Universality in multicomponent glass-forming liquids near the glass transition

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Universality in multicomponent glass-forming liquids near the glass transition

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I. INTRODUCTION

Understanding of the glass transition is one of the pioneering problems encountered in a wide variety of fields, such as soft-matter science and chemical engineering, which deal with complex systems [1–4]. With recent progress in science and technology the relaxation processes of viscous liquids near the glass transition are extensively studied by experiments and computer simulations [5,6]. Several interesting statistical-mechanical theories have been also proposed to study this problem, for example, by Götze et al. [4,7,8] and by Medina-Noyola and co-workers [9–11]. The former work is based on a mode-coupling theory (MCT), while the latter is based on a generalized Langevin equation description. Although their approaches are limited to a calculation of two-body correlations, their results are quite successful in some cases. However, it is well known that many-body correlations play an important role near the glass transition and cause a dynamic heterogeneity [12,13]. Hence, those correlations are indispensable to discuss the slow relaxation in complex systems. In general, however, it is difficult to deal with them from first principles. In the present paper, we focus only on the dynamics of a single particle. Instead of calculating those correlations, therefore, we investigate how many-body correlations lead to universal properties in the dynamics of a single particle by just analyzing available data for the mean-square displacement from a unified point of view based on the mean-field theory (MFT) recently proposed [14,15]. We do not discuss the dynamics of the non-Gaussian parameter here since precise data are not available yet.

In this paper, we discuss whether there exists a universality near the glass transition among diversely different glass-forming systems, including fragile glass formers and strong glass formers. In the previous papers [15,16], we have shown that there exists a universality among fragile glass formers. In the present paper, we analyze the simulation results on two different systems, bulk glass-forming Cu60Ti20Zr20 melt and network-forming SiO2 melt [17] and network-forming SiO2 melt [18], from a unified point of view based on MFT and compare them with the previous results. Thus, we show that the dynamical properties of the relaxation processes in those systems are also remarkably universal as in fragile systems. The first point is that any dynamical states of the systems are uniquely determined by a long-time self-diffusion coefficient \( D^L_t \) (or a universal parameter \( u \)). The second is that any simulation results for the mean-square displacements in different systems can be described by a single master curve given by MFT at a given value of \( u \). Thus, we show that MFT can describe not only the relaxation processes in fragile glass-forming systems but also those in strong glass-forming systems. This is also predicted from a first-principles theory recently proposed by the present author [19].

We begin in Sec. II by reviewing the theories, which are used in the present paper. In Sec. III we show the universal behavior among different systems from a unified point of view based on the MFT. We conclude in Sec. IV with a summary.

II. THEORIES

We consider three-dimensional multicomponent glass-forming systems, \( A_BC_z \ldots \), which consists of \( N_p \) particles with mass \( m_\alpha \) and diameter \( \sigma_{\alpha\alpha} \) in the total volume \( V \) at temperature \( T \), where \( \alpha \in \{A,B,C\ldots\}, N=\sum_\alpha N_\alpha \), and \( x+y+z+\cdots=100 \). Let \( X^{(\alpha)}(t) \) and \( P^{(\alpha)}(t) \) denote the position vector of \( i \)th particle of component \( \alpha \) and its momentum at time \( t \).

A. First-principles theory

We first review the first-principles theory recently proposed by the present author [19]. The particle obeys the Newton equation

\[
\frac{d}{dt} P^{(\alpha)}(t) = F^{(\alpha)}(t),
\]

where \( F^{(\alpha)}(t) \) is a force acting on the \( i \)th particle of component \( \alpha \) from the other particles. Equation (1) holds on the time scale of order \( t_d=\sigma_{\alpha\alpha} v_{th} \), where \( v_{th}=(k_B T/m_\alpha)^{1/2} \) is an average particle velocity.
In this paper, we are only interested in the single-particle dynamics near the glass transition, whose space-time scales are much larger than those of microscopic processes. Then, the useful physical quantities to describe the relaxation of a single particle near the glass transition are given by the self-intermediate scattering function

\[ F^{(2)}_s(q,t) = \langle \exp[iq \cdot (X^{(1)}(t) - X^{(1)}(0))] \rangle \]  

and the mean-square displacement

\[ M^{(2)}_2(t) = \langle (X^{(1)}(t) - X^{(1)}(0))^2 \rangle, \]  

both of which are related through the relation

\[ F^{(2)}_s(q,t) = \exp\left[ -\frac{q^2}{6} M^{(2)}_2(t) + \frac{q^2}{2} \left( \frac{M^{(2)}_2(t)}{6} \right)^2 \alpha^{(3)}(t) + \cdots \right], \]  

where \( \alpha^{(3)}(t) \) is the non-Gaussian parameter \[20\].

As shown in the previous paper \[19\], using the Tokuyama-Mori projection operator method \[21\], one can transform Eq. (1) into a time-convolutionless generalized Langevin equation

\[ \frac{d}{dt} \Pi^{(a)}_i(t) = -\int_0^t \psi^{(a)}(s)ds \Pi^{(a)}_i(t) + f^{(a)}_i(t) \]  

with the memory function

\[ \psi^{(a)}(t) = \frac{\langle f^{(a)}_i(t) \cdot f^{(a)}_j(0) \rangle}{\langle \Pi^{(a)}_i(t) \cdot \Pi^{(a)}_j(0) \rangle}, \]  

where \( f^{(a)}_i(t) \) denotes the fluctuating force and is given by

\[ f^{(a)}_i(t) = F^{(a)}_i(t) + \int_0^t \psi^{(a)}(s)ds \Pi^{(a)}_i(t). \]  

Here, \( \Pi^{(a)}_i(t) \) satisfies

\[ \langle f^{(a)}_i(t) \cdot \Pi^{(a)}_j(0) \rangle = \langle f^{(a)}_i(t) \rangle = 0. \]  

The use of Eqs. (5) and (8) then leads to

\[ \langle \Pi^{(a)}_i(t) \cdot \Pi^{(a)}_j(0) \rangle = \exp\left[ -\int_0^t ds \int_0^t d\tau \psi^{(a)}(\tau) \right] \langle \Pi^{(a)}_i(\tau) \rangle^2. \]  

Equation (5) is a starting equation to discuss the dynamics of a single particle.

By using Eqs. (3) and (5), one can derive the equation for the mean-square displacement \( M^{(2)}_2(t) \) as \[19\]

\[ \frac{d}{dt} M^{(2)}_2(t) = 6D^{(a)}(t), \]  

where \( D^{(a)}(t) \) denotes the time-dependent self-diffusion coefficient and is given by

\[ D^{(a)}(t) = \frac{(\sigma^{\alpha \alpha} u_0) \lambda^{\alpha \alpha}}{1 + t_0^2} \]  

Here, \( u_0 = (\epsilon/m_0)^{\frac{3}{2}} \) and \( t_0 = \sigma^{\alpha \alpha} u_0 \). Let \( t_0 \) denote a relaxation time of the memory function \( \psi^{(a)}(t) \). Then, one finds

\[ M^{(2)}_2(t) = \begin{cases} 3v^2 a_0^2 & \text{for } t \ll t_\beta, \\ 6D^2 t & \text{for } t \gg t_\beta. \end{cases} \]  

with the long-time self-diffusion coefficient

\[ D^2 = D^{(a)}(t = \infty) = \frac{\sigma^{\alpha \alpha} u_0}{t_0^2} \psi^{(a)}(s)ds. \]  

Thus, there are different time stages, depending on time scales \[14\]. In an early stage (\( E \)) for \( t \leq t_\beta \), the particle obeys a ballistic motion. In an intermediate stage (or \( \beta \) stage) (\( \beta \)), for \( t_\beta < t < t_\beta \), it behaves as if it is trapped in a cage which is mostly formed by neighboring particles. This is the so-called cage effect. On the time scale of order \( t_\beta \), the particles can escape their cages and in a late stage (\( L \)) for \( t \gg t_\beta \), they obey a long-time diffusion process with \( D^2 \).

B. Long-time self-diffusion coefficient

In general, it is difficult to calculate the memory function up to higher order in \( F_i \). However, this is indispensable to discuss the slow dynamics of a single particle near the glass transition because the many-body correlations play an important role near the glass transition. As shown in the previous paper \[22\], the long-time self-diffusion coefficient \( D^2 \) is written as

\[ \frac{D^2}{\sigma^{\alpha \alpha}} = \kappa^{\alpha \alpha}_0 \left( \frac{\lambda^{\alpha \alpha}}{\lambda} \right) \left( 1 - \frac{\lambda}{\lambda^{\alpha \alpha}} \right)^2, \]  

where \( \lambda \) is a control parameter, such as an inverse temperature \( 1/T \) and a volume fraction \( \phi \). \( \lambda^{\alpha \alpha} \) is a singular point to be determined. The singular part of Eq. (14) results from the long-time correlation effects due to the many-body interactions between particles and is in general difficult to calculate. Hence, the singular point \( \lambda_c \) is only determined by fitting Eq. (14) with experimental data and simulation results. As is discussed later, however, there exists a universal rule to determine it.

On the other hand, the coefficient \( \kappa^{\alpha \alpha}_0 \) can be calculated analytically. The use of Eqs. (13) and (14) then leads to

\[ t_M \int_0^\infty \psi^{(a)}(s)ds = \kappa^{\alpha \alpha}_0 \left( \frac{\lambda^{\alpha \alpha}}{\lambda} \right) \left( 1 - \frac{\lambda}{\lambda^{\alpha \alpha}} \right)^{-2}, \]  

As discussed in the previous paper \[22\], the coefficient \( \kappa^{\alpha \alpha}_0 \) can be calculated analytically at lower values of \( \lambda \) for such systems that (i) the intermolecular force is of long range and/or (ii) the number density is nondiluted at lower \( \lambda \) as

\[ \kappa^{\alpha \alpha}_0 = \frac{\sigma^{\alpha \alpha}}{\epsilon} \left( -\frac{\partial U^{rep}_\alpha(r)}{\partial r} \right) \]  

where \( U^{rep}(r) \) denotes a repulsive part of the potential \( U^{rep}(r) \). For other systems in which the control parameter is the volume fraction \( \phi \) and the intermolecular force is of short range with a linear force range \( \sigma_{\alpha \alpha} \), an analytical prediction of \( \kappa^{\alpha \alpha}_0 \) is as follows. At lower volume fractions, the two-body repulsive interactions play an important role. In the following, therefore, we only discuss those interactions. By using Eqs. (6), (7), and (9), one can then write \( \psi^{(a)}(t) \), up to the lowest order in \( F_i \), as

\[ \psi^{(a)}(t) = \exp \left[ -\frac{q^2}{6} \left( \frac{M^{(2)}_2(t)}{6} \right)^2 \alpha^{(3)}(t) + \cdots \right]. \]
where \( \langle (P_i^{(\alpha)})^2 \rangle = 3m_i k_B T \). It is convenient to introduce the number densities by

\[
n_S^{(\alpha)}(r) = \delta (r - X_i^{(\alpha)}(0)),
\]

\[
n^{(\alpha)}(r) = \frac{N_a}{N_i} \delta (r - X_i^{(\alpha)}(0)).
\]

Then, the force \( F_i^{(\alpha)}(0) \) can be written as

\[
F_i^{(\alpha)}(0) = \sum_{\beta} \int dr_1 \int dr_2 F_{i2}^{(\alpha \beta)}(r_2) n_i^{(\beta)}(r_2),
\]

where \( F_{i2}^{(\alpha \beta)} \) denotes the force acting on the particle \( i \) of component \( \alpha \) from the particle \( j \) of component \( \beta \). As shown in the previous paper [22], the force term \( F_{i2}^{(\alpha \beta)} \) is only needed to determine \( \kappa_{aa} \) at lower values of \( \lambda \). In the following, therefore, we neglect the forces acting on particle of component \( \alpha \) from particles of other components. It is convenient to introduce the dimensionless variables as

\[
\hat{r} = r/\sigma_{aa}, \quad k_B T/\epsilon = 1, \quad \hat{n} = \sigma_{aa}^3 n,
\]

\[
F_{12}^{aa} = (\sigma_{aa}/\epsilon) F_{12}^{aa}, \quad \hat{\mathbf{p}}_i^{(a)} = \mathbf{P}_i^{(a)}(m_i k_B T)^{1/2}.
\]

The average distance between particles is of order \( \sigma_{aa}/\phi^{1/3} \), while the force range is of order \( \sigma_{aa} \). Hence, one can write

\[
\hat{r}_2 = \hat{r}_1 + \hat{r}_{21} = \hat{r}_1 + O(\phi^{1/3}),
\]

\[
\hat{n}_i^{(a)}(r_2) = \hat{n}_i^{(a)}(\hat{r}_1) + \hat{r}_{21} \cdot \nabla \hat{n}_i^{(a)}(\hat{r}_1) + O(\phi^{2/3}),
\]

where \( \hat{r}_{21} = \hat{r}_2 - \hat{r}_1 \). Thus, the memory integral can be written as

\[
t_m \int_0^\infty \psi(t) ds = t_m \frac{\langle P_i^{(\alpha)}(s) \cdot F_i^{(\alpha)}(0) \rangle}{3m_i k_B T}
\]

\[
= \int d\hat{r}_{21} \hat{F}_{i21}^{aa}
\]

\[
\times \int d\hat{r}_1 \frac{\langle P_i^{(\alpha)}(\hat{r}_1) \cdot \hat{F}_i^{(\alpha)}(\hat{r}_1) \rangle}{3}
\]

\[
= \left[ - \int d\hat{r}_{21} \hat{r}_{21} \frac{\partial \hat{U}^{re2}_{aa}(\hat{r}_{21})}{\partial \hat{r}_{21}} \right]
\]

\[
\times \left[ \int d\hat{r}_1 \frac{4\pi}{3} \hat{n}_i^{(a)}(\hat{r}_1) \hat{F}_i^{(\alpha)}(\hat{r}_1) \cdot \nabla \hat{n}_i^{(a)}(\hat{r}_1) \right].
\]

The second part of Eq. (25) is of order 1 and corresponds to the singular part of Eq. (15). Hence, we thus find

\[
\kappa_{aa} = \int_1^\infty d\hat{r} \hat{r} \hat{U}^{re2}_{aa}(\hat{r}) \frac{\partial \hat{U}^{re2}_{aa}(\hat{r})}{\partial \hat{r}}.
\]

As a simple example, we take \( U_{aa}(r) = k_B T (\sigma_{aa}/r)^n_{aa} \). Then, we obtain

\[
\kappa_{aa} = \frac{n_{aa}}{n_{aa} - d},
\]

where \( d=3 \) here. As \( n_{aa} \) increases, \( \kappa_{aa} \) decreases to 1. In fact, for hard spheres where \( U_{aa}(r) \) is given by the step function, we find \( \kappa_{aa} = 1 \).

In order to test Eq. (27), we analyze the simulation results from Refs. [23–27] for the long-time self-diffusion coefficient \( D_S^L \) on the polydisperse systems of soft spheres and quasishar spheres with \( \delta \% \) size polydispersity, where the potential is given by \( U(r) = k_B T (\sigma/r)^n \). For comparison, the hard-sphere systems with \( \delta \% \) size polydispersity are also considered. In Fig. 1, \( D_S^L/\sigma v_0 \) versus the volume fraction \( \phi(=\pi/6 N/\lambda^3) \) is plotted for different values of \( n \). It is thus shown that for soft spheres with \( n=8 \), \( \kappa_{aa} \) is given by Eq. (16), while for quasi-hard spheres with \( n=36 \) it is given by Eq. (27). On the other hand, for such systems with \( 9 \leq n < 36 \) that they are neither soft spheres nor hard spheres, \( \kappa_{aa} \) is determined by fitting since there is no theory for it. The coefficient \( \kappa_{aa} \) and the singular volume fraction \( \phi_s \) are listed in Table I. In order to check the consistency with Eq.
more clearly, we also show a log-log plot of $D_2(t)/\sigma_{\text{v}_0}$ versus $(\phi_0/\phi)(1-\phi/\phi_t)^2$ in Fig. 2. Thus, all the simulation results are shown to be well described by Eq. (14) within errors. Finally, we note here that the simulation results on the polydisperse system with $\delta = 10$ and the corresponding solutions of the MCT [23] are also well described by Eq. (14). In both cases $\kappa_{\text{na}}$ has the same value as 36/33 (=1.091), while the singular point $\phi_t$ is different from each other because the only two-body correlations are taken into account for MCT but the many-body correlations are done for the simulations. Finally, we note that the simulation results deviate from the mean-field line given by Eq. (14) at higher volume fractions. As is discussed later, this deviation always occurs around the same value of $D_2(t)/\sigma_{\text{na}}v_0$ even in different systems.

### C. Mean-field theory

Here, we briefly summarize the MFT of the glass transition for molecular systems recently proposed by the present author [14,15,28]. The mean-field theory consists of two essential points: (i) the mean-field equations for the mean-square displacement and (ii) the singular long-time self-diffusion coefficients.

#### Mean-field equations

The mean-square displacement $M_2^{(a)}(t)$ for molecular systems is described by a nonlinear equation [14]

$$\frac{d}{dt} M_2^{(a)}(t) = 6D_2^{(a)}(\lambda) + 6[v_f^2 - D_2^{(a)}(\lambda)]e^{-M_2^{(a)}(t)/\ell(\lambda)^2}, \quad (28)$$

where the mean-free path $\ell(\lambda)$ is a length in which a particle can move freely without any interactions between particles. Although it is originally related to the static structure factor $S(q)$ [28], it is determined by a fitting with data here. Equation (28) can be solved to give a formal solution

$$M_2^{(a)}(t) = 2dD_2^{(a)} + t^2 \ln \left[ e^{-2d/t_0} + \frac{1}{6} \left( \frac{t_0^2}{6} \right)^2 \right] \times \left[ 1 - \left( 1 + \frac{2d}{t_0} e^{-2d/t_0} \right)^2 \right], \quad (29)$$

where $t_0(=\ell^2/D_2^{(a)})$ denotes a time for a particle to diffuse over a distance of order $\ell$ with the diffusion coefficient $D_2^{(a)}$ and is identical to the so-called $\beta$-relaxation time. Here, $t_0(=\ell/v_0)$ is a mean-free time, within which each particle can move freely without any interactions between particles. As shown in the previous paper [15], the mean-free path $\ell$ is uniquely determined by $D_2^{(a)}/(\sigma_{\text{na}}v_0)$. Hence, solution (29) suggests that the dynamics is described by only one parameter $D_2^{(a)}/(\sigma_{\text{na}}v_0)$ if the length and the time are scaled by $\sigma_{\text{na}}$ and $t_0$, respectively.

Solution (29) also shows the asymptotic forms given by Eq. (12). As shown in the previous paper [14], for $\lambda \geq \lambda_s$, there exists a new time stage, the so-called $\beta$-relaxation stage ($\beta$) for $t_0 < t \leq t_0$, where $\lambda_s$ is a value at which a new time appears. In fact, one can find one more time scale, the caging time $t_c$, as follows. First, one can obtain the following asymptotic solutions from Eq. (29):

<table>
<thead>
<tr>
<th>Method</th>
<th>$n$</th>
<th>$\kappa_{\text{na}}$</th>
<th>$\phi_t$</th>
<th>$\delta$ (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD</td>
<td>8</td>
<td>8 [Eq. (16)]</td>
<td>1.245</td>
<td>0</td>
<td>[25]</td>
</tr>
<tr>
<td>MD</td>
<td>12</td>
<td>4 (fitting)</td>
<td>0.822</td>
<td>0</td>
<td>[25]</td>
</tr>
<tr>
<td>MD</td>
<td>18</td>
<td>3 (fitting)</td>
<td>0.6885</td>
<td>0</td>
<td>[25]</td>
</tr>
<tr>
<td>MD</td>
<td>144</td>
<td>144/141 [Eq. (22)]</td>
<td>0.5598</td>
<td>0</td>
<td>[25]</td>
</tr>
<tr>
<td>MCT</td>
<td>36</td>
<td>36/33 [Eq. (22)]</td>
<td>0.593</td>
<td>10</td>
<td>[24]</td>
</tr>
<tr>
<td>MD</td>
<td>36</td>
<td>36/33 [Eq. (22)]</td>
<td>0.593</td>
<td>15</td>
<td>[24]</td>
</tr>
<tr>
<td>MD</td>
<td>36</td>
<td>36/33 [Eq. (22)]</td>
<td>0.593</td>
<td>10</td>
<td>[23]</td>
</tr>
<tr>
<td>MD</td>
<td>$\infty$</td>
<td>1 [Eq. (22)]</td>
<td>0.583</td>
<td>6</td>
<td>[27]</td>
</tr>
<tr>
<td>MD</td>
<td>$\infty$</td>
<td>1 [Eq. (22)]</td>
<td>0.5908</td>
<td>15</td>
<td>[26]</td>
</tr>
</tbody>
</table>

FIG. 2. (Color online) A log-log plot of $D_2(t)/\sigma_{\text{v}_0}$ versus $(\phi_0/\phi)(1-\phi/\phi_t)^2$ for different $n$. The details are the same as in Fig. 1.
The single-particle dynamics is determined by only one parameter $D_s^0/(\sigma_{\alpha\alpha}v_0)$. Hence, it is convenient to introduce a parameter $u$ by

$$u = \log_{10}(\sigma_{\alpha\alpha}v_0/D_s^0).$$

As shown in the previous paper [15], as $\lambda$ is increased, the supercooled state and the glassy state appear at $\lambda_1 (u_1)$ and $\lambda_2 (u_2)$, respectively, where $\lambda_1 > \lambda_2 > \lambda_c$ ($u_1 > u_2$). Analyses of various data show that $u_2 \approx 2.6$, $u_1 \approx 5.1$, and $u_c \approx 1.06$ (Table II). As $\lambda$ increases, the time exponents $b_\gamma$ and $b_\beta$ decrease. In the supercooled region [S] for $u_2 \leq u < u_1$, the exponent $b_\beta$ reduces to 1.3301, while the exponent $b_\gamma$ reduces to 1 in the glassy region [G] for $u \approx u_c$. We should also mention here from the detailed analyses that, as $u$ increases, the long-time self-diffusion coefficients obtained by the simulations and the experiments start to deviate from Eq. (14) at $u=0.304$, while their mean-square displacements also show a deviation from Eq. (29) for $u > u_c$, but only in the $\beta$ stage. This concurrence may not be a coincidence because the systems are considered not to be in equilibrium for $u > u_c$.

### III. Universalities Near the Glass Transition

In this section, we analyze the mean-square displacements obtained in two different systems, Cu$_{60}$Ti$_{20}$Zr$_{20}$ and SiO$_2$, from a unified point of view based on MFT and explore universal behavior near the glass transition. Both systems satisfy the conditions that (i) the intermolecular force is of long range and/or (ii) the number density is nondiluted at lower $\lambda$. Hence, $\kappa_{\alpha\alpha}$ is calculated from Eq. (16).
A. Cu\textsubscript{60}Ti\textsubscript{20}Zr\textsubscript{20}

First, we analyze the simulation results for self-diffusion of Cu in Cu\textsubscript{60}Ti\textsubscript{20}Zr\textsubscript{20} melt \cite{17}, where $\lambda=1/T$. The molecular-dynamics (MD) simulations are performed at $m_{Cu}=m_{Ti}=m_{Zr}$ by the so-called NPT method by using the following Stillinger-Weber potential (SW) \cite{29}:

$$U_{ab}(r) = \begin{cases} c_{ab}r^2\left[\left(\frac{\sigma_{ab}}{r}\right)^{n_{ab}} - 1\right] & \text{for } r < R_{ab}\sigma_{ab} \frac{1}{r} \left[\left(\frac{r}{\sigma_{ab}} - R_{ab}\sigma_{ab}\right)^{1/n_{ab}} - 1\right] & \text{for } r > R_{ab}\sigma_{ab}. \end{cases}$$ (36)

where the potential parameters are listed in Table III. Here, the total number of particles is $N=4000$. The simulation is done at 1 atm. Length, time, and temperature are scaled by $\sigma_{CuCu}\sigma_{CuCu}(m_{Cu}/\epsilon)^{1/2}$, and $\epsilon/k_B$, respectively.

In Fig. 3, the mean-square displacement $M_2(t)$ for Cu is plotted versus time $t/t_0$ for different temperatures. The mean-field equation given by Eq. (29) agrees with the simulation results well, except for lower temperatures $T<T_c$. Here, two adjustable parameters $\ell$ and $D^2_0$ are used to fit Eq. (29) with the simulation results. For $T<T_c$ (or $u>u_c$), the simulation results deviate upward from the theoretical results only in $\beta$ stage. Hence, those simulation results are considered not to reach an equilibrium state yet. As mentioned before, such a deviation always occurs at $u>u_c$. In Fig. 4, the long-time self-diffusion coefficient $D^2_0$ is plotted versus inverse temperature. From Eq. (16), the coefficient $\kappa_{CuCu}$ is calculated as $\kappa_{CuCu}=9$ \cite{22}. The inverse singular temperature is obtained by fitting Eq. (14) with the simulation results as $1/T_c$ =5.92. Thus, Eq. (14) can describe the simulation results well, except for lower temperatures $T<T_c$ (or $u>u_c$). We note here that those simulation results also show a deviation from Eq. (14) for $u>u_c$. Hence, the simulation results do not reach an equilibrium state yet for $u>u_c$. The characteristic temperatures are listed in Table IV.

B. SiO\textsubscript{2}

Next, we analyze the simulation results for self-diffusion of O in SiO\textsubscript{2} melt \cite{18}, where $\lambda=1/T$. The molecular-dynamics simulations are performed by the so-called $NVT$ method by using the following potential given by Nakano et al. \cite{31}:

$$U = \sum_{a=0}^{\infty} U^{(2)}_{a\beta} + \sum_{a=\beta}^{\gamma} U^{(3)}_{a\beta\gamma}$$ (37)

with the two-body potential

$$U^{(2)}_{a\beta}(r) = \epsilon_{a} \left(\frac{a_{a\beta} + a_{a\beta}}{r}\right)^{n_{a\beta}} + Z_{a}Z_{\beta} e^{-r/A} - a_{a\beta}^{2} + a_{a\beta}^{2} e^{-r/A}$$ (38)

and the three-body potential

$$U^{(3)}_{a\beta\gamma} = B_{a} \exp\left[\frac{1}{r_{a\beta} - A_2} + \frac{1}{r_{a\gamma} - A_2}\right] \left(\frac{r_{a\beta} - r_{a\gamma}}{r_{a\beta} r_{a\gamma}}\right)^{2}$$ (39)

where $\theta(x)$ is a step function, $A_0=4.43$ (Å), $A_1=2.5$ (Å), and $A_2=5.5$ (Å). The potential parameters are listed in Table V. Here, the total number of particles is $N=5184$ and the system size is 42.8 Å. Length, time, and temperature are scaled by $\sigma_{OO}(2\epsilon_{OO})$, $\sigma_{OO}/v_0$, and $\epsilon/k_B$, respectively, where $m_{O}=2.66 \times 10^{-26}$ (kg) and $\sigma_{OO}v_0=7.52 \times 10^{-7}$ (m$^2$/s).

<table>
<thead>
<tr>
<th>$T_s$</th>
<th>$T_\beta$</th>
<th>$T_x$</th>
<th>$T_c$</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.399</td>
<td>0.196</td>
<td>0.185</td>
<td>0.169</td>
<td>0.146</td>
</tr>
<tr>
<td>2247 (K)</td>
<td>1104 (K)</td>
<td>1042 (K)</td>
<td>952 (K)</td>
<td>822 (K)</td>
</tr>
</tbody>
</table>

$\log_{10}(M_2(t)/\sigma_{CuCu})^2$ versus $t/t_0$ for different temperatures, $T=0.315$, 0.3, 0.27, 0.23, 0.2, 0.182, 0.167, 0.154, and 0.143 (from left to right). The filled circles indicate the simulation results for Cu from Ref. \cite{17}. The solid lines indicate the mean-field master curve given by Eq. (29).
In Fig. 5, the mean-square displacement \( M_\Sigma(t) \) for O is plotted versus time \( t/t_0 \) for different temperatures. The mean-field equation agrees with the simulation results well, except for lower temperatures \( T<T_s \) (or \( u>u_s \)). In Fig. 6, the long-time self-diffusion coefficient \( D_S^L \) is plotted versus inverse temperature. From Eq. (16), the coefficient \( \kappa_{OO} \) is calculated as \( \kappa_{OO}=15.31 \) [22]. The inverse singular temperature is obtained by fitting Eq. (14) with the simulation results as \( 1/T_s=6.0 \). Thus, Eq. (14) can describe the simulation results well, except for lower temperatures \( T<T_s \) (or \( u>u_s \)). This situation is the same as that discussed in Cu. The characteristic temperatures are listed in Table VI.

In order to show whether Eq. (14) holds for the other network glass formers, we analyze the data given by Hemmati and Angell for different model potentials of SiO\(_2\) [32]. As shown in the previous paper [22], the coefficient \( \kappa_{OO} \) should be the same as that obtained by using Eq. (37), even though the model potentials are different. Hence, we take \( \kappa_{OO}=15.31 \) and \( \sigma_{OO}T_0=7.52 \times 10^{-7} \) (m\(^2\)/s) to analyze seven different data discussed in Ref. [32]. In Fig. 7, we show a logarithmic plot of the oxygen self-diffusion coefficient \( D_S^{O}(t) \) versus the reduced temperature \( T/T_s \). The inverse singular temperatures are obtained by fitting Eq. (14) with the simulation results and are listed in Table VII. For comparison, the simulation results obtained by using Eq. (37) are also shown in Fig. 7. In Fig. 8, a log-log plot of \( D_S^{O}(t) \) versus \( (T/T_s)(1-T_s/T)^2 \) is also shown to check consistency with Eq. (14). All simulation results obtained by using different potentials are well described by a single master curve given by Eq. (14) up to \( u_s \). This is reasonable because most of those potentials have been made, so that their static structure factors describe realistic structural properties of SiO\(_2\). Here, we note that the potential difference appears only in the singular temperature.

C. Exponents \( b_\beta \) and \( b_\gamma \)

We now discuss the exponents \( b_\gamma \) and \( b_\beta \) obtained for Cu\(_{90}\)Ti\(_{20}\)Zr\(_{30}\) and SiO\(_2\). They are calculated numerically from Eqs. (31) and (32) by using fitting values of \( \ell \) and \( D_S^L \). In Fig.

<table>
<thead>
<tr>
<th>( \epsilon ) (eV)</th>
<th>( a_{\bar{a}\bar{a}} ) (Å)</th>
<th>( Z_{\bar{a}} ) (e)</th>
<th>( a_{\bar{a}} ) (Å(^3))</th>
<th>( n_{\bar{a}\bar{a}} )</th>
<th>( B_\bar{a} ) (eV)</th>
<th>( \bar{\theta}_\bar{a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>1.592</td>
<td>1.2</td>
<td>1.76</td>
<td>2.4</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Si-Si</td>
<td>1.592</td>
<td>0.47</td>
<td>-0.88</td>
<td>0.00</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>O-Si</td>
<td>1.592</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>O-Si-O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.993</td>
<td>109.47</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td></td>
<td>19.972</td>
<td>141.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE V. Potential parameters for SiO\(_2\).
agree with others in a liquid state. This would be because the MICHIO TOKUYAMA PHYSICAL REVIEW E 80 length scale dimensionless. We note that solid lines indicate the mean-field singular function given by Eq. (14), where \( \kappa_{OO} = 15.31 \) and \( 1/T_c = 6.0 \). A log-log plot of \( D_{S}^{(0)} \) versus \( (T/T_c)(1-T_c/T)^2 \) is given in the inset, where the dotted line indicates \(-\mu_c\),

9, they are plotted versus \( u \). As typical examples of fragile systems, the simulation results for the hard-sphere fluids with 15% size polydispersity [26] and 6% size polydispersity [27] and the Lennard-Jones (LJ) binary mixtures [33] are also plotted for comparison. As \( u \) increases, \( b_\beta \) and \( b_\gamma \) decrease and reduce to each the constant 1.3301 at a supercooled point \( u_c \) and 1.0 at a glass point \( u_g \), respectively. Although the systems are completely different from each other, all their exponents coincide with each other within error. This universality is already seen in fragile systems [15].

D. Mean-free path \( \ell \)

We next discuss the mean-free path \( \ell \) obtained for Cu60Ti20Zr20 and SiO2. In Fig. 10, it is plotted versus \( u \) for different systems. For comparison, the simulation results for the hard-sphere fluids and the Lennard-Jones binary mixtures are also shown. The lengths \( \ell \) of O and Cu do not agree with other fragile systems. But if one scales \( \ell \) of O and Cu by \( 1.8\sigma_{OO} \) and \( 1.5\sigma_{CuCu} \), respectively, then they agree with others. Those scaled fittings are needed because \( \sigma_{oa} \) is not a diameter of O or Cu but just a technical number to make the length scale dimensionless. We note that \( \ell \) of Cu does not agree with others in a liquid state. This would be because the simulations on Cu have been done by the NPT method, while the other simulations have been done by the NVT method.

E. Characteristic times \( t_\beta \) and \( t_\gamma \)

We also discuss the characteristic times \( t_\beta \) and \( t_\gamma \) obtained for Cu60Ti20Zr20 and SiO2. In Fig. 11, they are plotted versus \( u \). For comparison, the simulation results for the hard-sphere fluids and the Lennard-Jones binary mixtures are also shown. The \( u \) dependence of those times is similar to each other, where the results for O and Cu are also scaled by the times \( 1.8\sigma_{OO}/v_0 \) and \( 1.5\sigma_{CuCu}/v_0 \), respectively, as in Fig. 10.

F. Mapping

In this section, we discuss a dynamical mapping from one system to another at a given value of \( D_S^{(0)} \) [16]. We consider

\[ \begin{array}{lllll}
T_s & T_\beta & T_\alpha & T_\gamma & T_0 \\
0.500 & 0.203 & 0.188 & 0.167 & 0.136 \\
9242 (K) & 3752 (K) & 3475 (K) & 3087 (K) & 2514 (K)
\end{array} \]

TABLE VI. Characteristic temperatures for O.

\[ \begin{array}{llllll}
\text{Model} & \text{1000}/T \ (\text{K}^{-1}) & \text{Symbol} & \text{Ref.} \\
\hline
\text{Modified-Matsui} & 0.350 & \bigcirc & [32] \\
\text{Tsuneyuki} & 0.305 & \bigtriangledown & [32] \\
\text{BKS} & 0.285 & \bigcirc & [32] \\
\text{Horbach (BKS)} & 0.267 & \square & [32] \\
\text{Poole} & 0.200 & \blacktriangledown & [32] \\
\text{TRIM} & 0.1976 & \times & [32] \\
\text{Kubicki} & 0.1905 & + & [32] \\
\text{Nakano} & 0.324 & \bigcirc & [31] \\
\end{array} \]

TABLE VII. Singular temperatures for different models.
the following three cases. The first is a mapping from Cu to the hard-sphere fluid with 6% size polydispersity (HSF6%). In Fig. 12, the mean-square displacement $M_2(t)$ is compared at two different values of $\Delta T_L$; in a liquid state [L] at $\Delta T_L = 0.05$, where $\Delta T = 0.45$ for the hard-sphere fluid and $T = 0.27$ for Cu, and in a supercooled liquid state [SL] at $\Delta T_L = 0.0017$, where $\Delta T = 0.56$ and $T = 0.182$. At each value the simulation results are collapsed on the mean-field master curve. Here, we note that in a supercooled state the simulation results for Cu deviate from the mean-field theory because they do not reach an equilibrium state yet.

FIG. 8. (Color online) A log-log plot of $D^{(0)}_S$ versus $(T/T_c)(1 - T/T_c)^2$. The dashed line indicates $-u_c$. The details are the same as in Fig. 7.

FIG. 9. (Color online) A plot of $b_\gamma$ and $b_\beta$ versus $u$ for different systems. The open symbols indicate the exponent $b_\beta$ and the filled symbols indicate $b_\gamma$: (o) Cu, (□) O, (○) hard-sphere fluids with 15% size polydispersity from Ref. [26], (△) hard-sphere fluids with 6% size polydispersity from Ref. [27], and (∇) LJ from Ref. [33]. The horizontal dotted line indicates $b_\gamma = 1.0$ and the horizontal dashed line indicates $b_\beta = 1.33014$. The vertical dotted line indicates $u_\beta$ and the vertical dashed line indicates $u_\gamma$.

FIG. 10. (Color online) A plot of $\ell/\sigma$ versus $u$ for different systems. The open squares and circles indicate the original results for O and Cu, respectively, and the filled squares and circles the scaled ones. The details are the same as in Fig. 9.

$D^{(1)}_S/(\sigma v_0) = 0.05$, where $\phi = 0.45$ for the hard-sphere fluid and $T = 0.27$ for Cu, and in a supercooled liquid state [S] at $D^{(1)}_S/(\sigma v_0) = 0.0017$, where $\phi = 0.56$ and $T = 0.182$. At each value the simulation results are collapsed on the mean-field master curve. Here, we note that in a supercooled state the simulation results for Cu deviate from the mean-field theory because they do not reach an equilibrium state yet.

FIG. 11. (Color online) A plot of $t_\gamma$ and $t_\beta$ versus $u$ for different systems. The open symbols indicate the time $t_\beta$ and the filled symbols indicate $t_\gamma$. The details are the same as in Fig. 9.
The filled circles indicate the simulation results for hard spheres with 6% size polydispersity at [L] \( \phi = 0.45 \) and [S] 0.56 from Ref. [27] and the open squares for Cu at [L] \( T = 0.27 \) and [S] 0.182 from Ref. [17]. The solid lines indicate the mean-field master curve given by Eq. (29).

The second is a mapping from O to the hard-sphere fluid with 15% size polydispersity (HSF15%). In Fig. 13, the mean-square displacement \( M_2(t) \) is compared at two different values of \( D_2^L \) in a liquid state [L] at \( D_2^L/(\sigma v_0) = 0.0053 \), where \( \phi = 0.55 \) for the hard-sphere fluid and \( T = 0.2273 \) for O, and in a supercooled liquid state [S] at \( D_2^L/(\sigma v_0) = 0.00036 \), where \( \phi = 0.58 \) and \( T = 0.1678 \). At the same value of \( D_2^L \), the simulation results are collapsed on the corresponding mean-field master curves given by Eq. (29).

The last is a mapping from O and Cu to the LJ binary mixtures. In Fig. 14, the mean-square displacement \( M_2(t) \) is compared at two different values of \( D_2^L \) in a liquid state [L] at \( D_2^L/(\sigma v_0) = 0.01 \), where \( T = 1.0 \) for LJ and \( T = 0.23 \) for Cu, and in a supercooled liquid state [S] at \( D_2^L/(\sigma v_0) = 0.002 \), where \( T = 0.769 \) for LJ and \( T = 0.2165 \) for O. At the same value of \( D_2^L \) all the simulation results on fragile and strong glass formers are collapsed on the mean-field master curve given by Eq. (29). Hence, the dynamical behavior in different systems is identical to each other if \( D_2^L \) is the same. This universality is also true even for stronger glass formers, although this was discussed only in fragile glass formers in the previous paper [16].

G. Long-time self-diffusion coefficient

Finally, we discuss the universality among the long-time self-diffusion coefficients for diversely different glass-forming systems. In Fig. 15, \( D_2^L \) is plotted versus \( \lambda/\lambda_c \) for different systems. All simulation results are described by the master curve given by Eq. (14) well, except for higher values...
have then shown that if the long-time self-diffusion coefficient $D_2^L/\sigma v_0$ versus $\lambda/\lambda_c$ for different systems. The solid line indicates the mean-field master curve given by Eq. (14) at $\kappa_{CuCu}=9.0$, the dotted line at $\kappa_{OO}=15.31$, the dashed line at $\kappa=1$ for hard spheres, and the long-dashed line at $\kappa=48$ for Lennard-Jones (LJ). The horizontal solid lines indicate $u_\beta$ and $u_\infty$, while the horizontal dashed line indicates $-u_c$. [L] stands for a liquid state $0<u<u_\beta$ [S] for a supercooled state $u_\beta \equiv u < u_\infty$, and [G] for a glass state $u_\infty \equiv u$. The details are the same as in Fig. 9.

$\lambda/\lambda_c > 1$ (or $u > u_\infty$), where the systems do not reach an equilibrium state yet. In order to check consistency with Eq. (14) more clearly, we also show a log-log plot of $D_2^L/\sigma v_0$ versus $(\lambda_c/\lambda)(1-\lambda/\lambda_c)^2$ in Fig. 16. Thus, all the simulation results are shown to be described by Eq. (14) well up to $\lambda_c$ over which the deviation from Eq. (14) starts to occur. Hence, this suggests that the $\lambda/\lambda_c$ dependence of $D_2^L$ in any systems should be the same for $\lambda/\lambda_c \equiv 1$ [22]. This is clearly seen in Fig. 17, where $\kappa D_2^L$ is plotted versus $\lambda/\lambda_c$ for different systems. When $\lambda/\lambda_c > 1$ (or $u > u_\infty$), $\kappa D_2^L$ obeys a nonsingular function and its value is larger for stronger glasses. For $\lambda/\lambda_c > 1$, however, the systems are usually out of equilibrium. In order to calculate such a nonsingular function, therefore, one has to discuss the nonequilibrium relaxation processes separately from the equilibrium formulation discussed here.

IV. SUMMARY

In this paper, we have analyzed two different glass-forming systems, bulk glass-forming Cu$_{60}$Ti$_{20}$Zr$_{20}$ melt and network-forming SiO$_2$ melt, from a unified viewpoint based on the mean-field theory. We have first shown that the both simulation results for the mean-square displacement $M_2(t)$ are well described by the mean-field master curve given by Eq. (29), except for lower temperatures $T < T_\ast$ (or $u > u_\infty$) where the system does not reach an equilibrium state yet. We have then shown that if the long-time self-diffusion coefficient in different systems has the same value, those results are collapsed into a master curve given by Eq. (29). Second, we have shown that the simulation results for the long-time self-diffusion coefficient $D_2^L$ obey a mean-field singular curve given by Eq. (14) well, except for lower temperatures $T < T_\ast$ (or $u > u_\infty$). These situations are exactly the same as those discussed in fragile systems [15,16]. In fact, we have

FIG. 15. (Color online) A logarithmic plot of $D_2^L/\sigma v_0$ versus $\lambda/\lambda_c$ for different systems. The details are the same as in Fig. 9. Here, the data points for $\lambda/\lambda_c > 1$ are excluded for a simplicity.

FIG. 16. (Color online) A log-log plot of $D_2^L/\sigma v_0$ versus $(\lambda_c/\lambda)(1-\lambda/\lambda_c)^2$ for different systems. The details are the same as in Fig. 15. Here, the data points for $\lambda/\lambda_c > 1$ are excluded for a simplicity.

FIG. 17. (Color online) A logarithmic plot of $\kappa D_2^L/\sigma v_0$ versus $\lambda/\lambda_c$ for different systems. The solid line indicates the mean-field master curve given by Eq. (14) at $\kappa=1$. The details are the same as in Fig. 9.
compared the results with those obtained in fragile systems, such as hard-sphere fluids. Thus, we conclude that there exists a simple universal mechanism near the glass transition even among any diversely different glass-forming systems. Finally, we should mention that the mean-field theory holds only in an equilibrium state for $\lambda \leq \lambda_0$ (or $u \leq u_0$). For $\lambda > \lambda_0$ (or $u > u_0$), however, the dynamic (spatial) heterogeneity becomes more important. Hence, one has to formulate a new theory to discuss such a region. This will be discussed elsewhere.

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