopic level.

In contrast, in normal liquid states, where the correlation length does not exceed the particle size, the SE relation remains valid even at the particle scale, and the friction coefficient (per unit volume) is therefore given by ηd^{-2}, where d is the characteristic particle size. In normal liquid states, the hydrodynamic transport coefficients do not show significant differences between microscopic and macroscopic scales, which is because the particle-scale dynamics dominates the hydrodynamic transport properties. Consequently, the density fluctuations relax in an uncorrelated manner and follow the particle motions. Thus, Eq. (1) should be replaced by

$$D_{\mathrm{c}} \cong \frac{d^2}{\eta K_0}. \tag{2}$$

Furthermore, assuming that $1/K_0(\sim G_0) \sim T/d^3$, then $D_{\mathrm{c}} \sim T/\eta d$. Therefore, in normal liquid states, the density diffusion should be described by the single-particle diffusion coefficient.

To check the validity of the present argument, we plot $\tau_\rho(k)$ scaled by $\eta/k^2\xi^2T$ as a function of the scaled wave number $k\xi$ in Fig. 2(b). Figure 2(b) shows that in supercooled states ($T \lesssim 0.306$), $1/\tau_\rho(k)k^2 \sim \xi^2T/\eta$ for $k\xi \lesssim 1$; therefore, the relation (1) holds well. In contrast, in normal liquid states ($T \gtrsim 0.473$), the diffusion coefficient behaves as $\sim T/\eta$ as shown in Fig. 2(c). $T = 0.352$ is the marginal case in the present system. These simulation results are consistent with our argument. The recent self-diffusion experiment [11] shows that the self-diffusion coefficient of tracer molecules becomes enhanced by a factor of ~ 100 when approaching T_g. Therefore, we can estimate that the characteristic size of DH in that case is approximately 10 times the molecular size, which is reasonable.

Interestingly, Fig. 2(b) shows that in highly supercooled states ($T \lesssim 0.306$) $\tau_\rho(k)k^2\xi^2T/\eta$ almost lies on a single curve. Thus, ξ, which is the crossover length of the transverse viscous transport, also provides that of the longitudinal density diffusion. Additionally, in supercooled states, at higher wave numbers ($k\xi \gtrsim 1$), the deviation from diffusive decay becomes apparent and the density fluctuations survive for a longer time than $1/D_{\mathrm{c}}k^2$. We now speculate that the viscoelastic stress stored in the correlated less-mobile regions acts against the restoring force due to density fluctuations, which may prevent the density fluctuations from relaxing during the structural relaxation (frustration effect on $\hat{\rho}$).

Although the detailed arguments and theoretical description of this phenomena will be presented elsewhere [34], here we provide evidence for the link between the long-term viscoelastic stress and the cooperative structural relaxation as follows. First, we define the field variable $\hat{q}(\boldsymbol{r}) = \sum_{i=0}^{N}\Pi_i^{xy}\delta(\boldsymbol{r} - \boldsymbol{r}_i)$, where $\Pi_i^{xy} = \sum_{j\neq i}(\partial U_{ij}/\partial x_i)y_{ij}$ is the shear stress acting on particle i and $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$. The spatial correlation of $\hat{q}(\boldsymbol{r})$ is a measure of the static structural coherence relevant to the shear-stress response. In Fig. 3(a) we plot $S_q(k) = \langle|\hat{q}_{\boldsymbol{k}}|^2\rangle/N$ in supercooled states ($T \lesssim 0.306$), where $\hat{q}_{\boldsymbol{k}}$ is the Fourier transform of $\hat{q}(\boldsymbol{r})$. At all temperatures, hardly any long-range correlation is observed in $S_q(k)$, which indicates that there is no important static structure involving the mesoscopic mechanical response. Therefore, we instead speculate that the origin of the mesosocpic nature of the transport is a dynamic conformation associated with DH. To verify this speculation, we analyze the spatial correlations of another field variable: $\hat{Q}(\boldsymbol{r};\Delta t) = \sum_{i=0}^{N}\Pi_i^{xy}(\Delta t)\Pi_i^{xy}(0)\delta(\boldsymbol{r} - \boldsymbol{r}_i)$, whose correlation is a measure of the coherence of the structural relaxation event during the time duration Δt. Notice the following: Although DH is usually characterized by the correlation of the mobility field, which is quantified by measurements of the particle displacements [5–7], DH is described here through the "stress capability" of particle. Because the

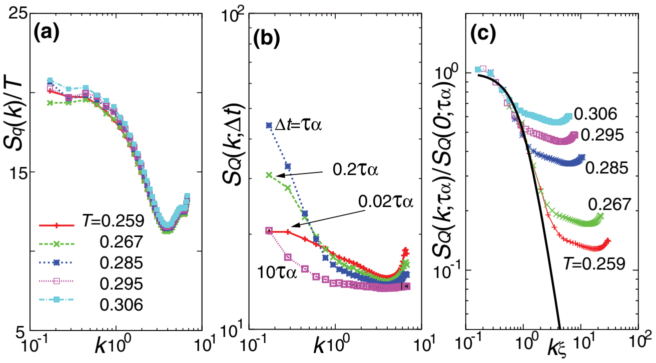

FIG. 3. (Color online) (a) $S_q(k) = \langle|\hat{q}_{\boldsymbol{k}}|^2\rangle/N$ in supercooled states ($T \lesssim 0.306$), which falls onto a single curve. (b) $S_Q(k;\Delta t) = \langle|\hat{Q}_{\boldsymbol{k}}|^2\rangle/N$ at a supercooled state ($T = 0.275$) for various Δt. (c) The scaled structure factor, $S_Q(k;\tau_\alpha)/S_Q(0;\tau_\alpha)$, as a function of the scaled wave number $k\xi$. The thick black solid curve represents the fitting function $1/[1 + (k\xi)^2]$.

relaxation of the longitudinal shear stress proceeds via large (translational) particle displacements for $\Delta t \gtrsim \tau_\alpha$ [16], both characterizations should provide similar information for DH in the long time regime (see also discussion below). In Fig. 3(b) the structure factor of $\hat{Q}$, $S_Q(k;\Delta t) = \langle |\hat{Q}_{\boldsymbol{k}}|^2\rangle/N$, is shown at the supercooled state ($T = 0.275$) for various Δt: $S_Q(k;\Delta t)$ at smaller k grows in time Δt, indicating that the structural relaxation takes place in a correlated manner, which is the most pronounced at $\Delta t \cong \tau_\alpha$. At much larger $\Delta t(\gg \tau_\alpha)$, such correlations diminish. These features are common to DH [5–7]. In Fig. 3(c), the scaled structure factor, $S_Q(k;\tau_\alpha)/S_Q(0;\tau_\alpha)$, is plotted against the scaled wave number $k\xi$, where ξ is the crossover length of the cooperative transport. At smaller wave numbers ($k \lesssim 1$), $S_Q(k;\tau_\alpha)/S_Q(0;\tau_\alpha)$ almost falls onto a single curve; therefore, the coherent length of the structural relaxation also coincides with ξ. These results strongly suggest that the growing dynamic correlation, which transmits the long-term viscoelastic stress, is responsible for the mesoscopic nature of the transport. In our previous study [17], it was found that the plateau shear modulus, G_0, only weakly depends on the temperature and the wave number: G_0 takes its macroscopic value at a wavelength comparable to the particle size, which is in marked contrast to the strong T and k dependences of the viscosity or the structural relaxation time [16,17]. Thus, we can state that although the shear-stress relaxation itself takes place via the coherent particle rearrangement over distances of $\sim\xi$ and times of $\sim\tau_\alpha$, the spatial correlation of the stored stress is much shorter than the cooperative length.

Before closing, we notice the following: Within the temperature range of our simulation, the T dependence of D_s (and thus of ℓ^*) is slightly stronger than that of D_c (of ξ) (not presented here). This slight difference might be due to direct and indirect reflections of the cooperative effects in the coherent and incoherent scattering functions, respectively; though D_c itself directly reflects the dynamical coherence, D_s does not. In addition, the T dependence of ξ is slightly stronger than that of ξ_4, which is the dynamic heterogeneity size measured using the usual four-point correlation function [16]. All of these length scales (ξ, ℓ^*, and ξ_4) reflect certain aspects of the cooperative effects associated with DH, and the physical meanings of these length scales are therefore very similar. However, precisely speaking, they are not the same due to the different nature of the characterization (see also the discussion in Ref. [9]). We remind the reader that in our paper, ξ denotes the coherence (cooperative) length of hydrodynamic transport. Further analysis will be presented elsewhere.

In conclusion, in this Rapid Communication, we have shown through the use of a three-dimensional molecular dynamics simulation that in highly supercooled states, the dynamic correlation length, ξ, could be identified as the crossover length between microscopic and macroscopic transport and that the cooperative nature of the anomalous transport could be characterized only by ξ. Moreover, in the context of this study, we have provided a simple explanation for the long-standing problem concerning the breakdown of the SE relation, which should be a direct result of the cooperative diffusion of the correlated structure with the size ξ in a medium with the macroscopic viscosity $\eta \propto \tau_\alpha$. Therefore, in a supercooled liquid, the SE relation should be restored at the mesoscopic level. The problem involving the breakdown of the SE relation is primarily about the self-diffusion of a tagged particle [the relationship between D_s and η (or τ_α)]. However, the very origin of this problem is the cooperative effect, and the problem is thus difficult to fully understand using only a particle-level analysis. Notice that the conventional theories, such as macroscopic hydrodynamics or mode coupling theory, cannot explain the mesoscopic nature of the anomalous hydrodynamic transport, which are explicitly shown in this Rapid Communication. Therefore, a new point of view is required. Our findings suggest that the anomalous transport in supercooled liquids has a dynamic origin in a mesoscopic length scale.

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[1] M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996).

[2] P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).

[3] K. Binder and W. Kob, *Glassy Materials and Disordered Solids* (World Scientific, Singapore, 2005).

[4] M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).

[5] L. Berthier and G. Biroli, Rev. Mod. Phys. **83**, 587 (2011).

[6] L. Berthier, Physics **4**, 42 (2011).

[7] Edited by L. Berthier *et al.*, *Dynamical Heterogeneities in Glasses, Colloids, and Granular Media* (Oxford University Press, Oxford, 2011).

[8] L. Berthier, Phys. Rev. E **69**, 020201(R) (2004).

[9] L. Berthier *et al.*, Europhys. Lett. **69**, 320 (2005).

[10] G. Szamel and E. Flenner, Phys. Rev. E **73**, 011504 (2006).

[11] S. F. Swallen *et al.*, J. Phys. Chem. B **113**, 4600 (2009).

[12] F. Fujara *et al.*, Z. Phys. B **88**, 195 (1992).

[13] M. T. Cicerone and M. D. Ediger, J. Chem. Phys. **104**, 7210 (1996).

[14] C. A. Angell *et al.*, J. Appl. Phys. **88**, 3113 (2000).

[15] J. Kim and T. Keyes, J. Phys. Chem. B **109**, 21445 (2005).

[16] A. Furukawa and H. Tanaka, Phys. Rev. Lett. **103**, 135703 (2009).

[17] A. Furukawa and H. Tanaka, Phys. Rev. E **84**, 061503 (2011).

[18] R. M. Puscasu *et al.*, J. Chem. Phys. **133**, 144907 (2010).

[19] R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, Oxford, 1999).

[20] A. Onuki, *Phase Transition Dynamics* (Cambridge University Press, Cambridge, 2002).

[21] K. Kawasaki, Ann. Phys. **61**, 1 (1970).

[22] F. Brochard and P. G. de Gennes, Macromolecules **10**, 1157 (1977).

[23] M. Doi and A. Onuki, J. Phys. II (Paris) **2**, 1631 (1992).

[24] A. Furukawa, J. Phys. Soc. Jpn. **72**, 209 (2003); **72**, 1436 (2003).

[25] A. Furukawa, J. Chem. Phys. **121**, 9716 (2004).

[26] B. Bernu *et al.*, Phys. Rev. A **36**, 4891 (1987).

[27] J.-N. Roux *et al.*, J. Phys.: Condens. Matter **1**, 7171 (1989); J.-L. Barrat *et al.*, Chem. Phys. **149**, 197 (1990).

[28] R. Yamamoto and A. Onuki, Phys. Rev. E **58**, 3515 (1998).

[29] D. C. Rapaport, *The Art of Molecular Dynamics Simulation* (Cambridge University Press, Cambridge, 2004).

[30] In the preset binary system, the effective one-component density is given by $\rho(\boldsymbol{r}) = d_1^3 n_1(\boldsymbol{r}) + d_2^3 n_2(\boldsymbol{r})$, where n_1 and n_2 are the number densities of species 1 and 2, respectively [28,31].

[31] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, Oxford, 1986).

[32] The conventional macroscopic hydrodynamics [31] cannot explain this anomalously slow density diffusion. In supercooled liquids, the heat transfer is a much faster process, and thus, the heat mode is decoupled from the structural relaxation and also the density diffusion.

[33] When adopting the stick (slip) boundary condition, the friction coefficient should be multiplied by a constant factor of 6π (4π). However, because the present discussion is qualitative rather than quantitative, the precise value of the factor is not important.

[34] A. Furukawa (unpublished).