

Nonlocal Nature of the Viscous Transport in Supercooled Liquids: Complex Fluid Approach to Supercooled Liquids

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Using molecular dynamics simulations, we show clear evidence for the nonlocal mesoscopic nature of the anomalous viscous transport in a supercooled liquid and its direct link to dynamic heterogeneity: (i) a distinct crossover from the microscopic to macroscopic viscosity at a mesoscopic length scale, which is comparable to the correlation length of dynamic heterogeneity and grows with an increase in the degree of supercooling; (ii) a strong anisotropic decay of the shear-stress autocorrelation at a finite wave number, which indicates intrinsic decoupling between the longitudinal and transverse dynamics. Our findings suggest the fundamental importance of the growing dynamic correlation in anomalous transport and shed new light on the nature of slow dynamics.

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Structural relaxation of a supercooled liquid dramatically slows and its viscosity steeply increases while approaching the glass transition point T_g . The origin of this viscous slowing down is the central problem of glass transition. One of the most successful theories is mode coupling theory (MCT), which has been considered to have a microscopic basis and to explain various key aspects of vitrification [1,2]. In this theory, jamming of density fluctuations with wavelengths comparable to the cage size (\sim particle size d) is the origin of the excessive slowing down of macroscopic structural relaxation, and thus there is no mesoscopic length scale in the theory. Thus, in the ideal MCT framework, glass transition is regarded as a particle-scale phenomenon. This is a natural consequence of the fact that the current MCT for supercooled liquids is a direct extension of that for simple liquids: In a simple liquid the only characteristic length is the interparticle distance ($\sim d$), and there is no characteristic structure beyond this length [3,4]. Consequently, the viscous transport does not exhibit any significant dependences on wave number k for $kd \lesssim 1$. That is, in a simple liquid, macroscopic hydrodynamics can be applied even for particle-scale phenomena [5].

This “simple liquid” picture may not cover all aspects of the anomalous dynamic features: In the last decade, the concept of dynamic heterogeneity (DH) has been established by experiments [6,7] and simulations [8–10]. In a supercooled liquid, structural rearrangement occurs in a spatially heterogeneous and correlated manner, whose size grows while approaching T_g and becomes much larger than the cage size [8–12]. This is suggestive of the existence of a dynamical hierarchical structure beyond the cage size in a supercooled liquid. How the presence of such a dynamical heterogeneity is linked to the viscous transport anomaly of a supercooled liquid remains elusive. In this Letter, we show that what is known in the field of complex fluids (or soft matter), which also exhibit slow dynamics, sheds new light on this problem.

Unlike simple liquids, complex fluids frequently possess conspicuous mesoscopic internal structures (size ξ), which lead to slow structural relaxation (relaxation time τ) [13,14]. This results in a viscoelastic response, which is characterized by a marked frequency (ω) dependence of the transport coefficient for $\omega\tau \gtrsim 1$. In addition to this temporal nonlocality, the viscous transport of complex fluids also exhibits spatial nonlocality. The shear viscosity η of a complex fluid with mesoscopic internal structures exhibits a marked k dependence for $k\xi \gtrsim 1$ [14]: $\eta(k)$ increases with a decrease in k within a cooperative length scale ($k\xi \gg 1$), as a consequence of the renormalization of smaller-scale ($\lesssim k^{-1}$) fluctuations. For $k\xi \ll 1$, on the other hand, such fluctuations are completely renormalized and averaged, and thus $\eta(k)$ becomes equal to its macroscopic ($k = 0$) value. Nonlocal viscous transport in critical fluids is such a typical example [14,15].

Here we note that this nonlocality is not limited to a system with a static mesoscopic structure. For example, entangled polymer solutions are characterized by the viscoelastic length ξ_{ve} [14,16–18], whose origin is the coexistence of topological entanglement and dynamic asymmetry between polymer and solvent and thus purely dynamical. In this case, even without “static” spatial heterogeneity or correlation, the viscous transport exhibits significant nonlocality, which is characterized by a crossover from microscopic (solvent) to macroscopic (polymer) viscosity at $k\xi_{ve} \sim 1$ and a strong decoupling between longitudinal and transverse dynamics at a finite k [19–21].

The above example suggests that we may examine the possible relevance of DH with a mesoscopic length scale in the viscosity anomaly of a supercooled liquid by studying the nonlocality of the viscous transport. In this Letter, thus, we systematically investigate the k dependence of $\eta(k)$ and the wave-vector (\mathbf{k}) dependence of shear-stress autocorrelation function. Previously, Kim and Keyes investigated $\eta(k)$ of a supercooled liquid in relation to the breakdown of the Stokes-Einstein relation and reported a nonlocal nature

of the viscous dissipation [22]. Here we will show (a) an intimate link between the nonlocal viscous transport and DH and (b) evidence of strong decoupling between longitudinal and transverse shear-stress relaxation. We also discuss implications of these findings on the origin of slow dynamics.

We used a three-dimensional glass-forming model liquid, which is a mixture of two atomic species, A and B with $N_A = N_B = 20\,000$. The particles interact via the soft-core potentials $v_{ij}(r) = \epsilon(d_{ij}/r)^{12}$ with $d_{ij} = (d_i + d_j)/2$, where r is the distance between two particles, d_i is the particle size, and $i, j = A, B$. The mass and size ratios are $m_B/m_A = 2$ and $d_B/d_A = 1.2$, respectively. We fixed the particle number density at a value of $(N_A + N_B)/V = 0.8/d_A^3$, where V is the system volume. Space and time were measured in units of d_A and $\tau_0 = (m_A d_A^2/\epsilon)^{1/2}$, respectively. So the linear dimension of the system is $L = 36.84$. The temperature and viscosity were measured in units of ϵ/k_B and $\epsilon\tau_0/d_A^3$, respectively. The simulation was carried out using velocity Verlet algorithms, in the NVE ensemble.

We quantify DH and the associated correlated dynamics by the four-point correlation function [11]: The time-dependent ‘‘order parameter’’ that measures the number of overlapping particles in two configurations separated by a time interval t is defined as $Q(t) = \int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1, 0)\rho(\mathbf{r}_2, t)w_{12}$, where $\rho(\mathbf{r}, t) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i(t))$ is the density. Here $w_{12} = w(|\mathbf{r}_2 - \mathbf{r}_1|)$, where $w(|\mathbf{r}|) = 1$ (0) for $|\mathbf{r}| < 0.3$ (> 0.3). The mean square variance of $Q(t)$ measures the degree of the cooperativity of structural relaxation: $\chi_4(t) = (V/TN^2)[\langle Q^2(t) \rangle - \langle Q(t) \rangle^2]$. It can be written in the form of spatial integration as $\chi_4(t) = (V/TN^2) \int d\mathbf{r} \tilde{G}_4(\mathbf{r}, t)$, where $\tilde{G}_4(\mathbf{r}, t) = \sum_{i,j,k,l} \langle \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_k(0))w_{ij}w_{kl} \rangle - \langle Q(t) \rangle^2$. Its Fourier transformation yields the following structure factor $S_4(\mathbf{k}, t) = (1/TN\rho) \langle \tilde{\rho}(\mathbf{k}, t)\tilde{\rho}(-\mathbf{k}, t) \rangle$, where $\tilde{\rho}(\mathbf{k}, t) = 1/N \sum_{i,j} e^{i\mathbf{k}\cdot\mathbf{r}_i(0)} w_{ij}$. Figure 1(a) shows the intermediate scattering function (self-part) for A particles, $F_s(\mathbf{k}_0, t) = \sum_{i=1}^{N_A} \langle e^{-i\mathbf{k}_0 \cdot [\mathbf{r}_i(t) - \mathbf{r}_i(0)]} \rangle / N_A$, where $|\mathbf{k}_0| = 2\pi$. We also show $\chi_4(t)$ in Fig. 1(b).

The k -dependent shear viscosity can be calculated from the autocorrelation function of the transverse momentum current density [3,4,23,24], which is defined as $\mathbf{j}_T(\mathbf{k}, t) = 1/\sqrt{N} \sum_i^N m_i \mathbf{v}_i^T(t) e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}$, where $\mathbf{v}_i^T(t)$ is the transverse part

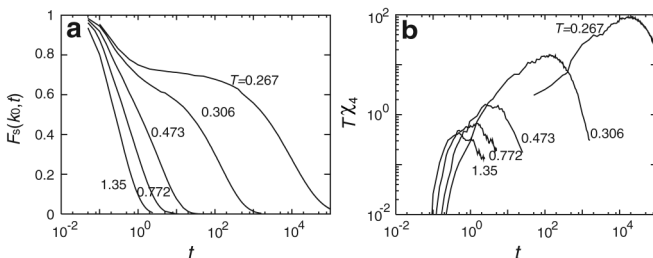


FIG. 1. (a) $F_s(\mathbf{k}_0, t)$ and (b) $\chi_4(t)$ for several temperatures.

of the velocity of particle i [i.e., $\mathbf{v}_i^T(t) \cdot \mathbf{k} = 0$]. Then the autocorrelation function is defined as $c_{\text{tr}}(\mathbf{k}, t) = \langle \mathbf{j}_T(\mathbf{k}, t) \cdot \mathbf{j}_T(-\mathbf{k}, 0) \rangle$. Thus, we have $\eta(k) = (\rho_m/k^2) \times [\int_0^\infty dt c_{\text{tr}}(\mathbf{k}, t)/c_{\text{tr}}(\mathbf{k}, 0)]^{-1}$, where ρ_m is the mass density.

Figure 2(a) shows the k dependence of $\eta(k)$ for several temperatures. At high-temperature normal-liquid states ($T \geq 0.473$), $\eta(k)$ smoothly approaches its macroscopic ($k = 0$) value with a decrease in k , already at a wavelength comparable to the particle size. This suggests that there is no important length scale beyond the cage size in a normal-liquid state. On the contrary, in supercooled states ($T \leq 0.306$) the k dependence of $\eta(k)$ becomes more pronounced for lower T . In a highly supercooled state ($T = 0.267$), $\eta(k)$ increases almost 10^4 times when k decreases from the microscopic ($k \sim 2\pi/d$) to the macroscopic value ($k = 0$). This highly nonlocal nature of the viscosity means that the transverse viscous stress is not determined only by the local strain rate but is severely influenced by velocity fluctuations of a wide range of k . That is, macroscopic hydrodynamics is valid only for $k \lesssim 2\pi/\xi$. This nonlocality strongly suggests that a growing dynamic correlation dominates the viscosity anomaly. To verify this, we study a standard measure of dynamic correlation length, ξ_4 , which is the characteristic length of DH [11]. Figure 2(b) shows the behavior of ξ_η and ξ_4 , which are determined by the half-value widths of $\eta(k)$ and $S_4(k, t = \tau_\chi)$, respectively. Here τ_χ is defined as a time when $\chi_4(t)$ takes its peak. Interestingly, ξ_η and ξ_4 grow in quite a similar manner. This indicates an intimate link between the nonlocality of the viscous transport and DH. Here we note that ξ_η characterizing the k dependence of $\eta(k)$ should not be confused

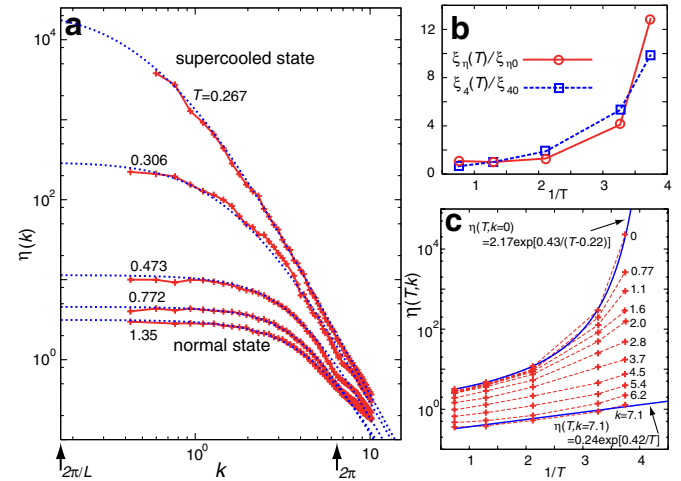


FIG. 2 (color online). (a) The k dependence of η , $\eta(k)$, for several temperatures (red solid curves). $\eta(k)$ can be well fitted by the empirical function, $\eta(k = 0, T)/[1 + (\xi_\eta(T)/k)^2 + (\lambda_\eta(T)k)^4]$ (blue dashed curves), where $\eta(k = 0, T)$ is the macroscopic shear viscosity obtained by the Green-Kubo formula. (b) ξ_η and ξ_4 scaled by their values at $T = 1.15$ are plotted against $1/T$. (c) T dependence of $\eta(k, T)$ for different values of k . The upper and lower solid curves represent Vogel-Fulcher and Arrhenius fitting, respectively.

with the so-called hydrodynamic length, which is the persistence length of a propagating shear elastic wave. In our binary soft-core system, even in a normal-liquid state ($T \sim 0.473$) the hydrodynamic length much exceeds our system size ($L = 36.84$) [25].

Figure 2(c) plots $\eta(k, T)$ against $1/T$ for different k 's. For a small enough k ($k\xi_\eta \ll 1$) $\eta(k, T)$ approaches the usual Vogel-Fulcher law. For a microscopic scale ($k\xi_\eta \gg 1$), on the other hand, $\eta(k, T)$ shows the Arrhenius-type T dependence, indicating that the relaxation of the transverse modes on a microscopic scale does not exhibit any anomaly (slowing down) even in a highly supercooled state. This can be more clearly seen in Fig. 3, where the shear-stress autocorrelation function, $H(\mathbf{k}, t) = \langle \sigma_{xy}(\mathbf{k}, t) \sigma_{xy}(-\mathbf{k}, 0) \rangle$, is plotted for several k 's both for a supercooled and normal state. Here $\sigma_{xy}(\mathbf{k}, t)$ is calculated using the microscopic expression of the xy component of the shear stress [3]. For $\mathbf{k} = (k/\sqrt{2}, k/\sqrt{2}, 0)$, $\sigma_{xy}(\mathbf{k}, t)$ is directly coupled to the longitudinal modes [26]: In a supercooled state, $H(\mathbf{k}, t)$ very slowly decays in a time scale of the α relaxation and nearly collapses on a single curve for long time ($t \geq \tau_\alpha$) [see Fig. 3(a)]. For $\mathbf{k} = (k, 0, 0)$, on the other hand, $\sigma_{xy}(\mathbf{k}, t)$ is the almost purely transverse shear stress [26]: Along this direction, $H(\mathbf{k}, t)$ decays very quickly within the β -relaxation time scale, while exhibiting a pronounced anticorrelation [see Fig. 3(b)]. This strong anisotropy of the shear-stress relaxation is a consequence of decoupling between the longitudinal (structural) and transverse relaxation modes at finite k : The longitudinal relaxation requires highly cooperative rearrangements of many particles, whereas the transverse relaxation can proceed only by local dissipative rotational or pure shear motions, which do not require translational particle diffusion. It is worth

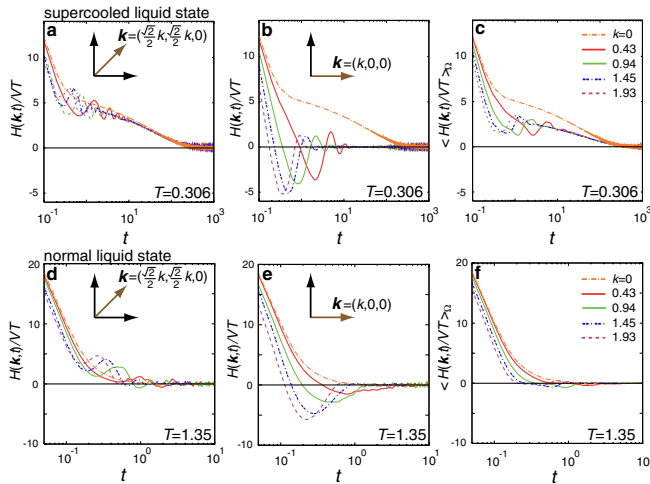


FIG. 3 (color online). The upper row: the decay of the shear-stress autocorrelation function $H(\mathbf{k}, t) = \langle \sigma_{xy}(\mathbf{k}, t) \sigma_{xy}(-\mathbf{k}, 0) \rangle$ for a supercooled state ($T = 0.306$). (a) is for $\mathbf{k} = (k/\sqrt{2}, k/\sqrt{2}, 0)$, and (b) is for $\mathbf{k} = (k, 0, 0)$. The angular average, $\langle H(\mathbf{k}, t) \rangle_\Omega$, is plotted in (c). The lower row: the same plots for a normal-liquid state ($T = 1.35$).

noting that this decoupling becomes more pronounced for lower T . In a normal-liquid state, where there is no separation between the α and β regime, $H(\mathbf{k}, t)$ decays with the same time scale in all directions [see Figs. 3(d)–3(f)]. For $\mathbf{k} = (k, 0, 0)$ we can also see distinct anticorrelation [see Figs. 3(e)]. Thus, we may conclude that the strong decoupling between longitudinal and transverse dynamics is characteristic of a supercooled liquid.

Here we consider whether these findings can be explained by a microscopic caging mechanism, or in the framework of MCT. MCT assumes that the dominant stress (or force density) is specified by density fluctuations. In a supercooled state, density fluctuations with wavelengths near the first peak of the structure factor (\sim cage size) become the longest-lived modes. Thus, their nonlinear (jamming) interactions are considered to play a crucial role in the slowing down of dynamics and the resulting transport anomalies. To elucidate the basic feature of $\eta(k)$ in a MCT picture, we compute $\eta(k)$ of a one-component hard-sphere system rather than a binary soft sphere system, by using the ideal MCT [27,28]. Here the structure factor is evaluated by the Percus-Yevick theory [3]. As can be seen in Fig. 4(b), even in a supercooled state, $\eta(k)$ approaches the macroscopic value $\eta(0)$, when the wavelength becomes comparable to the cage size. This is a direct consequence of the fact that in MCT there is no important length scale beyond the cage size. This means that the viscosity anomaly is really a particle-scale phenomenon in MCT. However, this strongly contradicts our findings [compare Fig. 4(b) with Fig. 2(a)]. In relation to this, we stress the following point. In MCT the generalized Maxwell relation $\eta(k) = G(k)\tau_\alpha(k)$ qualitatively holds even up to the particle scale. Here $G(k)$ and $\tau_\alpha(k)$ are the k -dependent shear modulus and α -relaxation time, respectively [29]. This is simply because in MCT $\eta(k) \sim \eta(0)$, $G(k) \sim G(0)$, and $\tau_\alpha(k) \sim \tau_\alpha(0)$ for $kd \lesssim 1$. On the other hand, our results clearly show that the Maxwell relation is apparently violated at a finite wave number ($k\xi_\eta \gtrsim 1$) [30].

Furthermore, in MCT the relaxation of the dominant stress is entirely determined by the dynamics of the scalar

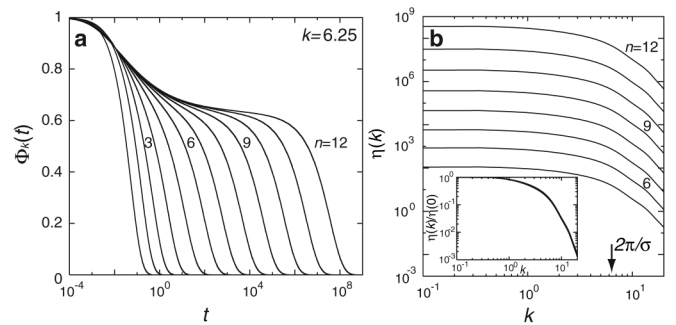


FIG. 4. MCT results: (a) the density autocorrelation function $\Phi(k, t)$ at $k = 6.25$ for several volume fractions $\phi = \phi_c \times (1 - 10^{-n/3})$, where $\phi_c \cong 0.516$ and $n = 1, 2, \dots$; (b) the k -dependent shear viscosity $\eta(k, \phi)$. $\eta(k, \phi)/\eta(0, \phi)$ can be collapsed onto a single curve as shown in the inset.

density field. Thus, the shear-stress autocorrelation should decay with the longest (longitudinal) relaxation time in all directions: isotropic decay. Thus, MCT cannot reproduce the strong angular dependence of the relaxation of $H(\mathbf{k}, t)$ shown in Figs. 3(a)–3(c). These discrepancies may be directly related to the failure in describing the breakdown of the Stokes-Einstein relation by MCT. Recently there have been several efforts to incorporate DH into MCT [31,32]. However, we speculate that a framework beyond the scalar-field description may be necessary for explaining the decoupling between longitudinal and transverse modes in a supercooled liquid.

In the field of complex fluids, a MCT-like scalar-field description is often not capable of describing the whole aspects of complex viscoelastic phenomena: For example, in polymeric liquids the (thermodynamic) osmotic stress due to concentration fluctuations is not sufficient to describe complex mesoscopic dynamics. One should also consider the (mechanical) viscoelastic stress that arises from dynamic coupling between strain field and geometrical conformation (bond-orientation, entanglement, etc.) [33]. For entangled polymer solutions, a new length scale, ξ_{ve} , sets in [16,17], which leads to a crossover from the microscopic to macroscopic viscosity at $k\xi_{ve} \sim 1$ and strong decoupling between longitudinal and transverse dynamics for $k\xi_{ve} \gg 1$ [19,20], quite similarly to our findings. This suggests that even in supercooled liquids such a mechanical viscoelastic stress may play an essential role in addition to the scalar density field. A promising candidate of the origin of such a stress is a dynamical conformation associated with DH [30].

In summary, in the light of the mesoscopic nature of the viscous transport, our study suggests that a supercooled liquid cannot be categorized into a simple liquid, but should be regarded as a complex fluid with a mesoscopic length scale: The spatiotemporal hierarchical structures revealed here share many features common to those of complex fluids. We emphasize that a macroscopic hydrodynamic description is valid only for $k\xi_{\eta} \ll 1$: For $k\xi_{\eta} \gg 1$, the spatiotemporal hierarchical nature of a system dominates the viscous transport properties. We note that the nonlocal nature of the viscous transport may be key to many unsolved problems, e.g., translational-rotational decoupling (the breakdown of the Stokes-Einstein relation) and the origin of the slow β mode. We speculate that the strong decoupling between the longitudinal and transverse dynamics [see Figs. 3(a)–3(c)] is responsible for the translational-rotational decoupling in a supercooled state [34,35]. Microrheological measurements may provide important information on this problem [20,36]. We believe that an approach from the physics of complex fluids may shed new light on the very origin of slow dynamics associated with glass transition.

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