A relationship between diffusivity and cooperativity of supercooled liquids in the proximity of glass transition

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A B S T R A C T

In structurally disordered glass-forming liquids, the Stokes–Einstein (SE) law for translational diffusivity is violated, in particular, in the proximity of the glass transition temperature. Usually, the violation of the SE law is explained as due to the decoupling of the diffusivity from the viscous flow. Meanwhile, one of the prominent features observed in the supercooled liquids is the drastic increase of the viscosity with the decrease of temperature. The origin of the increase of the viscosity is attributed to the increase of the molecular motion cooperativity. In the present study, it is shown that the translational diffusivity of glass-forming liquids can be correlated with the cooperativity involved in the thermally activated viscous flow. In the present analysis, the cooperativity is defined in the framework of the bond strength–coordination number fluctuation (BSCNF) model of the viscosity. The result of the analysis suggests that the translational diffusivity is driven by the bond-breaking and bond-switching between the structural units that compose the network structure.

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1. Introduction

The understanding of the diffusion mechanisms in structurally disordered substances near the melting temperature T_m and the glass transition temperature T_g is of crucial importance for practical applications such as the suppression of devitrification in silicate glasses [1], in phase change materials [2], in pharmaceutical science [3], etc. From a fundamental point of view, the microscopic transport properties of the melts and glasses have been investigated directly through the measurements of the diffusion coefficients by means of NMR [4,5], radio-tracer [6], electrochemical methods [7,8], molecular dynamic (MD) simulations [9–11], and other techniques [12,13]. Concerning the relation between the diffusion coefficient and the viscosity, the validity of the Stokes–Einstein (SE) relation [14,15] remains a subject of intensive debates [3,6–10]. The SE relation for translational diffusivity is given by $D = k_B T/6\pi r_s \eta$ [3,6,7,16] in the case of "stick" boundary condition, where D is the self-diffusion coefficient, k_B is the Boltzmann's constant, T is the absolute temperature, r_s is the spherical radius of the diffusive species and η is the viscosity, respectively. The SE relation has been used widely in the discussion of atomic transport in liquids [17]. However, it has been revealed that the SE relation is violated, in particular, in the proximity of the glass transition temperature [6,7,12,18–21]. In these cases, the fractional Stokes–Einstein (FSE) law which is given by

$$D \propto \left(\frac{T}{\eta}\right)^p \quad (0 < p \le 1),\qquad (1)$$

describes the relation between the translational diffusivity and the viscosity. Here p gives the degree of deviation from the original SE law. As has been reported in many studies, p takes a value of less than unity for various glass-formers [10,12,16]. The FSE law given by Eq. (1) indicates the "decoupling" of the diffusive motions from the viscous flow. The FSE law is observed especially in fragile liquids in the temperature range lower than the crossover temperature [16,18]. It has been discussed that the origin of the FSE law could be attributed to the spatial heterogeneity of the liquids under supercooling [22]. On the other hand, other authors have cast doubt on the general validity of the FSE law [23].

It should be also noted that one of the prominent features observed in supercooled liquids is the drastic increase of viscosity or relaxation time with the decrease of temperature [24]. This process is accompanied by the increase of the molecular motion cooperativity among the constituent elements of the supercooled liquid. In our previous study [25], it was discussed that the self-diffusion coefficients of cations and anions in room temperature ionic liquids (RTILs) can be correlated with the cooperativity involved in the thermally activated viscous flow. There, the cooperativity of the RTILs was evaluated by the quantity N_B which was defined in the framework of the bond strength–coordination number fluctuation (BSCNF) model of the viscosity [26]. The result suggested that the diffusivity of cations and anions in the RTILs is driven by the bond-breaking and bond-switching between the constituent elements of the liquids, which leads to the cooperative motion of the diffusivity [27].

The main objective of the present work is to investigate if the above picture of the correlation between the diffusivity and the cooperativity is common in other glass-forming liquids as well. In

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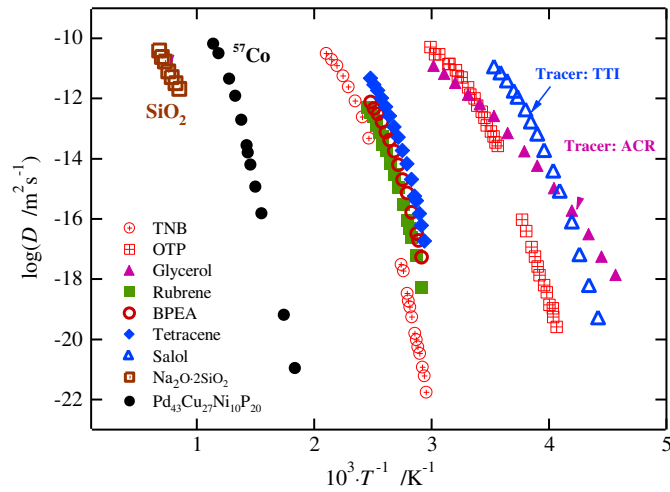
Fig. 1. Temperature dependence of diffusion coefficients for the materials investigated in the present study. The methods used in the measurements of the diffusion coefficient and the references where the experimental data are taken are listed in Table 1.

Fig. 1, the temperature dependence of the diffusion coefficient is shown for the materials investigated in the present study. It includes various materials as indicated in Table 1. The experimental data of the diffusion coefficient D are taken from the literatures [12,16,18–20]. As mentioned in the beginning, understanding the mechanism of viscous flow near T_g is of fundamental importance for the clarification of the mechanisms of glass transition [22], as well as the crystallization process in glassy state and melts [1–3,21,22]. In the following, the validity of the relation mentioned above, as well as the implications of the results to the exponent p of the FSE law will be discussed.

2. Evaluation of the cooperativity of the melt

The viscous flow of a liquid occurs by involving a large number of molecules or structural units that form the liquid. In such flow process, the connectivity of the structural units depends on the nature of the chemical bonds and affects greatly the behavior of the structural relaxation [24]. In one of our previous studies, with the objective to understand the viscous flow of the melt, a model for the temperature dependence of the viscosity has been proposed by one of the authors [26]. The model has been called bond strength–coordination number fluctuation (BSCNF) model and describes the viscosity behaviors in terms of the mean bond strength E_0, the coordination number Z_0, and the fluctuations, ΔE and ΔZ, of the structural units that form the melt. The BSCNF model of the viscosity is given by [26,28]

$$\eta = \frac{\eta_0}{\sqrt{1-Bx^2}} \exp\left[\frac{Cx + Cx^2\left[\left\{\ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \frac{1}{2}\ln(1-B)\right\}\frac{(1-B)}{C} - 1\right]}{1-Bx^2}\right], \quad (2)$$

where

$$B = \frac{(\Delta E)^2(\Delta Z)^2}{R^2 T_g^2} \quad \text{and} \quad C = \frac{E_0 Z_0}{RT_g}. \quad (3)$$

Here, x is the inverse temperature normalized by T_g, $x = T_g/T$. η_0 and η_{T_g} are the viscosity at the high temperature limit and at T_g, respectively. R is the gas constant. In the BSCNF model, the glass-forming liquids are characterized with the parameters B and C, whose numerical values are determined from the viscosity analysis. Intuitively, B gives the degree of the fluctuation, and C gives the degree of the mean binding energy between the structural units against the thermal disturbance at T_g. The explanations of the model have been given in detail elsewhere [25–29].

The atomic and molecular cooperative rearrangement involved in the viscous flow plays an important role in the agglomeration process of the melt [21,30,31]. In our previous study [29], a quantity N_B which gives the number of structural units involved in the thermally activated viscous flow has been introduced in the light of the BSCNF model. This quantity is defined as $N_B = E_\eta/(E_0 Z_0)$, where E_η is the activation energy for the viscous flow and $E_0 Z_0$ is the average binding energy per structural unit. In other words, N_B gives the ratio between the thermally activated energy (or enthalpy) and the average binding energy that depends on the materials. From the theoretical point of view, it has been also shown [32] that N_B is closely related with the notion of cooperatively rearranging region (CRR) in the theory of Adam and Gibbs [33]. In the present analysis, the temperature dependence of the cooperativity in glass-forming liquids is evaluated by the relation

$$N_B(T) = \frac{\ln(10)}{C} \frac{d}{d\left(T_g/T\right)} \log\eta(B, C, T). \quad (4)$$

Here, the viscosity η is given by Eq. (2). Note that at T_g, the term $d\log\eta/d(T_g/T)$ reduces to the fragility index m [34]. Eq. (4) is obtained by extending the original definition of N_B. The quantity N_B which is given by Eq. (4) increases with the decrease of temperature. The growth behavior of the cooperativity described by this equation is consistent with the results by other studies [30,31]. However, concerning the number of correlated units involved in glass-forming liquids, i.e., the number of molecules or structural units that are involved during supercooling depends on theoretical models [31,35]. It would be interesting to perform a detailed comparative study on the temperature dependence of cooperativity based on different models. In the present analysis, we have focused on the rate of increment of the cooperativity described by N_B in the range of temperature close to T_g, since it is closely related with the activation energy.

Table 1
Materials, glass transition temperature T_g, values of the parameters B and C used in this study, shift factor $a_T = \ln(\eta_{Tg}/\eta_0)$ or $a_T^* = \ln(\tau_{Tg}/\tau_0)$, exponent p of the FSE law, methods used in the measurements of the diffusion coefficients D and the references where the data of the viscosity η or the relaxation time τ are provided. The acronyms used in the list stand for, MS (mass spectrometry), IS (isothermal desorption), and FRAP (fluorescence recovery after photobleaching), respectively.

Materials	T_g [K]	B	C	a_T	p	Method or the diffusive species (D)	η or τ (*)
Tris-naphthylbenzene (TNB)	343	0.34	27.6	66.3	0.84	MS [18]	[38]
o-Terphenyl (OTP)	243	0.31	37.4	85.3	0.74	NMR, IS [16,39,40]	[16,41]
Rubrene	337	0.64	8.5	43.5	0.73	FRAP [12]	[12]
9,10-Bis(phenylethynyl)anthracene (BPEA)	337	0.64	8.5	43.5	0.66	FRAP [12]	[12]
Tetracene	337	0.64	8.5	43.5	0.63	FRAP [12]	[12]
Na$_2$O·2SiO$_2$	728	0.29	17.5	35.9	0.71	SiO$_2$ in Na$_2$O·2SiO$_2$ [20]	[20]
Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$	582	0.09	50.8	72.1	0.74	Tracer (^{57}Co) [16,6]	[16,42]
Glycerol	185	0.52	11.2	40.3*	0.98	Tracer (ACR) [19]	[43]*
Salol	218	0.51	15.2	53.6*	0.95	Tracer (TTI) [19]	[43]*