Universality in Self-Diffusion among Distinctly Different Glass-Forming Liquids

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Self-diffusion of a single particle in distinctly different multi-component glass-forming liquids, AₙBₙCₙ…, is studied from a unified point of view based on the mean-field theory recently proposed by the present author. Let T denote temperature. In an equilibrium liquid, the long-time self-diffusion coefficient D(T) for a component α is then described by a singular function

\[ \frac{D(T)}{d_0} = (1 - x)^{2/0} / x, \quad (x = T / T_c), \quad (1) \]

where \( T_c \) is a singular temperature to be determined, and \( d_0 \) a positive constant. We assume that even in an equilibrium supercooled liquid, the diffusion coefficient D(T) also obeys a singular function

\[ \frac{D(T)}{d_0} = (1 - x)^{2/0} / x, \quad (x = T / T_f), \quad (2) \]

where \( T_f \) is a fictive singular temperature to be determined, η an exponent caused by many-body correlations. The simulation results and the experimental data are then analyzed consistently by using Eqs. (1) and (2). Thus, it is shown that they are all collapsed onto a master curve, which is well described by a regression equation

\[ D(T) / d_0 = x^{-1} (1 - x)^{2/0} \exp[\beta x^{3/0} (1 - x)^{2/0}], \quad (3) \]

where \( \beta \approx 0.62 \). In order to find the exponent η, we use the power law dependence of a β-relaxation time on D. Then, analyses of many simulation results lead to η = 0 for hard spheres, 4/3 for fragile liquids, and 5/3 for strong liquids. In Fig. 1, a log plot of D(T) versus \( T / T_f \) is shown for fragile liquids, where 1/T_f is listed in Table I. The same situation holds for other systems. Thus, we emphasize that all data start to deviate from Eq. (3) and obey an Arrhenius law.

![Fig. 1 A log plot of D(T) for fragile liquids versus T/T_f. The solid line indicates the master curve given by Eq. (3) and the dotted line the mean-field result given by Eq. (1). The symbols indicate the experimental data and the simulation results; (○) Lennard-Jones, (□) confined Lennard-Jones, (▲) Cu₉₀Ti₇₀Zr₂₀, (○) hydration water, (●) Zr₄₁₂Ti₁₃₃Cu₁₂₂Ni₁₀Be₂₂₅, and (▼) OTP.](image)

when they become nonequilibrium. Hence we suggest that such a temperature must be a glass transition temperature, which is roughly estimated as \( T_f / T_s \approx 0.9356 \) for water.

<table>
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<th>System</th>
<th>1/T_f</th>
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Table I. \( T_f \) in fragile liquids.

References