



A novel difference between strong liquids and fragile liquids in their dynamics near the glass transition



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HIGHLIGHTS

- The dynamics of fragile liquids and that of strong liquids is compared consistently.
- A novel difference between their dynamics is found near glass transition.
- Existence of master curve in each type of liquids is proposed.

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ABSTRACT

The systematic method to explore how the dynamics of strong liquids (S) is different from that of fragile liquids (F) near the glass transition is proposed from a unified point of view discussed recently by Tokuyama. The extensive molecular-dynamics simulations are performed on different glass-forming materials. The simulation results for the mean- n th displacement $M_n(t)$ are then analyzed from the unified point of view, where n is an even number. Thus, it is first shown that in each type of liquids there exists a master curve $H_n^{(\alpha)}$ as $M_n(t) = R^n H_n^{(\alpha)}(v_{th}t/R; D/Rv_{th})$ onto which any simulation results collapse at the same value of D/Rv_{th} , where R is a characteristic length such as an interatomic distance, D a long-time self-diffusion coefficient, v_{th} a thermal velocity, and $\alpha = F$ and S . The master curves $H_n^{(F)}$ and $H_n^{(S)}$ are then shown not to coincide with each other in the so-called cage region even at the same value of D/Rv_{th} . Thus, it is emphasized that the dynamics of strong liquids is quite different from that of fragile liquids.

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1. Introduction

It has been known for a long time since Angell [1] has proposed a famous classification in viscosities of glass-forming materials that there exist two types of glass-forming liquids, fragile liquids (F) and strong liquids (S), near the glass transition [2–12]. The systems with short-range interactions such as *o*-terphenyl and glycerol are typical examples of fragile liquids, while the covalently bonded network glass formers such as SiO₂ and GeO₂ are known as typical examples of strong liquids. Thus, it has been understood commonsensically since then that the transport coefficients of both liquids, such as viscosity and self-diffusion coefficient, are well described by the Vogel–Fulcher–Tammann (VFT) law [13–15], although the fitting temperature range for strong liquids is shorter than that for fragile liquids. However, it is not clear yet how the dynamics of strong liquids is different from that of fragile liquids in a supercooled state. Thus, it is still important to clarify it not only qualitatively but also quantitatively from a unified point of view.

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In order to classify the long-time self-diffusion coefficient $D(T)$ into two types of glass forming liquids from a unified point of view consistently, Tokuyama [16–18] has recently shown that the α - and β -relaxation times, τ_α and τ_β , obey power laws in a supercooled state

$$\tau_\alpha \sim D^{-(1+\mu)}, \quad \tau_\beta \sim D^{-(1-\mu)}, \quad (1)$$

where the exponent μ is given by $\mu \simeq 1/5$ for (F) and $2/11$ for (S). Then, the following master curve $f(x; \eta)$ for $D(T)$ has been proposed:

$$D(T) = d_0 f(T_f/T; \eta), \quad (2)$$

$$f(x; \eta) = \frac{(1-x)^{2+\eta}}{x} \exp[62x^{3+\eta}(1-x)^{2+\eta}], \quad (3)$$

where T_f is a fictive singular temperature to be determined and d_0 a positive constant to be determined. Here the exponent η is given by $\eta = 2(1-3\mu)/3\mu$, which leads to $\eta \simeq 4/3$ for (F) and $5/3$ for (S). Thus, it has been shown by analyzing many different data that both types of liquids are well described by two types of master curves up to the deviation point T_n , below which all the data start to deviate from them and obey the Arrhenius law, where $T_n > T_f$. Here we note that T_n coincides with the so-called thermodynamic glass transition temperature T_g and the master curves can be also fitted by the VFT law well for $T \geq T_n$ [17,18]. Thus, all the diffusion data in each type collapse onto each single master curve $f(x; \eta)$ (see Fig. 1). Their material differences are just characterized by a set of parameters (T_f, d_0, η) . From this viewpoint, therefore, those parameters may correspond to the so-called degree of fragility usually discussed among different systems [2,6,19–21]. Here we should mention that the present approach gives a mathematical tool to distinguish two types of liquids from each other and the classified results agree with those obtained by Angell.

In the present paper we only discuss the dynamics of two different types of glass-forming materials, fragile glass formers (F) and network strong glass formers (S), from a unified point of view [22]. In order to compare the dynamics of F with that of S, it is convenient to use the mean- n th displacement $M_n(t)$ given by $M_n(t) = \langle |\mathbf{X}_i^\alpha(t) - \mathbf{X}_i^\alpha(0)|^n \rangle$, where $\mathbf{X}_i^\alpha(t)$ is a position vector of i th atom α at time t , the brackets an average over the equilibrium ensemble, and n even numbers. Analyses of many data then suggest an existence of a master curve $H_n^{(\alpha)}$ for $M_n(t)$ in each type as

$$M_n(t) = R^n H_n^{(\alpha)}(v_{th}t/R; D/Rv_{th}), \quad (4)$$

where R is the characteristic length such as an interatomic distance, v_{th} the average thermal velocity, and $\alpha = F$ and S . Any data in each type are thus shown to collapse onto a single master curve $H_n^{(\alpha)}$ at the same value of D/Rv_{th} . Then, we also show that even at the same value of D/Rv_{th} the master curve $H_n^{(\alpha)}$ for type α does not coincide at all with $H_n^{(\beta)}$ for other type $\beta (\neq \alpha)$ in the cage region for $\tau_f \leq t \leq \tau_\beta$, in which each particle behaves as if it is trapped in a cage mostly formed by neighboring particles, where τ_f is a mean-free time before which each particle undergoes a ballistic motion. On the other hand, $H_n^{(\alpha)}$ and $H_n^{(\beta)}$ ($\alpha \neq \beta$) are easily shown to coincide with each other both for a short-time region ($t \ll \tau_f$) and for a long-time region ($\tau_\beta \ll t$) at the same value of D/Rv_{th} . In fact, for both time regions we have

$$H_n^{(\alpha)}(\tau) = \frac{(n+1)!(3!)^{-n/2}}{(n/2)!} H_2^{(\alpha)}(\tau)^{n/2} \quad (5)$$

with

$$H_2^{(\alpha)}(\tau) \simeq \begin{cases} 3\tau^2, & (t \ll \tau_f) \\ 6(D/Rv_{th})\tau & (t \gg \tau_\beta), \end{cases} \quad (6)$$

where $\tau = v_{th}t/R$. Thus, we emphasize that an explicit disagreement between different types appears only in the cage region. Finally, we note that although the even number n is taken up to 6 here for simplicity, the same results as those discussed in the present paper also hold for $n \geq 8$.

We begin in Section 2 by briefly reviewing the mean-field theory recently proposed. We first discuss the mean-field equation for the mean-square displacement and its related characteristic times. Then, we show two types of master curves for the long-time self-diffusion coefficient. One is a master curve for fragile liquids and another is for strong liquids. In Section 3, we introduce several potentials to perform extensive molecular-dynamics simulations. In Section 4, we briefly review how physical quantities satisfy the universality near the glass transition. Based on such a universality, we then show that there exist a master curve $H_n^{(i)}$ for the mean- n th displacement in each liquid, (F) and (S). In Section 5, we show that the master curves $H_n^{(\alpha)}$ and $H_n^{(\beta)}$ in different types α and $\beta (\neq \alpha)$ do not coincide with each other in the cage region even at the same value of D/Rv_{th} . We conclude in Section 6 with a summary.

2. Mean-field theory

Here we briefly summarize the mean-field theory of the glass transition (MFT) for molecular systems recently proposed by Tokuyama [16,17,22–25]. The mean-field theory consists of the following two essential points: (A) Mean-field equation

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