Simple picture of supercooled liquid dynamics: Dynamic scaling and phenomenology based on clusters

Akira Furukawa[*]

Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan[†]
and School of Physics and Astronomy, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3J, United Kingdom

Although it is now well established that in glassy liquids, slow structural relaxation accompanies a correlated structural rearrangement, the role of such a correlation in the transport anomaly, and thus in the slow dynamics, remains unclear. In this paper, we argue from a hydrodynamic viewpoint that a correlated structure (cluster) with a characteristic size ξ sustains the long-lived stress and dynamically couples with the hydrodynamic fluctuations; therefore, the dynamics of this cluster is the origin of the mesoscopic nature of anomalous hydrodynamic transport. Based on this argument, we derive a dynamic scaling law for τ_α (or η, where η is the macroscopic shear viscosity) as a function of ξ: τ_α ($\propto \eta$) $\propto \xi^4$. We provide a simple explanation for basic features of anomalous transport, such as the breakdown of the Stokes-Einstein relation and the length-scale-dependent decoupling between viscosity and diffusion. The present study further suggests a different physical picture: Through the coarse graining of smaller-scale fluctuations ($\lesssim \xi$), the supercooled liquid dynamics can be regarded as the dynamics of normal (cluster) liquids composed of units with a typical size of ξ. Although the correlation length of hydrodynamic transport ξ and the dynamic heterogeneity size ξ_{DH}, which is determined by the usual four-point correlation function, reflect some aspects of the cooperative effects, the correspondence between ξ and ξ_{DH} is not one to one. We highlight the possibility that ξ_{DH} overestimates the actual collective transport range at a low degree of supercooling.

PACS number(s): 66.20.Cy, 66.10.C−, 61.43.Fs

I. INTRODUCTION

As a supercooled liquid approaches the glass transition point T_g, the structural relaxation slows dramatically and the viscosity increases steeply. The origin of this viscous slowdown remains the central issue in glass physics [1–4]. Over the past two decades, the concept of dynamic heterogeneity (DH) has been extensively explored in experimental studies [5–7] and simulations [8–12] (see recent reviews [13,14] and the references therein). In glassy liquids, a slow structural relaxation accompanies the spatially heterogeneous and correlated particle rearrangement whose characteristic size grows as the system approaches T_g.

Dynamic heterogeneity and its associated phenomena strongly suggest the significance of spatial correlations over a mesoscopic length scale and raises two fundamental questions. The first question of what the underlying mechanism is behind this growing correlation length is the focus of intensive study in this field. To elucidate this question, many theoretical and numerical efforts have been made recently, particularly from the viewpoint of the static origin (see recent reviews [15–18] and papers [19–22] as well as the aforementioned reviews [13,14] and the references therein). Although such approaches are appealing, there are still uncertainties and thus further investigations are necessary to definitively identify the origin of the correlated structure. Another important question is whether this spatial correlation substantially affects anomalous transport and the subsequent slow dynamics. Although some dynamical effects characteristic of supercooled liquids are believed to be a consequence of DH, such as the breakdown of the Stokes-Einstein (SE) relation [23–26], no consensus exists on the role of DH in the transport properties of supercooled liquids. These two questions should be closely related to each other, but we cannot generally expect that solving one problem will automatically solve the other [27]. In this paper, as our strategy, we do not discuss the first problem, the origin of the dynamic correlation; instead, we assume there is a well-defined correlated structure with a characteristic size ξ and we discuss the possible fundamental roles of this correlation in anomalous hydrodynamic transport.

Accumulating evidence suggests a link between the dynamic correlation and length-scale-dependent anomalous transport. One of the most studied phenomena directly related to the growing length scale is the crossover from Fickian to non-Fickian diffusion of a tagged particle [28–33]; the wave-number- (k-) dependent relaxation rate of the self part of the intermediate scattering function behaves as $\sim D_s k^2$ and $\sim 1/\tau_\alpha$ for $k\ell^* \ll 1$ and $k\ell^* \gg 1$, respectively, where D_s is the self-diffusion coefficient and τ_α is the α-relaxation time. The length scale for the crossover to Fickian particle diffusion is given by $\ell^* \cong \sqrt{D_s \tau_\alpha}$. In all systems investigated thus far, ℓ^* is found to grow monotonically as the temperature is lowered. This crossover behavior is intrinsically linked to the breakdown of the SE relation; thus this behavior should reflect some aspect of the cooperative effects associated with DH. Note, however, that it is difficult to fully understand and interpret the cooperative effects, which are expected to cause anomalous transport, through the analysis of the single-particle transport only; therefore, a hydrodynamic viewpoint is necessary.

There have been few attempts to investigate the spatiotemporal hierarchical structures of hydrodynamic transport, such as viscous transport and viscoelasticity [34–40], even though this anomaly itself characterizes the glass transition. Recently, in a series of studies [36–38], using a three-dimensional

---

[*]furu@iis.u-tokyo.ac.jp
[†]Permanent address.

molecular dynamics simulation, we revealed evidence for the nonlocal mesoscopic nature and the scaling properties of hydrodynamic transport in supercooled liquids by directly analyzing the k-dependent hydrodynamic transport coefficient. Both the (longitudinal) density diffusion and the (transverse) viscous relaxation exhibit a distinct crossover between microscopic and macroscopic transport and are characterized by a single length scale ξ. This ξ can be identified as the correlation length of the nonlocal hydrodynamic transport and is found to be apparently comparable to the dynamic heterogeneity length (see the discussion in Sec. II C). We also showed that shear stress relaxation occurs through coherent particle rearrangement over distances of $\sim\xi$ and time scales of $\sim\tau_\alpha$. These findings suggest that a correlated structure with a characteristic size ξ that sustains a long-lived stress dynamically couples with density and velocity fluctuations, thus giving rise to the mesoscopic nature of hydrodynamic transport.

In most soft materials (or complex liquids), a mesoscopic cooperative structure is the essential origin of the slow structural relaxation [41,42]. This cooperative nature results in marked frequency and wave-number dependence in the hydrodynamic transport coefficients, in which the time and length scales for the crossover from microscopic to macroscopic transport directly measure the cooperative time and length scales, respectively (more examples can be found in the literature [41–48]). Notably, such spatiotemporally nonlocal properties of hydrodynamic transport are not limited to systems with static mesoscopic structures but are also found in systems with mesoscopic dynamic correlation [45,46]. The examination of whether such a physical description remains valid in supercooled liquids is also interesting and important. The purpose of this paper is to further interpret the role of the dynamic correlation in anomalous transport through hydrodynamic arguments and to provide an initial step toward the construction of a hydrodynamic theory for supercooled liquids.

II. DYNAMIC SCALING

A. Dynamic scaling behavior of hydrodynamic transport

We begin by discussing the dynamic scaling behavior of hydrodynamic transport. Here we provide a theoretical argument for the scaling relation between the growth of the length and time scales based on our previously obtained simulation results described in Ref. [38]; please refer to Ref. [38] for simulation details.

1. Longitudinal diffusion

Figure 1(a) shows the dynamic scaling behavior of the k-dependent collective density diffusion coefficient $D(k)$; in highly supercooled states the scaled diffusion coefficient $D(k)/D_c$ as a function of the scaled wave number $k\xi$ almost falls on a single master curve, where D_c is the collective density diffusion coefficient given by the limit of $D(k)$ at long wavelengths. Thus $D(k)$ can be characterized by ξ only. We subsequently write $D(k)$ in the scaling form as

$$D(k) = D_c \Phi(k\xi), \tag{1}$$

where the scaling function $\Phi(x)$ behaves as
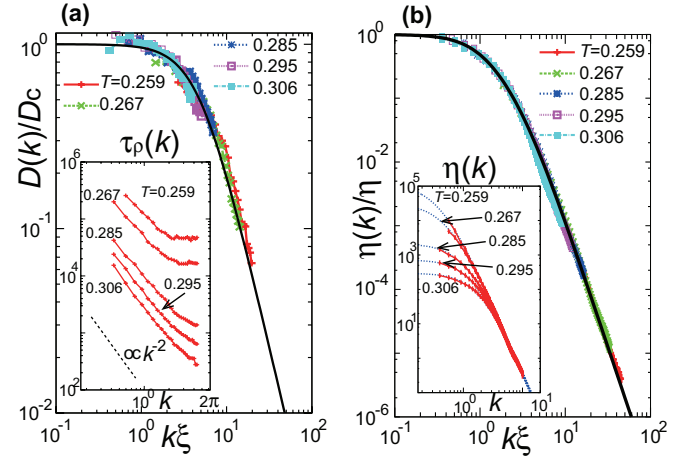
$$\Phi(x) \sim 1 \quad (x \ll 1) \tag{2}$$

FIG. 1. (Color online) Scaled plots of (a) the k-dependent collective diffusion coefficient $D(k)/D_c$ and (b) the viscosity $\eta(k)/\eta$ in highly supercooled states as functions of the scaled wave number $k\xi$. Here D_c and η are the long-wavelength limits for $D(k)$ and $\eta(k)$, respectively, and ξ is the correlation length for hydrodynamic transport; $D(k)$ is calculated from the simulation data for the k-dependent relaxation time of the density fluctuations shown in the inset of (a). Here we use the relation $\tau_\rho(k) \cong 1/D(k)k^2$. In the inset of (b), the unscaled data for $\eta(k)$ are shown. Both $\eta(k)/\eta$ and $D(k)/D_c$ almost lie on master curves (the thick black solid curves) given by $1/[1 + x^2 + (0.53x)^4]$ and $1/[1 + (0.21x)^2]$, respectively, in which $x = k\xi$. These plots are similar to Figs. 1 and 2 of Ref. [38]; please refer to Ref. [38] for simulation details. Note that similar scaling plots were previously reported in Refs. [28–30,33] for the k-dependent relaxation rate of the (self) intermediate scattering function.

$$\sim x^{-2} \quad (x \gg 1). \tag{3}$$

This scaling behavior can be understood through the length-scale-dependent decoupling between diffusion and viscosity [28]: In the long-wavelength regimes ($k\xi \ll 1$), the density fluctuations decay through diffusion with a diffusion coefficient of D_c; in contrast, at the microscopic scale $k\xi \gg 1$, the relaxation time $\sim 1/D(k)k^2$ is nearly equal to the α-relaxation time $\tau_\alpha \propto \eta$. Consequently, the density diffusion coefficient D_c can be given by

$$D_c \sim \frac{\xi^2}{\tau_\alpha}. \tag{4}$$

However, as discussed in Ref. [38], this expression for D_c should not be merely a consequence of the decoupling or the crossover but should also describe the dynamical coherence of hydrodynamic transport. We emphasize that in Ref. [38], crossover in longitudinal transport was not investigated with the self part of the intermediate scattering function but with the full part, which directly reflects the cooperative effects. The incoherent scattering function (the self part) measures the motion of the tagged particle; this single-particle analysis cannot directly describe the cooperative effects. In contrast, the coherent scattering function at wave number k measures the relaxation of the density fluctuations of size $\sim 1/k$. As further discussed below, the expression for the collective diffusion coefficient [Eq. (4)] should describe the cooperative diffusion

of correlated fluctuations (structures) of size ξ in a medium with macroscopic viscosity η.

2. Transverse viscous transport

Likewise, we show the scaled shear viscosity $\eta(k)/\eta$ as a function of $k\xi$ in Fig. 1(b); $\eta(k)/\eta$ almost lies on a single master curve as well. Thus viscous transport in highly supercooled states can also be characterized by ξ alone and the k-dependent viscosity $\eta(k)$ is written in the scaling form as

$$\eta(k) = \eta\Psi(k\xi), \tag{5}$$

where the scaling function $\Psi(x)$ behaves as follows:

$$\Psi(x) \sim 1 \quad (x \ll 1) \tag{6}$$
$$\sim x^{-4} \quad (x \gg 1). \tag{7}$$

From this scaling behavior we derive the scaling relation between $\eta\ (\propto\tau_\alpha)$ and ξ. Here we make use of the fact that for $k\xi \gg 1$, $\eta(k)$ is almost independent of T, as shown in the inset of Fig. 1(b). Therefore, viscous transport at smaller scales ($k\xi \gg 1$) should not be sensitive to the macroscopic transport properties; namely, $\eta(k)$ at $k\xi \gg 1$ is almost independent of η and ξ. This fact leads to the following scaling relation:

$$\eta \cong \eta_0\left(\frac{\xi}{\lambda}\right)^4, \tag{8}$$

where λ is the particle size and η_0 is the viscosity at the particle scale. In our previous simulations, we found that η_0 exhibits an Arrhenius-like weak temperature dependence [36,37].

B. Simple scaling argument: Link between the growth of the length and time scales

Although many similar scaling relations have been reported to date, there is no clear physical explanation for these relations, even at the phenomenological level. An understanding of the scaling relation (8) would immediately provide insight into the link between the growth of the length and time scales. Here, from our observations we construct a general dynamic scaling theory for the supercooled liquid dynamics based on clusters. In the present argument, the only necessary assumption is that the particle rearrangements occur cooperatively in the form of clusters of size ξ at the longer length scale ($k\xi \lesssim 1$) that accompanies stress relaxation. Such cooperative particle rearrangements are generally expected to occur in the usual glass formers; thus the present assumption can be applied to a wide range of molecular systems.

First, let us consider a correlated structure or cluster with a typical size ξ that is composed of microscopic constituents (particles) of size λ. The velocity fluctuations of the cluster are estimated from the equipartition law as $\langle v_\xi^2 \rangle \sim T/\rho\xi^3$, where T is the temperature in units of Boltzmann's constant and ρ is the mass density. The mean frequency of the random rattling motions of a cluster is $c/\xi \sim \sqrt{E/\rho}/\xi$, where c and $E \sim T/\lambda^3$ are typical values for the speed of sound and the elastic modulus, respectively. Here ξ/c is the mean turnover time for the momentum autocorrelation at $k\xi \cong 1$; after this time, the direction of the motion of the cluster randomly changes. By averaging such random motions of the cluster over long enough times ($\gg\xi/c$), we observe diffusive motions. Therefore, the

diffusion constant of the cluster is given by

$$D_\xi \sim \langle v_\xi^2 \rangle \frac{\xi}{c} \sim \frac{T}{\xi^2\sqrt{E\rho}} \sim \frac{1}{\tau_0}\frac{\lambda^4}{\xi^2}, \tag{9}$$

where $\tau_0 \sim \eta_0/E$ is a microscopic time scale, and the microscopic viscosity η_0 can be evaluated as $\eta_0 \sim \sqrt{T\rho}/\lambda$ [49,50]. Assuming that cooperative particle rearrangements involve relaxation of the stress stored in the cluster, we identify τ_α as the average cluster relaxation time, during which the cluster diffuses a distance of $\sim\xi$. Thus we obtain

$$\tau_\alpha \sim \frac{\xi^2}{D_\xi} \sim \tau_0\left(\frac{\xi}{\lambda}\right)^4. \tag{10}$$

This relation is supported by our previous simulation results [38]; the α-relaxation time nearly coincides with the self-diffusion time of the correlated fluctuations (thus $D_c \sim D_\xi$).

From the Maxwell relation, we obtain the viscosity as

$$\eta \sim E\tau_\alpha \sim \eta_0\left(\frac{\xi}{\lambda}\right)^4. \tag{11}$$

Under the present scaling argument, the dissipative flux is on the order of $\sim\xi/\tau_\alpha$; therefore, the dissipation rate per cluster is estimated to be $(\eta\xi)(\xi/\tau_\alpha)^2$, where $\eta\xi$ is the friction coefficient of the cluster. This dissipation rate coincides with the rate of stress relaxation for the cluster $E\xi^3/\tau_\alpha$.

The relations in Eqs. (9)–(11) can clearly be reduced to those for normal liquids by replacing ξ with λ. In particular, Eq. (9) reduces to $D_\lambda \sim T/\eta_0\lambda$. This expression for the diffusion constant is the SE relation for the self-diffusion of a single particle; this relation arises from the almost uncorrelated motions of particles in a normal liquid state. In contrast, in a supercooled state, particles cannot diffuse independently, but instead move coherently by forming clusters. With this description, the resulting dynamics can be regarded as the self-diffusion of clusters and this observation is supported by our previous simulation [38]. Thus we may conclude that in supercooled liquids, the SE relation is violated at the particle level, but is restored at the mesoscopic level.

To end this subsection, we should mention the following. In Monte Carlo (or Brownian) dynamics without particle inertia, a different scaling relation between the cluster size and the α-relaxation time should be predicted by an argument similar to that used in this section for the usual molecular liquids: The average random displacement of a cluster with size ξ in each Monte Carlo step Δt_{MC} is proportional to $\sim\xi^{-3}$, and after Δt_{MC}, because of the Markovian nature of Monte Carlo dynamics, randomization of the direction of the cluster motion occurs. Therefore, the diffusion constant of the cluster is proportional to $D_\xi \sim \xi^{-3}$ and the structural relaxation time should behave as $\tau_\alpha \sim \xi^5$.

C. Comparison of ξ to ξ_{DH}

The dynamic scaling $\tau_\alpha \sim \xi^4$ is apparently comparable to the previously reported relation $\tau_\alpha^{(s)} \sim \xi_{\mathrm{DH}}^{4.6}$ [51], where ξ_{DH} is the dynamic heterogeneity size, which is determined by the usual four-point correlation function, and $\tau_\alpha^{(s)}$ is defined to be the relaxation time of the self-intermediate scattering function ($\tau_\alpha \sim \tau_\alpha^{(s)}$ [37]). However, recent studies have shown stronger ξ_{DH} dependence for the α-relaxation time [52–54]. In fact,

within the temperature range investigated in our simulation, it was also found that the temperature dependence of ξ is stronger than that of ξ_{DH} [36,38,55]. This difference in the scaling relations should be explained by the different natures of the characterization.

In our previous studies [36–38], the dynamic correlation was characterized by the correlations in the transport coefficients. By definition, the nonlocal response can be written as

$$\boldsymbol{j}_\rho^\parallel(\boldsymbol{r}) = \int d\boldsymbol{r}' D(\boldsymbol{r} - \boldsymbol{r}) \nabla' \hat{\rho}(\boldsymbol{r}'), \tag{12}$$

$$\overset{\leftrightarrow\perp}{\boldsymbol{\sigma}}_{\text{vis}}(\boldsymbol{r}) = \int d\boldsymbol{r}' \eta(\boldsymbol{r} - \boldsymbol{r}')\{\nabla' \boldsymbol{v}^\perp(\boldsymbol{r}') + [\nabla' \boldsymbol{v}^\perp(\boldsymbol{r}')]^\dagger\}, \tag{13}$$

where $D(\boldsymbol{r} - \boldsymbol{r})$ and $\eta(\boldsymbol{r} - \boldsymbol{r}')$ are the inverse Fourier transforms of $D(k)$ and $\eta(k)$, respectively. Equations (12) and (13) with Fig. 1 explicitly show that the hydrodynamic fluxes (the longitudinal diffusive flux $\boldsymbol{j}_\rho^\parallel$ and the transverse viscous stress $\overset{\leftrightarrow\perp}{\boldsymbol{\sigma}}_{\text{vis}}$) are not determined by the local fluctuations (the longitudinal density $\hat{\rho}$ and the transverse velocity $\boldsymbol{v}^\perp$, respectively), but are dominated by fluctuations in the distance $|\boldsymbol{r} - \boldsymbol{r}'| \sim O(\xi)$. Thus the nonlocal transport coefficient directly measures the coherence of the collective motions involved in hydrodynamic transport.

In contrast, the usual four-point correlation function method characterizes the dynamic correlation by correlations in the mobility field defined by the absolute value of the particle displacement in a time interval $\sim\tau_\alpha$ and ξ_{DH} is given by the characteristic length scale of the spatially heterogeneous pattern of the mobility field. However, such a spatial pattern of mobile (or immobile) regions results from the accumulation of some individual events with a size smaller than ξ_{DH} over the time $\sim\tau_\alpha$; while some of these events are correlated, others are not. Thus this pattern does not necessarily reflect the actual size of the collective transport range in a direct way. That is, the usual determination of the mobility field may not be sufficient to distinguish between correlated and uncorrelated (or anticorrelated) events. To examine this speculation, in the Appendix we analyze the spatiotemporal coherence of the mobility field for the time interval τ_α. Based on simulation results, we suggest the following interpretation: At a lower degree of supercooling, the individual cooperative rearrangement events are smaller, but they occur at a greater number of locations with less correlation; thus the resultant ξ_{DH} is larger than ξ. In contrast, with an increase in the degree of supercooling, the difference between ξ_{DH} and ξ becomes smaller. Therefore, although the cluster size does not exceed ξ_{DH} in the relevant temperature range (see the Appendix), the temperature dependence of ξ_{DH} is weaker than that of ξ; namely, the usual four-point correlation method may overestimate the actual cooperative length scale or the collective transport range at lower degrees of supercooling.

Here we emphasize that although both ξ and ξ_{DH} reflect some aspects of the cooperative effects in supercooled liquids, the relation of ξ to ξ_{DH} is not precisely one to one. The usual four-point correlation function measures the spatial distribution of the mobility or the activity defined during a time interval $\sim\tau_\alpha$, but indirectly measures the correlation length of the nonlocal transport itself. Despite the great success of the four-point correlation method in describing the

statistical properties of spatiotemporally fluctuating particle dynamics and its collective kinetic features in supercooled liquids, it is difficult to elucidate the link between DH and anomalous hydrodynamic transport. This difficulty arises because in the conventional four-point correlation approach, there is an ambiguity in relating the hydrodynamic transport coefficients to the correlation function of the mobility field.

Previously, decoupling of the characteristic length of DH and that of the Fickian crossover for the self-diffusion of a probe was analytically shown in the Fredrickson-Andersen model and the EAST model [29]. This decoupling is ascribed to the specific dynamic features of these lattice models. Structural relaxation proceeds through the slow motion of excitation lines at the mesoscopic length scale (comparable to the dynamic heterogeneity size), whereas the self-diffusion of a probe is governed by the *a priori* local spin-flipping rules [56]. Thus these dynamical processes have different time scales and this difference results in decoupling of the characteristic length scales. However, in molecular systems, such as the Lennard-Jones system, the structural relaxation is the cooperative particle rearrangement, which also determines the coherence of hydrodynamic transport, so the characteristic lengths of DH and the transport crossover should be more closely related (but would not be one to one because of the different characterizations, as discussed above).

The understanding of the relationships among these length scales is far from sufficient, but is left for future studies.

III. LENGTH-SCALE-DEPENDENT ANOMALOUS TRANSPORT: SLOW DYNAMICS OF CLUSTERS

In the previous section we indicated that the primary features of the anomalous transport in supercooled liquids can be captured with a dynamic scaling argument based on the cluster picture. In particular, we would like to emphasize that cooperative structural rearrangements can be idealized as the self-diffusion of a correlated structure (cluster) of size ξ in a medium with macroscopic viscosity η.

However, at length scales much smaller than the cooperative length ($k\xi \gg 1$), the relaxation time of the density fluctuations is not given by the diffusion time $1/D_c k^2$ but by the macroscopic structural (α-)relaxation time τ_α [3]. This coincidence between the relaxation time for microscopic ($k\lambda \sim 1$) fluctuations and the macroscopic ($k = 0$) structural relaxation time seems odd, but has been shown in many numerical simulations and neutron scattering experiments. In this section, with a continuum-mechanics-based approach, we will further interpret such length-scale-dependent anomalous transport in terms of clusters and we conclude that the correspondence between these time scales may be a consequence of the stress-diffusion coupling at $k\xi \gtrsim 1$.

The present phenomenology was inspired by the apparent analogy between supercooled liquids and entangled polymer solutions; that is, the essential features of mesoscopic transport in supercooled liquids and entangled polymer solutions are apparently analogous. In the following subsection, we will first provide a short summary of this analogy.

A. Apparent analogy with entangled polymer solutions

In entangled polymer solutions, cooperative transport is characterized by the mesoscopic length scale, the "magic length" (or viscoelastic length) ξ_p [44,45], which is typically significantly larger than the static correlation length (blob size) defined by the static two-body correlation function or the static (Flory–Huggins–de Gennes) free energy functional. The magic length is a dynamical correlation length that originates from the coexistence of topological constraints (entanglements) and the asymmetric stress division between the polymer and solvent; the magic length can be regarded as the correlation length of the stress relaxation [46,47] during the (longest) structural relaxation time τ_p that originates from the reptation dynamics of entanglement relaxation [57,58]. This situation is similar to that of supercooled liquids, where the dynamical correlation length ξ is usually defined as the spatial correlation length of the structural relaxation or particle rearrangement event during the time duration τ_α. In addition, the dynamical correlation length ξ cannot be obtained from an ordinary static two-body correlator such as the density-density correlation function.

In entangled polymer solutions, for $k\xi_p \ll 1$, the concentration fluctuations decay through diffusion with a diffusion coefficient of $D_p \sim \xi_p^2/\tau_p$. In contrast, for $k\xi_p \gg 1$, the force from the gel-like network that is transiently formed for time τ_p dominates the longitudinal modes (stress-diffusion coupling) [44,45]. As a result, the relaxation time for the concentration fluctuations is on the order of τ_p, which is much longer than that expected from the diffusive decay, $1/D_p k^2 \ll \tau_p$. As shown in our previous study [38], the slowly varying density fluctuations exhibit similar behavior.

This analogy is also relevant in the transverse modes. We predicted that, in entangled polymer solutions, the viscous transport and viscoelasticity would exhibit significant non-locality [46–48]. With a decrease in k, the (k-dependent) viscosity $\eta(k)$ increases from the solvent viscosity η_s for $k\xi_p \gg 1$ to the polymeric viscosity η_p ($\gg\eta_s$) for $k\xi_p \ll 1$. The marked k dependence in $\eta(k)$ is essential for connecting the transport properties at the various length scales [46–48]. Recently, similar behavior has been reported for spatially nonlocal viscous transport in supercooled liquids [35–39]. In our previous work [36–38], we demonstrated that a distinct crossover from microscopic to macroscopic viscosity occurs at the dynamic correlation length ξ.

These analogies do not necessarily indicate that the same origin or mechanism underlies the slow dynamics; however, they at least lead us to expect a common physical description for hydrodynamic transport. In both systems, the long-lived topological constraints (entanglement in polymer solutions and dynamical conformations of particles in supercooled liquids, which are both transient structures) and the stress associated with these constraints cause the correlated dynamics and severely restrict the structural rearrangements over the cooperative length and time scales.

B. Cluster picture

This subsection describes our cluster picture for the slow structural relaxation of supercooled liquids.

1. Diffusive decay ($k\xi \lesssim 1$)

For $k\xi \lesssim 1$, as shown in Fig. 1, the slowly relaxing density fluctuations, which we refer to as $\hat{\rho}$, obey the diffusion equation

$$\frac{\partial \hat{\rho}}{\partial t} \cong D_c \nabla^2 \hat{\rho}. \tag{14}$$

We suppose that this collective diffusive decay of density fluctuations at longer length ($k\xi \lesssim 1$) and time ($\omega\tau_\alpha \lesssim 1$) scales, where ω is the frequency, reflects the mutual diffusion of correlated fluctuations (clusters). Here, on the basis of this physical picture, we reevaluate the collective diffusion coefficient D_c through a simple hydrodynamic argument as follows: For $k\xi \lesssim 1$, we assume that the restoring (or pressure gradient) force associated with the density fluctuations balances the friction force as

$$0 \cong -\zeta \boldsymbol{w} - \frac{1}{K_0}\boldsymbol{\nabla}\frac{\hat{\rho}}{\hat{\rho}_0}, \tag{15}$$

where $\zeta \sim \eta\xi^{-2}$ is the friction coefficient (per unit volume), K_0 is the compressibility in the long-wavelength regime, and $\hat{\rho}_0$ is the average value of $\hat{\rho}$. Hereafter, $\boldsymbol{w}$ represents the average velocity of the slowly moving collective fluctuations in which the fast time scale ($\omega\tau_\alpha \gg 1$) motions are assumed to be coarse grained and $\hat{\rho}\boldsymbol{w}$ thus provides the diffusive current. The dynamical correlation length ξ cannot be identified through the static two-body density correlator or through the free energy functional. Therefore, although the thermodynamic force (and thus K_0) should be insensitive to ξ, the friction force (and thus ζ) directly reflects the cooperative effect. Because $\hat{\rho}$ evolves by the continuity equation

$$\frac{\partial \hat{\rho}}{\partial t} \cong -\hat{\rho}_0 \boldsymbol{\nabla} \cdot \boldsymbol{w}, \tag{16}$$

we obtain

$$D_c \sim \frac{1}{K_0}\frac{1}{\eta\xi^{-2}} \sim \frac{\xi^2}{\tau_\alpha}, \tag{17}$$

where the Maxwell relation $\eta \cong E\tau_\alpha$ is employed and the relation $K_0 E \sim 1$ is assumed. Notably, this expression of the collective diffusion coefficient D_c corresponds to the cluster diffusion constant D_ξ derived in Sec. II B.

In the present argument, $\boldsymbol{w}$ is tacitly assumed to differ from the total velocity $\boldsymbol{v}$. On a faster time scale $\omega\tau_0 \gtrsim 1$, where τ_0 is again the microscopic time scale, the less-correlated (thermally driven) motions are dominant. However, on a slower time scale ($\omega\tau_0 \ll 1$), the cooperative nature becomes pronounced and slow cluster dynamics cannot be simply described by the local $\boldsymbol{v}$. We assume that $\boldsymbol{w}$ reflects the coarse graining of the fast time scale motions. In this sense, we may view the slow cluster diffusion at the longer length scale ($k\xi \lesssim 1$) as similar to the usual diffusive dynamics of (normal) colloidal suspensions, where the positional degrees of freedom of the colloidal particles themselves are slow variables and where the velocity of the colloidal particles is obtained by coarse graining the fast (solvent) degrees of freedom. Our view is schematically shown in Fig. 2.
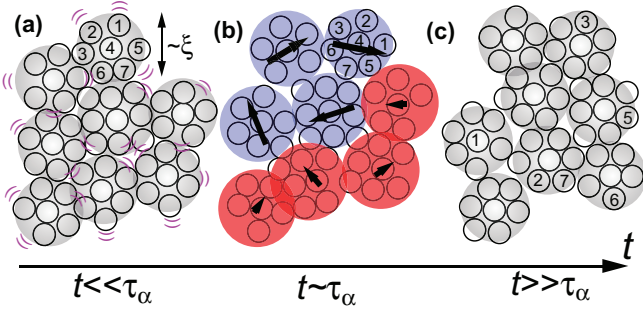
FIG. 2. (Color online) Schematic of cooperative particle rearrangements based on clusters. (a) For $t \ll \tau_\alpha$, almost none of the particles can move far, although small-amplitude thermal rattling motions are shown. (b) For $t \sim \tau_\alpha$, the particles move by forming clusters. Structural rearrangements over a period of τ_α accompany stress relaxation. In (b), the relatively mobile (immobile) clusters are indicated with a bright-blue (dark-red) shaded color and the thick arrows represent the average displacement of the clusters over $\sim\tau_\alpha$. We assume that the dynamic properties of the clusters (mobile and immobile) change on a time scale of $\sim\tau_\alpha$; these changes are observed as DH. For longer time scales ($t \gtrsim \tau_\alpha$), the supercooled liquid dynamics can be regarded on average as cluster diffusion. After a long time ($t \gg \tau_\alpha$), the particles are redistributed among new clusters.

2. Stress-limited decay ($k\xi \gtrsim 1$)

For $k\xi \gtrsim 1$, the deviation from diffusive decay becomes apparent and the density fluctuations survive longer than $1/D_c k^2$ (see Fig. 1 as well as Fig. 2 of Ref. [38]). We speculate that the transiently formed steric constraints associated with the dynamic correlation act against the restoring force caused by the density fluctuations: During structural relaxation, the long-lived longitudinal stress $\overset{\leftrightarrow}{\boldsymbol{\sigma}}^{\parallel}$ may prevent the density fluctuations from relaxing. The resultant force balance for $\omega\tau_\alpha \gtrsim 1$ and $k\xi \gtrsim 1$ is expressed as

$$0 \sim -\frac{1}{K_0}\boldsymbol{\nabla}\frac{\hat{\rho}}{\hat{\rho}_0} + \boldsymbol{\nabla} \cdot \overset{\leftrightarrow}{\boldsymbol{\sigma}}^{\parallel}. \tag{18}$$

In the framework of mode coupling theory (MCT), $\boldsymbol{\nabla} \cdot \overset{\leftrightarrow}{\boldsymbol{\sigma}}^{\parallel}$ is specified by the nonlinear term for the force density $-\hat{\rho}\boldsymbol{\nabla}(\delta\mathcal{F}/\delta\hat{\rho})$, where $\mathcal{F}\{\hat{\rho}\}$ is the free energy functional [4]; the dominant stress is assumed to be uniquely specified by the spontaneous density fluctuations. However, such an approach had not yet succeeded in consistently describing the mesoscopic nature of the anomalous hydrodynamic transport in deeply supercooled states. Here we critically consider this MCT approach in terms of the crossover of hydrodynamic transport: In MCT, both the longitudinal and transverse stress relaxations are determined by the relaxation of the scalar density field on the particle scale and these stress fluctuations then govern density relaxation over a wide range of length scale. Thus $\hat{\rho}$, $\overset{\leftrightarrow}{\boldsymbol{\sigma}}^{\parallel}$, and $\overset{\leftrightarrow}{\boldsymbol{\sigma}}^{\perp}$ have the same time scale $\sim\tau_\alpha$ for relevant wave numbers. However, this property is inconsistent with the strong decouplings between the (transverse) shear viscosity and the (longitudinal) structural relaxation for $k\xi \gtrsim 1$ and between the density diffusion and the structural relaxation for $k\xi \lesssim 1$ (see Fig. 1). These discrepancies should be closely related to the failure in describing the breakdown of the

SE relation and the translation-rotation decoupling by MCT. The observed transport crossover indicates that the density and the longitudinal and transverse stress relaxations each have different spatiotemporal hierarchical properties; thus the stress tensor contains components that cannot be directly expressed in terms of the density field. We speculate that such stress components reflect the topological conformation of the particle configurations; these configurations are transiently formed in supercooled liquids and their dynamical properties are not conserved, but alternately appear and disappear on the time scale of τ_α. In the present paper, instead of representing $\overset{\leftrightarrow}{\boldsymbol{\sigma}}$ with the density field as in MCT, we treat $\overset{\leftrightarrow}{\boldsymbol{\sigma}}$ as an independent nonconserved tensor variable [36,37,59]. Furthermore, the length-scale-dependent dynamical coupling ($k\xi \gtrsim 1$) and decoupling ($k\xi \lesssim 1$) between the density and stress fluctuations can be described through a set of coupled linear transport equations.

In soft matter systems, such as polymer solutions, to describe complex mesoscopic dynamics, it is essential to consider the mechanical viscoelastic stress tensor, which arises from dynamic coupling between internal strain and geometrical conformation, as an independent coarse-grained (hydrodynamic) variable separate from the density (or concentration) field [41,42]. Of course, in supercooled liquids, such a treatment is difficult to justify *a priori*, so it would be highly desirable to evaluate the relevance of this speculation with a first-principles approach. However, as shown in the following subsection, the phenomenological inclusion of the nonconserved stress tensor field $\overset{\leftrightarrow}{\boldsymbol{\sigma}}$ in addition to the conserved scalar density field ensures coherent dynamics for $k\xi \gtrsim 1$.

C. Decoupling ($k\xi \lesssim 1$) and coupling ($k\xi \gtrsim 1$) between diffusion and viscosity (α relaxation): Possible role of mechanical stress

As described so far, a dynamical cooperative length scale ξ exists; above this length scale, the density fluctuations decay by diffusion with a diffusion coefficient $D_c \sim \xi^2/\tau_\alpha$, and below this length scale, relaxation of density fluctuations is limited during the α-relaxation time. Here we again recall the analogy to the mesoscopic dynamics of entangled polymer solutions [44,45] surveyed in Sec. III A, where stress-diffusion coupling (decoupling) is observed at $k\xi_p \gtrsim 1$ ($k\xi_p \lesssim 1$). This coupling arises from topological constraints (entanglement); the mechanical stress relaxation requires cooperative structural rearrangements on the length scale of ξ_p and these rearrangements result in the cooperative diffusion of concentration fluctuations. These dynamical properties are quite similar to those observed in supercooled liquids; thus one should expect that a similar description of the mesoscopic dynamics holds. In this subsection, using this analogy, we propose a minimal model based on a cluster picture; this model consistently describes length-scale-dependent anomalous transport in supercooled liquids.

The longitudinal force balance equation for the dynamics over the entire range of wavelengths is represented in Fourier space as

$$0 \cong -\zeta(k)\boldsymbol{w_k} - \frac{1}{\hat{\rho}_0 K_0}i\boldsymbol{k}\hat{\rho}_k + i\boldsymbol{k} \cdot \overset{\leftrightarrow}{\boldsymbol{\sigma}}_{\boldsymbol{k}}. \tag{19}$$

Thus the longitudinal part of the mechanical stress $\overset{\leftrightarrow}{\sigma}$ induces the dissipative flux, as the pressure gradient (the restoring force due to density fluctuations) does. In structural fluids or soft materials, it is often the case that the longitudinal part of the mechanical stress is inevitably coupled to the density or concentration fluctuations. The strong k dependence of $\eta(k)$ [36,37] leads to the nonlocal friction coefficient $\zeta(k)$, which should follow $\zeta(k) = \zeta \sim \eta \xi^{-2}$ and $\zeta(k) \sim \eta(k)k^2$ for $k\xi \ll 1$ and $k\xi \gg 1$ [60], respectively. However, the explicit form of $\zeta(k)$ does not affect the final result. Note that here we neglect the weak k dependence of the isothermal compressibility (and the shear modulus) at larger k. As shown in this subsection, Eq. (19) includes Eqs. (15) and (18) for $k\xi \lesssim 1$ and $k\xi \gtrsim 1$, respectively, and thus is the generalization of Eqs. (15) and (18).

Assuming that a cluster is a transient viscoelastic body, the slow internal distortion of the cluster causes mechanical stress $\overset{\leftrightarrow}{\sigma}$, which, for simplicity, is assumed to obey the following simple constitutive equation:

$$\overset{\leftrightarrow}{\sigma}_{\boldsymbol{k}}(t) = \int^t dt' h(t-t') \overset{\leftrightarrow}{\kappa}_{\boldsymbol{k}}(t'), \qquad (20)$$

where $\overset{\leftrightarrow}{\kappa} = \nabla \boldsymbol{w}^\dagger + \nabla \boldsymbol{w} - 2(\nabla \cdot \boldsymbol{w})\overset{\leftrightarrow}{\boldsymbol{\delta}}/3$ is the traceless strain-rate tensor that describes the slow cluster deformation. The bare response function $h(t)$ is usually well approximated by the Kohlrausch-Williams-Watts (KWW) form as $h(t) = E \exp[-(t/\tau_\alpha)^\psi]$. In this relation, ψ is the KWW exponent.

In frequency space, Eq. (20) is rewritten as

$$\overset{\leftrightarrow}{\sigma}_{ve}(\boldsymbol{k},\omega) = \frac{G^*(\omega)}{i\omega} \overset{\leftrightarrow}{\kappa}(\boldsymbol{k},\omega), \qquad (21)$$

where $G^*(\omega) = i\omega h(\omega)$ is the complex shear modulus [57] and $\eta = h(\omega = 0)$. From Eqs. (16), (19), and (21) we can derive the following:

$$\hat{\rho}(\boldsymbol{k},\omega) \cong \frac{1}{i\omega + \frac{k^2}{\zeta(k)K_0}\frac{1}{1 + \frac{4}{3}k^2 \frac{G^*(\omega)}{i\omega\zeta(k)}}} \hat{\rho}_{\boldsymbol{k}}(t=0), \qquad (22)$$

For $\omega\tau_0 \ll 1$, where τ_0 is the microscopic time scale, which is comparable to the momentum relaxation time, $|G^*(\omega)/i\omega\eta| \lesssim 1$. Thus, for $k\xi \ll 1$,

$$\hat{\rho}(\boldsymbol{k},\omega) \cong \frac{1}{i\omega + \frac{k^2}{\zeta K_0}} \hat{\rho}_{\boldsymbol{k}}(t=0), \qquad (23)$$

which provides the diffusive decay with a diffusion coefficient of $D_c \cong 1/\zeta K_0 \sim \xi^2/\tau_\alpha$. Here $\zeta(k) \cong \zeta$ at smaller $k\xi \ll 1$. In contrast, for $k\xi \gg 1$ and $\omega\tau_\alpha \gtrsim 1$, we determine that

$$\hat{\rho}(\boldsymbol{k},\omega) \cong \frac{1}{i\omega\left[1 + \frac{3}{4K_0 G^*(\omega)}\right]} \hat{\rho}_{\boldsymbol{k}}(t=0), \qquad (24)$$

which indicates that the density fluctuations are dominated by the mechanical relaxation. When the simple Maxwell model ($\psi = 1$) is adopted, $G^*(\omega)/i\omega = E\tau_\alpha/(1 + i\omega\tau_\alpha)$ and Eq. (24) reduces to

$$\hat{\rho}(\boldsymbol{k},\omega) \cong \frac{1}{1+\gamma} \frac{1}{i\omega + \frac{\gamma}{(1+\gamma)\tau_\alpha}} \hat{\rho}_{\boldsymbol{k}}(t=0), \qquad (25)$$

where $1/\gamma = 4K_0 E/3$.

Equations (24) and (25) indicate that the density fluctuations decay with the α-relaxation time within the cooperative

length scale ($k\xi \gg 0$); i.e., unless the topological constraints on the size of ξ are relaxed, the microscopic constituents (particles) cannot relax (stress-limited decay). This mechanism for the rearrangements of particles is almost the same as the stress-diffusion coupling in entangled polymer solutions [44,45]; however, this mechanism is completely different from that predicted by MCT, where caging at the particle scale causes the slowing down.

D. Brief remarks

The dynamic properties of clusters over the time period $\sim\tau_\alpha$ are distributed, that is, some clusters are mobile while others are immobile, and this distribution should be observed as DH (schematically shown in Fig. 2). Although the populations of mobile and immobile particles (or clusters) are not permanent but interchange after $\sim\tau_\alpha$, by averaging the mobile and immobile motions of a cluster over times longer than τ_α, we should observe well-averaged diffusive motions [61].

It should be noted that the present diffusive mechanism is different from that predicted by conventional macroscopic hydrodynamics (or the theory of simple liquids), which cannot explain the anomalously slow density diffusion [or the expression for D_c, Eq. (17)] observed in supercooled liquids. Conventional macroscopic hydrodynamics predict that the relaxation time for the density fluctuations at long wavelengths is given by $1/D_T k^2$, where D_T is the thermal diffusion coefficient [49,50]. However, in supercooled liquids, a much slower structural relaxation process dominates the transport properties; thus the heat mode is decoupled from the structural relaxation and from the density diffusion.

Even within the framework of MCT, recent efforts to explore the higher-order dynamical correlations of density fluctuations have indicated the existence of a growing length scale associated with a diverging relaxation time [65–67]. However, in the present MCT, it is an input assumption that the nonlinear interactions of density fluctuations at wavelengths near the first peak of the structure factor dominate anomalous hydrodynamic transport. Consequently, macroscopic transport coefficients are observed already at the particle scale and the correlation of hydrodynamic transport is therefore microscopic. In this sense, caging on the particle scale should be the primary effect and the mesoscopic dynamical correlation observed in a multipoint density correlation function in MCT might be a by-product of the slow dynamics.

This feature of MCT can be associated with the fact that the present mathematical framework of MCT for the supercooled liquid dynamics originates from the theory of simple liquids. In normal simple liquids, the hydrodynamic transport coefficients do not exhibit significant differences between the microscopic and macroscopic scales [49,50]. In normal simple liquids, the macroscopic transport coefficients can be applied over a wide range of spatiotemporal scales because no important characteristic length scale exists beyond that of the particle size and particle-scale dynamics dominate the hydrodynamic transport properties. However, in realistic supercooled liquids, this situation does not hold. For example, our simulation studies [36–38] strongly indicate that in supercooled liquids, a slow dynamical process at the mesoscopic scale governs hydrodynamic transport.

IV. CONCLUSION

Based on simulation results presented in the literature [36–38], we have constructed a dynamic scaling theory for anomalous hydrodynamic transport in supercooled liquids. The most important prediction is the scaling relation between the dynamic correlation length and the structural relaxation time, $\tau_\alpha \sim \xi^4$. In Sec. II we have also shown that the basic transport properties can be captured by simple scaling arguments. In addition, a continuum mechanics model has been provided to describe the length-scale-dependent anomalous hydrodynamic transport. We indicated that a nonconserved tensor field should be introduced to describe coherent dynamics for smaller length scales ($\lesssim\xi$).

We have assumed that fluctuations with a typical size of ξ behave as transiently correlated clusters. Smaller-scale ($\lesssim\xi$) fluctuations are subordinate to the cluster dynamics, which result in $\tau_\rho(k) \sim \tau_\rho(k=1/\xi) \sim \tau_\alpha$, where $\tau_\rho(k)$ is the k-dependent relaxation time of the (collective) density fluctuations. In contrast, the relaxation of larger-scale ($\gtrsim\xi$) fluctuations can be understood as diffusive decay, where the cluster is regarded as a unit; thus the relaxation time is given by $\tau_\rho(k) \sim 1/k^2 D_c \sim \tau_\alpha/(k\xi)^2$. These dynamic behaviors are clearly shown by previous simulation results in the literature [38]. In the derivation of the scaling relation, we tacitly assumed that densely packed clusters with a typical sizes of ξ diffuse in an almost uncorrelated manner. By coarse graining the fluctuations at wavelengths smaller than ξ, we can idealize the supercooled liquid dynamics with the dynamics of a normal (cluster) liquid composed of effective particles with a size of ξ. Based on this simple coarse-grained cluster view, we can essentially understand anomalous hydrodynamic transport. Although our results are purely qualitative, the present study should shed light on this field.

The most fundamental and difficult problem remaining is to determine the temperature dependence of ξ (thus that of τ_α) or to determine why clusters are preferentially formed when rearrangements of particle configurations occur in supercooled states. Moreover, theoretical studies are still needed to determine how ξ grows at low temperatures. Further theoretical investigations on the development of a general theory for the slow dynamics of structural glasses are the subject of another study [68].

APPENDIX

We argue in Sec. II C that the dynamic heterogeneity size $\xi_{\rm DH}(\Delta t)$ reflects the spatial distribution of the accumulation of the displacement events during a time interval Δt, but does not necessarily coincide with the actual cluster size of comoving particles or the collective transport range. Here, based on simulation results, we further discuss this point.

We use the same three-dimensional model of glass-forming liquids employed in Refs. [36–38]; this model has been thoroughly studied by many authors [10,69,70] (for details of the model, please see these papers). As mentioned in the preceding text, the mobility field for a time interval Δt is usually defined in terms of the displacement during the time; here the mobility field is defined as [12]

$$Q(\boldsymbol{r},t_0;\Delta t) = \sum_i q_i(t_0;\Delta t)\delta(\boldsymbol{r} - \boldsymbol{r}_i(t_0)), \quad \text{(A1)}$$

where $q_i(t_0;\Delta t) = q(|\boldsymbol{r}_i(t_0 + \Delta t) - \boldsymbol{r}_i(t_0)|)$ and $|\boldsymbol{r}_i(t_0 + \Delta t) - \boldsymbol{r}_i(t_0)|$ is the absolute value of the displacement of particle i over time Δt. Here $q(|\boldsymbol{u}|) = 1$ for $|\boldsymbol{u}| > a$ and $q(|\boldsymbol{u}|) = 0$ otherwise, which is opposite to the usual convention for q [12,36,53]. In the following analysis, we set $a = 0.3$, which is slightly larger than the plateau value of the mean square displacement of a particle in supercooled states. Hereafter, the particle of $q_i(t_0;\Delta t) = 1$ is referred as a mobile particle for the time interval $[t_0,t_0 + \Delta t]$. The structure factor of Q_k, $S_Q(k;\Delta t) = (1/N)\langle|Q_k|^2\rangle$, where $Q_k(t_0;\Delta t)$ is the Fourier transform of $Q(\boldsymbol{r},t_0;\Delta t)$, is a measure of the mobility correlation and its characteristic length determines the dynamic heterogeneity size $\xi_{\rm DH}(\Delta t)$ for the time interval Δt.

To analyze the spatiotemporal coherence of the rearrangement dynamics during $\Delta t = \tau_\alpha$ with a shorter time resolution, we first divide the time interval $[t_0,t_0 + \tau_\alpha]$ into subintervals $[t_0 + m\delta t,t_0 + (m + 1)\delta t]$ $(m = 0,1,2,\ldots,\tau_\alpha/\delta t - 1)$, where $\delta t < \tau_\alpha$. Then we introduce another field variable

$$P(\boldsymbol{r},m;t_0,\delta t)$$
$$= \sum_i q_i(t_0;\tau_\alpha)q_i(t_0 + m\delta t;\delta t)\delta(\boldsymbol{r} - \boldsymbol{r}_i(t_0 + m\delta t)), \quad \text{(A2)}$$

where $q_i(t_0;\tau_\alpha)q_i(t_0 + m\delta t;\delta t)$ selects mobile particles at the mth subinterval among those for the total interval $[t_0,t_0 + \tau_\alpha]$. Thus the spatiotemporal correlation of $P(\boldsymbol{r},m;t_0,\delta t)$ reflects the coherence properties of the mobility for $\Delta t = \tau_\alpha$ with the time resolution of δt. In supercooled states of our model system [36,37], on a time scale $\gtrsim 0.1\tau_\alpha$, rearrangements that have a relatively large particle displacement ($\gtrsim 0.3$) become pronounced, which are expected to cooperatively occur. On a much shorter time scale, however, less-correlated small-amplitude ($\ll 0.3$) thermal motions are dominant. Therefore, in the following analysis, we set $\delta t = \tau_\alpha/8$ and $\tau_\alpha/4$ for the subinterval. The present selection of δt is arbitrary, but does not affect the qualitative property of our results for $0.1\tau_\alpha \lesssim \delta t \ll \tau_\alpha$.

We present the temperature T and the time interval Δt dependences of the spatial coherence of the mobility field. In Fig. 3(a), $S_Q(k;\tau_\alpha) = (1/N)\langle|Q_k|^2\rangle$ and $S_P(k;\delta t) = (1/N)\langle|P_k|^2\rangle$ ($\delta t = \tau_\alpha/4$ and $\tau_\alpha/8$) scaled by $S_Q(0;\tau_\alpha)$ are plotted as a function of the scaled wave number $k\xi_{\rm DH}(\tau_\alpha)$. The dynamic heterogeneity size $\xi_{\rm DH}(\tau_\alpha)$, which is the correlation length of $Q(\boldsymbol{r},t_0;\tau_\alpha)$, can be determined by fitting $S_Q(k;\tau_\alpha)$ to the Ornstein-Zernike form [12,36,53,71]. The correlation length of $P(\boldsymbol{r},m;t_0,\delta t)$, $\bar\xi_{\rm DH}(\delta t)$, is determined in the same manner. With increasing T and decreasing δt, the ratios
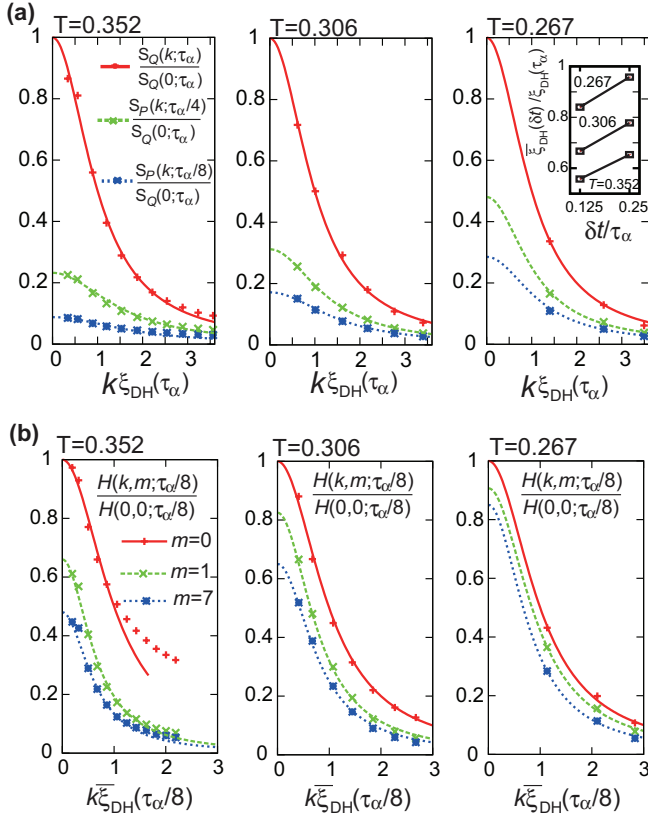
FIG. 3. (Color online) (a) $S_Q(k; \tau_\alpha)$ and $S_P(k; \delta t)$ scaled by $S_Q(0; \tau_\alpha)$ for several T and δt. The curves are determined by fitting $S_Q(k; \tau_\alpha)$ and $S_P(k; \delta t)$ to the Ornstein-Zernike form. The inset presents the ratios $\bar{\xi}_{DH}(\delta t)/\xi_{DH}(\tau_\alpha)$. With increasing T and decreasing δt, the ratios $S_Q(0; \tau_\alpha)/S_P(0; \delta t)$ and $\xi_{DH}(\tau_\alpha)/\bar{\xi}_{DH}(\delta t)$ increase. As demonstrated in Refs. [36–38], $T = 0.267$ and 0.306 correspond to the temperatures of high and low supercooling states, respectively. However, at $T = 0.352$, the system hardly exhibits the characteristic features of supercooled states. While in supercooled states ($T = 0.267$ and 0.306), for $\delta t = \tau_\alpha/8$ ($\tau_\alpha/4$), more than 90% (80%) of the mobile particles for a total period $[t_0, t_0 + \tau_\alpha]$ are mobile in at least one subinterval, at $T = 0.352$, the ratio is smaller [∼80% (70%)]. (b) Correlation between the mobility fields defined at different shorter periods $H(k, m - m'; \tau_\alpha/8) = \langle P_k(m; t_0, \tau_\alpha/8) P_{-k}(m'; t_0, \tau_\alpha/8) \rangle / N$ ($m - m' = 0, 1,$ and 7), for low and high degrees of supercooling, which is scaled by $H(0,0; \tau_\alpha/8)$.

$S_Q(0; \tau_\alpha)/S_P(0; \delta t)$ and $\xi_{DH}(\tau_\alpha)/\bar{\xi}_{DH}(\delta t)$ increase, which suggests that the spatiotemporal coherence of the particles motion is further weakened at higher temperatures. A similar tendency is observed in the analysis of the temperature T and the time interval Δt dependences of dynamic heterogeneity in Refs. [12,53]. To further examine the time coherence of the cooperative rearrangement motions for the long-term ($\Delta t =$

τ_α) accumulation, we analyze the correlation of $P_k(m; t_0, \delta t)$ at different shorter periods

$$H(k, m - m'; \delta t) = \frac{1}{N} \langle P_k(m; t_0, \delta t) P_{-k}(m'; t_0, \delta t) \rangle, \quad (A3)$$

which is presented in Fig. 3(b) for $\delta t = \tau_\alpha/8$. We observe that, at a higher degree of supercooling, the time coherence decays much more slowly. For $\Delta t \lesssim \tau_\alpha$, the average value of the particle displacement during Δt is much less than the dynamic heterogeneity size $\xi_{DH}(\tau_\alpha)$; thus this decay is not due to the advection of the mobility field but rather due to the temporal change of the mobile properties of particles during τ_α. Previously, Kim and Saito systematically revealed that as the temperature decreases toward the glass transition point, the lifetime of DH increases [62,63].

This simple investigation suggests the following picture: The spatially heterogeneous pattern of the mobility field is constructed from many cooperative rearrangement events during τ_α. At a low degree of supercooling, the individual cooperative events are smaller, but occur at a greater number of locations with less correlation. However, in the usual measurement of $\xi_{DH}(\tau_\alpha)$, neighboring regions that have cooperative events occurring during a time interval τ_α are counted as one cooperative region, even if those events are not actually correlated. This practice occurs because a measurement of the absolute value of the particle displacement cannot precisely distinguish between correlated and less-correlated or anticorrelated rearrangement modes [72]. Thus $\xi_{DH}(\tau_\alpha)$ may overestimate the actual size of the cooperative range of hydrodynamic transport or the clusters of comoving particles at a low degree of supercooling. At a high degree of supercooling, however, $\xi_{DH}(\tau_\alpha)$ may approach the actual cooperative length scale and the time coherence between each event is enhanced.

In our simulation, ξ grows as $\xi \cong 0.25\tau_\alpha^{1/4}$ within the range of τ_α of our simulations ($10 \lesssim \tau_\alpha \lesssim 10^5$). In contrast, $\xi_{DH}(\tau_\alpha)$ is found to grow more slowly but with a larger coefficient as $\xi_{DH}(\tau_\alpha) \cong 2.1\tau_\alpha^{1/8}$ [36]. Here the relaxation time of a normal state is ∼1. Thus, although the correlation length of hydrodynamic transport ξ exhibits a stronger T dependence than that of $\xi_{DH}(\tau_\alpha)$, ξ is still comparable to $\xi_{DH}(\tau_\alpha)$ at $\tau_\alpha \sim 10^8$. However, in such an extremely supercooled state, the relevance of the present simple phenomenological argument and simulation results is not clear (a change of eight orders of magnitude in the viscosity or the α-relaxation time greatly exceeds the results of existing simulation studies).

Though the dynamic heterogeneity size at $\Delta t = \tau_\alpha$ has usually been considered to be a dynamic correlation length, the physical meaning of this correlation is not clear. In this appendix, we critically addressed this problem by extending the usual four-point correlation function method. However, further analysis will be required to clarify the meaning and the relation between ξ and $\xi_{DH}(\tau_\alpha)$ [68].

[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] W. Götze, *Complex Dynamics of Glass-Forming Liquids: A Mode-Coupling Theory* (Oxford University Press, Oxford, 2009).

[5] H. Sillescu, J. Non-Cryst. Solids. **243**, 81 (1999).

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

[7] E. R. Weeks, J. C. Crocker, A. C. Levitt, A. Schofield, and D. A. Weitz, Science **287**, 627 (2000).

[8] M. M. Hurley and P. Harrowell, Phys. Rev. E **52**, 1694 (1995).

[9] W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **79**, 2827 (1997).

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

[11] B. Doliwa and A. Heuer, Phys. Rev. Lett. **80**, 4915 (1998).

[12] N. Lačević, F. W. Starr, T. B. Schrøder, and S. C. Glotzer, J. Chem. Phys. **119**, 7372 (2003).

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

[14] *Dynamical Heterogeneities in Glasses, Colloids, and Granular Media* edited by L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, and W. van Saarloos, (Oxford University Press, Oxford, 2011).

[15] H. Tanaka, Eur. Phys. J. E **35**, 113 (2012).

[16] V. Lubchenko and P. Wolyness, Annu. Rev. Phys. Chem. **58**, 235 (2007).

[17] A. Cavagna, Phys. Rep. **476**, 51 (2009).

[18] G. Tarjus, S. A. Kivelson, Z. Nussinov, and P. Viot, J. Phys.: Condens. Matter **17**, R1143 (2005).

[19] H. Tanaka, T. Kawasaki, H. Shintani, and K. Watanabe, Nat. Mater. **9**, 324 (2010).

[20] W. Kob, S. Roldan-Vargas, and L. Berthier, Nat. Phys. **88**, 164 (2012).

[21] L. Berthier and W. Kob, Phys. Rev. E **85**, 011102 (2012).

[22] C. Cammarota and G. Biroli, Proc. Natl. Acad. Sci. USA **109**, 8850 (2012).

[23] F. Fujara, B. Geil, H. Sillescu, and G. Fleischer, Z. Phys. B **88**, 195 (1992).

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

[25] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).

[26] D. N. Perera and P. Harrowell, Phys. Rev. Lett. **81**, 120 (1998).

[27] These fundamental questions regarding the spatial correlation pose a chicken-and-egg problem for the origin of the slowing down: Does the microscopic slowing down cause the mesoscopic (and thus the macroscopic) slowing down, or vice versa?

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

[29] L. Berthier, D. Chandler, and J. P. Garrahan, Euro. Phys. Lett. **69**, 320 (2005).

[30] A. C. Pan, J. P. Garrahan, and D. Chandler Phys. Rev. E. **72**, 041106 (2005).

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

[32] P. Chaudhuri, L. Berthier, and W. Kob, Phys. Rev. Lett. **99**, 060604 (2007).

[33] S. F. Swallen, K. Traynor, R. J. McMahon, M. D. Ediger, and T. E. Mates, J. Phys. Chem. B **113**, 4600 (2009).

[34] J. G. Amar and R. D. Mountain, J. Chem. Phys. **86**, 2236 (1987).

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

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

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

[38] A. Furukawa and H. Tanaka, Phys. Rev. E **86**, 030501(R) (2012).

[39] R. M. Puscasu, B. D. Todd, P. J. Daivis, and J. S. Hansen, J. Chem. Phys. **133**, 144907 (2010).

[40] V. A. Levashov, J. R. Morris, and T. Egami, J. Chem. Phys. **138**, 044507 (2013).

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

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

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

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

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

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

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

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

[49] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (Dover, New York, 1991).

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

[51] S. Whitelam, L. Berthier, and J. P. Garrahan, Phys. Rev. Lett. **92**, 185705 (2004).

[52] E. Flenner and G. Szamel, Phys. Rev. E **79**, 051502 (2009).

[53] E. Flenner, M. Zhang, and G. Szamel, Phys. Rev. E **83**, 051501 (2011).

[54] E. Flenner and G. Szamel, J. Chem. Phys. **138**, 12A523 (2013).

[55] A. Furukawa (unpublished).

[56] Y. J. Jung, J. P. Garrahan, and D. Chandler, Phys. Rev. E **69**, 061205 (2004).

[57] M. Doi and S. F. Edwards, *Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).

[58] P. G. de Gennes, *Scaling Concepts of Polymer Physics* (Cornell University Press, Ithaca, 1979).

[59] R. A. MacPhail and D. Kivelson, J. Chem. Phys. **90**, 6549 (1989); **90**, 6555 (1989).

[60] A scaling behavior for $\zeta(k)$ can be written as $\zeta(k) = \zeta\Theta(kx)$, where $\Theta(x) \sim 1$ for $x \ll 1$ and $\Theta(x) \sim x^{-2}$ for $x \gg 1$. Equation (8) yields the friction coefficient on the particle scale as $\zeta(k = 1/\lambda) \cong \eta_0\lambda(1/\lambda)^3$. The scaling form of $\zeta(k)$ suggests that the dissipation at smaller scales ($k\xi \gg 1$) should also be insensitive to the cooperative properties.

[61] Recent studies show that the lifetime of DH is comparable to or slightly longer than τ_α [62,63]. The slowly varying correlated cluster may be defined over much longer periods. In fact, as shown in the literature [64], the neighboring particles around a tagged particle remain almost unchanged for considerably longer than τ_α. However, the present view of slow cluster diffusion is established (on average) as long as a cluster is defined for at least τ_α.

[62] K. Kim and S. Saito, Phys. Rev. E **79**, 060501(R) (2009).

[63] K. Kim and S. Saito, J. Chem. Phys. **133**, 044511 (2010).

[64] H. Shiba, T. Kawasaki, and A. Onuki, Phys. Rev. E **86**, 041504 (2012).

[65] G. Biroli and J.-P. Bouchaud, Europhys. Lett. **67**, 21 (2004).

[66] G. Biroli, J.-P. Bouchaud, K. Miyazaki, and D. R. Reichman, Phys. Rev. Lett. **97**, 195701 (2006).

[67] L. Berthier, G. Biroli, J.-P. Bouchaud, W. Kob, K. Miyazaki, and D. R. Reichman, J. Chem. Phys. **126**, 184503 (2007).

[68] A. Furukawa (unpublished).

[69] B. Bernu, J. P. Hansen, Y. Hiwatari, and G. Pastore, Phys. Rev. A **36**, 4891 (1987).

[70] J.-N. Roux, J.-L. Barrat, and J. P. Hansen, J. Phys.: Condens. Matter **1**, 7171 (1989); J.-L. Barrat, J.-N. Roux, and J. P. Hansen, Chem. Phys. **149**, 197 (1990).

[71] The available range of wave numbers for the fit becomes narrower as the temperature decreases. This situation makes

the precise determination of ξ_{DH} difficult. In fact, in almost all existing simulation studies of deeply supercooled states, $\xi_{DH}k_0 \gtrsim 1$, where $k_0 = 2\pi/L_0$ is the minimum wave number of the computation determined by the system size L_0.

[72] In Ref. [38], we characterized DH not by the absolute value of the particle displacement but by the change in shear stress over a time interval $\sim\tau_\alpha$. Then the characteristic size of the heterogeneous stress relaxation was found to be almost given by the correlation length for hydrodynamic transport ξ: Because anticorrelated or less-correlated rearrangements exhibit different stress changes, such rearrangement events are somewhat distinguished by a measurement of the coherence of the stress relaxation [38]. However, within the usual characterization of DH, the absolute value of the particle displacement cannot distinguish such different rearrangements; this lack of distinction results in a different characteristic length scale $\xi_{DH}(\tau_\alpha)\ (> \xi)$.