Alternative Explanation of the Difference between Translational Diffusion and Rotational Diffusion in Supercooled Liquids

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We offer an alternative explanation of the breakdown of Debye–Stokes–Einstein and Stokes–Einstein relations observed as enhanced translational diffusion compared with rotational diffusion of probe molecules in supercooled liquids and polymers close to the glass transition temperature. By showing that the breakdowns of Debye–Stokes–Einstein and Stokes–Einstein relations in glass-forming liquids are special cases of a more general phenomenon, it becomes clear that a more general explanation than spatially heterogeneous dynamics is needed. In the framework of the coupling model, the explanation is based on the fact that different dynamic variables μ weigh the intermolecular cooperativity differently and have different coupling parameters (i.e., degrees of intermolecular cooperativity), n_μ, which enter into the stretch exponents of their correlation functions, $\langle\mu(0)\mu(t)\rangle = \exp[-(t/\tau_\mu)^{1-n_\mu}]$, represented in the Kohlrausch form. In some of the applications we made, the values of n_μ's are known from experiment and the difference between them is absolutely clear. The explanation of the difference between the τ_μ's and their temperature dependencies then becomes quantitative, requiring no adjustable parameter (Ngai, K. L.; Mashimo, S.; Fytas, G. *Macromolecules* **1988,** *21,* 3030). An exception is the present explanation of the breakdown of Stokes–Einstein relation where experimental technique has not yet been developed to determine the microscopic correlation function and, hence, the coupling parameter of translational diffusion. The explanation from the coupling model is based on the assumption that the known coupling parameter of rotational diffusion is larger than that of translational diffusion, which has been justified on theoretical grounds and can be falsified experimentally when the latter becomes known in the future. The effect depends on the degree of probe participation in the cooperative dynamics with the host molecules characterized by the ratio, τ_c/τ_α, of the probe rotational relaxation time τ_c to the α-relaxation time of the neat host τ_α. The observed variation in the magnitude of the enhanced translation with the size of the probes in supercooled liquids and polymers is explained. In the process, we have established a correlation between the enhanced translation and τ_c/τ_α as well as a correlation between the Kohlrausch exponent β of the rotation correlation function and τ_c/τ_α. These two correlations when combined give rise to the correlation between enhanced translational diffusion and $(1-\beta)$ established earlier by Ediger and co-workers. The present explanation of enhanced translational diffusion can also explain the recent findings of (a) a parallel enhancement of dielectric relaxation in supercooled liquids by Chang and Sillescu and (b) a breakdown of the Debye–Stokes–Einstein relation of depolarized light scattering data of diglycidyl ether of bisphenol A by Comez et al. On the other hand, the spatially heterogeneous dynamics explanation of enhanced translation no longer can explain these results.

1. Introduction

Fujara and co-workers[1,2] studied the translational and rotational diffusion in the small molecule supercooled liquid, *o*-terphenyl (OTP), above its glass temperature, $T_g \approx 244$ K. The rotational diffusion coefficient, D_r, of neat OTP followed the temperature dependence of the Debye–Stokes–Einstein (DSE) equation,

$$D_r \equiv \frac{1}{6\langle\tau_c\rangle} = \frac{kT}{8\pi\eta r_s^3} \qquad (1)$$

practically at all temperatures above T_g where the viscosity η changes by 12 orders of magnitude. In eq 1, $\langle\tau_c\rangle$ is by definition the mean rotational correlation time and r_s the spherical radius of the molecule. On the other hand, the translational diffusion coefficient, D_t, of a tracer molecule similar in size to OTP follows the temperature dependence of the Stokes–Einstein (SE) relation

$$D_t = \frac{kT}{6\pi\eta r_s} \qquad (2)$$

only at high temperatures down to T_B, which is approximately equal to $1.2T_g \approx 290$ K. Below T_B, the temperature dependence of D_t is significantly weaker than D_r and η, which indicates that there is a pronounced enhancement of translational diffusion in comparison with rotational diffusion and shear viscosity. The phenomenon has been cast sometimes in the form,[1–3]

$$D_t \propto T/\eta^\xi \qquad (3)$$

where $\xi < 1$. The exponent ξ was observed to increase with increasing tracer size to approach unity as shown by D_t of large

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polystyrene network spheres. The phenomena were confirmed in OTP by Ediger and co-workers[4,5] by comparing the diffusion of probe molecules which are the same size as OTP molecules with their rotational time correlation functions, $r(t)$. The time dependence of $r(t)$ was fitted to the Kohlrausch−Williams−Watts (KWW) function as

$$r(t) = r(0)\exp[-(t/\tau_c)^\beta] \qquad (4)$$

where β increases toward 1 as the temperature rises. To quantify translational enhancement, Ediger and co-workers[4−11] used the product $D_t\tau_c$ normalized to the value of this product predicted by the SE and the DSE equations, i.e., $(D_t\tau_c)_{SE,DSE} = 2r_s^2/9$. In OTP, the enhancement of tetracene translation measured by log-$[D_t\tau_c/(D_t\tau_c)_{SE,DSE}]$ is about 2.5 decades near T_g. Different behaviors are shown by larger probe molecules such as rubrene in OTP where the enhancement of translational diffusion becomes negligible as evidenced by D_t, T/η, and $\langle\tau_c\rangle$ all having about the same temperature dependence, and log$[D_t\tau_c/(D_t\tau_c)_{SE,DSE}]$ is small for all temperatures down to T_g. The study of the rotational motion and translational diffusion of probe molecules was extended[7−12] to several polymer matrixes: a strong correlation was observed between the enhanced translational diffusion and the exponent β near T_g. Probes that showed more enhanced translation had smaller β values.

This interesting correlation, the dependencies of ξ, log$[D_t\tau_c/(D_t\tau_c)_{SE,DSE}]$, and β on probes and matrixes and the origin of the enhancement of translational diffusion in the first place are interesting and fundamental problems of molecular motion of supercooled liquids. Several different explanations of some of these effects have been offered.[1,2,5,6,11−17] Most are models based on spatial heterogeneity of relaxation. In this work, we give an alternative explanation of the phenomena based on a different look of the cooperative or coupled molecular motion of the probe molecule with the host molecules. Here, the concept of cooperativity is used in the sense of the author's coupling model (CM).[18−25] All the features of probe molecule translational and rotational diffusions found experimentally can be explained by the cooperative molecular dynamics described in the framework of the CM.

2. Difference between Translational and Rotational Diffusions

The difference between translational diffusion and rotational diffusion is a special case of the difference between two different dynamic processes both related to the α-relaxation found in glass-forming liquids. There are other examples where two dynamic processes, none of which involves the translational diffusion, were found to have different relaxation times and temperature dependencies. In a paper published more than 10 years ago,[26] this difference was shown for dielectric relaxation, dynamic light scattering, and mechanical relaxation of several glass-formers. Although not explicitly stated therein, the results showed that there is a breakdown of the DSE relation (eq 1) for dielectric relaxation and/or dynamic light scattering data from their different temperature dependencies when compared with that of the viscosity. Moreover, there is an attendant difference between the stretch exponents of the KWW functions that fits the time dependence of the correlation function for dielectric relaxation, light scattering, and mechanical relaxation, although all three dynamic processes probe the α-relaxation through the rotational motion of the molecules. In the framework of the coupling model,[18−25] the explanation was based on the fact that different dynamic variables μ weight the intermolecular coop-

erativity differently and have different coupling parameters (i.e., degrees of intermolecular cooperativity), n_μ, which enter into the stretch exponents of their correlation functions, all having the KWW form

$$\langle u(0)u(t)\rangle = \exp[-(t/\tau_\mu)^{1-n_\mu}] \qquad (5)$$

There[26] we worked out the consequences of different coupling parameters, n_μ, on the temperature dependencies of the corresponding correlation times, τ_μ. In the CM, the KWW time dependence is the result of "cooperative" or "coupled" motions of the fundamental molecular units due to their mutual interactions. However, this holds only at sufficiently long times. There exists a crossover time t_c before which the fundamental units relax independently of each other and hence all $\langle u(0)u(t)\rangle$'s decays exponentially, i.e.,

$$\langle u(0)u(t)\rangle = \exp(-t/\tau_{o\mu}), \; t < t_c \qquad (6)$$

where all the "primitive" correlation times, $\tau_{o\mu}$, are free of intermolecular interaction and they have one and the same temperature dependence. Their temperature dependences are governed by a common friction factor $\varsigma_o(T)$, i.e.,

$$\tau_{o\mu}(T) \propto \varsigma_o(T) \qquad (7)$$

The existence of a rather sharp crossover time t_c is supported by theoretical models[18−20] and found in experimental data.[20,27−36] Quasi continuity of the KWW function (eq 10) and the exponential function (eq 11) at $t = t_c$ leads to the important relation between τ_μ and $\tau_{o\mu}$

$$\tau_\mu = [t_c^{-n_\mu}t_{o\mu}]^{1/1-n_\mu} \qquad (8)$$

It follows from eqs 7 and 8 that

$$\tau_\mu(T) \propto [\varsigma_o(T)]^{1/1-n_\mu} \qquad (9)$$

Therefore, τ_μ will have different temperature dependencies whenever their n_μ's are different. Shear mechanical relaxation (viscosity), dielectric relaxation, and photon correlation spectroscopy data in several polymers were used to show[26] that the data are consistent with eq 9. These data provide both $\tau_\mu(T)$'s and the values of the n_μ's. Therefore this satisfactory test of the relations between the temperature dependencies of the τ_μ-(T)'s via eq 9, i.e.,

$$\log[\tau_\mu(T)] \propto \left(\frac{1-n_{\mu'}}{1-n_\mu}\right)\log[\tau_{\mu'}(T)] \qquad (10)$$

was carried out *without* any arbitrarily chosen parameter. Equation 10 indicates that a larger n_μ or smaller KWW exponent $(1-n_\mu)$ is accompanied by a stronger temperature dependence of τ_μ, a quantitative relation that is supported by experimental data.[26]

The same approach from the CM is now employed to discuss the enhancement of translational diffusion comparing with rotational diffusion or viscosity. This is natural because the velocity v_x of the tracer, the correlation function of which determines D_t according to $D_t = (kT/M)\int_0^\infty \langle v_x(0)\cdot v_x(t)\rangle \, dt$, is just one dynamics variable among many of the tracer molecule. For rotation of deuterated OTP measured by NMR, the correlation function involves the second-order Legendre polynomial, $P_2[\cos\Theta(t)]$, where the angle between the C−^{2}H bond and the applied field direction,[5,6] Θ, is another dynamic variable of the deuterated OTP molecule. The correlation time τ_c is

determined from the correlation function by $\tau_c = \int_0^\infty \langle P_2[\cos \Theta(0)] \cdot P_2[\cos \Theta(t)] \rangle \, dt$. The time-resolved optical spectroscopy used to observe probe molecule rotation measure the orientation anisotropy function, $r(t) = (2/5)\langle P_2[\vec{u}(0) \cdot \vec{u}(t)] \rangle$, where $\vec{u}$, the transition dipole of the probe molecule, is the dynamic variable and the correlation time τ_c in eq 4 is calculated as $\tau_c = \int_0^\infty [r(t)/r(0)] \, dt$. The viscosity is calculated from the correlation function of another dynamic variable, the shear stress, σ^{xz}, as $\eta = (kT)^{-1} \int_0^\infty \langle \sigma^{xz}(0) \sigma^{xz}(t) \rangle \, dt$. One obvious difference between D_t and τ_c or η is that D_t involves the correlation of the center of mass of the tracer (one point), while τ_c is determined by the time correlation of the transition dipole of the probe molecule, $\vec{u}$, a vector, and η involves a tensor quantity. The vector $\vec{u}$ and the stress tensor σ^{xz} are defined by two or more points in space, including possibly the center of mass. Thus, one can expect intermolecular constraints will have stronger slowing effect on the rotation of $\vec{u}$[37] or relaxation of the stress tensor than the motion of the center of mass, which is only a point. This intuitive deduction can be justified on a firmer ground from the theoretical consideration of a constraint entropy formulation of the coupling model (CM) based on the Dirac constraint dynamics.[38] The coupling parameters for rotation, n_r, shear viscosity, n_η, and translational diffusion, n_t, appear in the KWW form of the correlation functions, $\exp[-(t/\tau_c)^{1-n_r}]$, $\exp[-(t/\tau_\eta)^{1-n_\eta}]$, and $\exp[-(t/\tau_t)^{1-n_t}]$, respectively. The correlation time τ_t is related to D_t by the equation $D_t = (r_s^2/6\tau_t)$. Here we follow closely the steps taken in ref 38d, where a similar situation of the diffusion of a tracer in a matrix was considered, to show that

$$n_t \leq n_r, \, n_t \leq n_\eta \qquad (11)$$

The dynamic constraint entropy for translational diffusion, $S_{c,t}$, and for rotation diffusion, $S_{c,r}$, according to ref 38d have the forms of $S_{c,t} = S_{max} - kn_t \ln(\omega_c t)$ and $S_{c,r} = S_{max} - kn_r \ln(\omega_c t)$, respectively, for $t > \omega_c^{-1}$. Here k is the Boltzmann constant and ω_c^{-1} is t_c multiplied by constant $(1-n)^{1/n}$. We assume the transition dipole vector of the probe molecule, $\vec{u}$, defined by two points in space one of which is the center of mass. There are more dynamic constraints imposed by the host molecules on the tracer molecule when considering $\vec{u}$ (i.e., rotational diffusion) than the center of mass because of the extra point. Either from this argument or formally through a mathematical procedure like that given by eqs 11–18 in ref 38d and replacing the subscript f and f' therein by t and r, respectively, we arrive at the result that $S_{c,r} \leq S_{c,t}$, or $n_t \leq n_r$. Therefore, the inequality (eq 11) is not an ad hoc assumption because it has been obtained from a theoretical consideration.

One should not identify $\exp[-(t/\tau_t)^{1-n_t}]$ with the exponential translational relaxation function usually obtained from holographic fluorescence recovery after photobleaching technique[5] because the characteristic length scale for diffusion is the holographic grating period, a distance equal to few micrometers. In fact, technique has not been introduced to measure the microscopic $\exp[-(t/\tau_t)^{1-n_t}]$ directly. Hence, the exact value of n_t has not been experimentally determined. Although n_r is known from experiment (see eq 4, where $\beta \equiv 1 - n_r$, and refs 5–11), the inequality, $n_t < n_r$, cannot be verified experimentally at this time. Nevertheless, it should be considered in the positive light as a prediction afforded by the present explanation that can be *falsified by experiment*. The fact that no one has yet invented the experimental technique to obtain n_t and check the prediction of $n_t < n_r$ should not be used negatively against our explanation. It is possible that critics may even trivialize our explanation as equivalent to making arbitrary assumption of the parameters n_t

and n_r to explain the enhancement of translational diffusion. We disagree with this view because n_r was determined already The only remaining unknown parameter is n_t. When it is determined in the future by a new experimental technique to measure the velocity–velocity correlation function $\langle v_x(0) v_x(t) \rangle$ of translational diffusion, we will see whether it falsifies or verifies our basic assumption (eq 11). In science, a theory with an assumption that can be falsified is an acceptable practice. If one compares the present explanation with other ones in the literature,[1,2,5,6,11–17] it should be pointed out there are also assumptions made and/or fitting parameters used in the latter, which cannot be directly verified at this time. For example, in a simulation of the spatially heterogeneous dynamics model[39] various values of the parameter, τ_{ex}/τ_c, between 1 and ∞ are needed to account for the entire set of the experimental data.

The primitive relaxations (eq 6) for translation, rotation and shear stress are given by $\exp(-t/\tau_{ot})$, $\exp(-t/\tau_{oc})$, and $\exp(-t/\tau_{o\eta})$, respectively. By their simple (i.e., noncooperative) nature of the primitive relaxations, the translational diffusion coefficient, $D_{ot} = (r_s^2/6\tau_{ot})$, the rotational diffusion coefficient, $D_{or} = 1/6\tau_{oc}$, and the shear viscosity, $\eta_o = G_\infty \tau_{o\eta}$, obey the DSE and the SE equations (eqs 1 and 2). Written out explicitly, these relations are $D_{or} \equiv 1/6\tau_{oc} = kT/8\pi\eta_o r_s^3$, $D_{ot} \equiv r_s^2/6\tau_{ot} = kT/6\pi\eta_o r_s$. The product $(D_{ot}\tau_{oc})$ is equal to $(r_s^2/6)(\tau_{oc}/\tau_{ot})$, as required by the DSE and the SE equations, i.e., $D_{ot}\tau_{oc} = (r_s^2/6)(\tau_{oc}/\tau_{ot}) = 2r_s^2/9$. From eq 7, these primitive relaxation times have the same temperature dependence, i.e., $\tau_{ot}(T) \approx \tau_{oc}(T) \approx \tau_{o\eta}(T) \approx \zeta_o(T)$. Applying eq 8 separately to translation, rotation and shear flow, one obtains the relations, $\tau_t = [t_c^{-n_t}\tau_{ot}]^{1/(1-n_t)}$, $\tau_c = [t_c^{-n_r}\tau_{oc}]^{1/(1-n_r)}$, and $\tau_\eta = [t_c^{-n_\eta}\tau_{o\eta}]^{1/(1-n_\eta)}$. Then, with $D_t = (r_s^2/6\tau_t)$, from eqs 20 and 22 and $\eta = G_\infty \tau_\eta$, it follows that the exponent ξ in eq 3 used by Fujara and co-workers[1-3,17] to characterize the enhancement of translational diffusion is given by

$$\xi = [(1 - n_\eta)/(1 - n_t)] \leq 1 \qquad (12)$$

It follows that ξ is less than or equal to 1 because $n_t \leq n_r$ and $n_t \leq n_\eta$ from inequality (eq 11). If indeed n_t is less than n_r and n_η, then ξ is less than 1 and translational diffusion has a weaker temperature dependence than rotation diffusion and viscosity as observed experimentally.

Likewise, from $D_t\tau_c = (r_s^2/6)(\tau_c/\tau_t)$, we obtain the following expression

$$D_t\tau_c = \left(\frac{2r_s^2}{9}\right)\frac{[\tau_{oc}/t_c]^{n_c/(1-n_c)}}{[\tau_{ot}/t_c]^{n_t/(1-n_t)}} \qquad (13)$$

Recognizing that the first factor on the right-hand-side of eq 13 is just $(D_t\tau_c)_{SE,DSE}$, the last equation can be rewritten in terms of the quantity

$$\log[D_t\tau_c/(D_t\tau_c)_{SE,DSE}] = \left(\frac{n_r}{1-n_r}\right)\log(\tau_{oc}/t_c) - \left(\frac{n_t}{1-n_t}\right)\log(\tau_{ot}/t_c) \qquad (14)$$

introduced by Ediger and co-workers. The primitive relaxation times, τ_{ot} and τ_{oc}, may not be exactly equal but they are expected to have comparable values because they obey the DSE relation. For $T < 1.2T_g$, they are much longer than $t_c \approx 2$ ps, a result which follows from eq 8. Thus, from eq 14, if n_r is larger than n_t, we have $\log[D_t\tau_c/(D_t\tau_c)_{SE,DSE}]$ larger than 0, i.e., enhanced translation. The value of $\log[D_t\tau_c/(D_t\tau_c)_{SE,DSE}]$ is greater for larger n_r and has a bigger difference between n_r and n_t. This

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property rationalizes the origin of what Ediger and co-workers have found experimentally that a larger $\log[D_t\tau_c/(D_t\tau_c)_{\text{SE,DSE}}]$ is correlated with a smaller KWW exponent β of the probe rotation correlation function, because their β is exactly our $(1 - n_r)$ here. Assuming that τ_{ot} and τ_{oc} are equal and using eq 8, the right-hand side of eq 14 can be rewritten in terms of the experimentally observed rotational relaxation time, τ_c, as

$$\log[D_t\tau_c/(D_t\tau_c)_{\text{SE,DSE}}] = \left(\frac{n_r - n_t}{1 - n_t}\right)\log(\tau_c/t_c) \qquad (15)$$

In eq 15, n_r and τ_c are known from experiment,[4–11] $t_c = 2$ ps is also from experiment,[20,27–36] and the only unknown is n_t. For tetracene in OTP at T_g, $\tau_c \approx 100$ s and $n_r = 0.40$. For a reasonable value of $n_t = 0.30$, eq 15 gives $\log[D_t\tau_c/(D_t\tau_c)_{\text{SE,DSE}}] = 2$, which is not far from the experimental value of about 2.3.

The explanation of enhanced translation given here is that the proposed difference between n_r and n_t cannot be directly verified quantitatively at this time because an experiment has not yet been performed to measure the velocity–velocity correlation function $\langle v_x(0)v_x(t)\rangle$ of translational diffusion and to determine n_t. Fortunately, there is supporting evidence for this proposal from the comparison by Chang and Sillescu[17] of dielectric relaxation and shear viscosity data on several of the supercooled liquids in which translational enhancements were found. These authors examined the quantity, $\eta/T\tau_{\text{diel}}$, where τ_{diel} is the dielectric relaxation time determined from the frequency $f_{\max}$ of the maximum of the dielectric loss peak by the expression $1/(2\pi f_{\max})$. They found that an increase of $\eta/T\tau_{\text{diel}}$, on decreasing temperature to approach T_g, *parallels* that of $D_t\eta/T$ for self-diffusion describable by eq 3 with $\xi < 1$. Since τ_c obtained from ^{2}H NMR in deuterated OTP scales with η in this T regime and follows the DSE equation, they found that τ_{diel} is shorter than τ_c by about 1 order of magnitude. This enhancement of τ_{diel} compared with τ_c of the same order of magnitude has also recently been seen in supercooled toluene.[40] In some other liquids, such as salol, the increase of $\eta/T\tau_{\text{diel}}$ down to T_g is even larger[17] and about one and a half decades. This parallel behavior indicates that *there is not only enhanced translational diffusion but also enhanced dielectric relaxation* compared with rotational diffusion and viscosity. The time correlation function of dielectric relaxation in supercooled liquids has been deduced by fitting the complex dielectric susceptibility, $\epsilon^*(f)$, by the Fourier transform of the derivative of the KWW function $\exp[-(t/\tau_{\text{diel}})^{1-n_{\text{diel}}}]$. Dielectric measurement of neat OTP was carried out recently by Wagner and Richert.[41] Their data when fitted to the KWW function gives approximately the same value of $n_{\text{diel}} = 0.50$. On the other hand, by fitting of the ^{2}H NMR measurement of the rotational correlation function to a KWW function, $\exp[-(t/\tau_c)^{1-n_r}]$, Fujara et al.[1] and Chang et al.[2] reported at 254 K a value of the stretched exponent $(1 - n_r) \approx 0.35$. This value of $(1 - n_r)$ is significantly smaller than any other measurements of small molecule glass-formers ever reported and it could have considerable error which was not given.[1,2] Nevertheless, this result indicates that $n_r > n_{\text{diel}}$. Similar steps such as that used before to arrive at eq 12, now applied to dielectric relaxation instead of translational diffusion, lead to the result $\tau_{\text{diel}} \propto (\tau_c)^\lambda$, where $\lambda = [(1 - n_r)/(1 - n_{\text{diel}})] < 1$. Since τ_c obtained from ^{2}H NMR in deuterated OTP scales with η in this T regime and follows the DSE equation, we have $(\eta/T\tau_{\text{diel}}) \propto (\eta/T)^{1-\lambda}$. Substituting $(1 - n_r) \approx 0.35$ and $(1 - n_{\text{diel}}) = 0.50$ in $\lambda = [(1 - n_r)/(1 - n_{\text{diel}})] < 1$, one gets $\lambda = 0.70$. If error allows one to take a smaller value of $(1 - n_r) = 0.40$, then $\lambda = 0.80$. This result is qualitatively consistent with the increase of $\eta/T\tau_{\text{diel}}$ with decrease in T on approaching T_g, discovered by Chang and Sillescu[17] in several supercooled liquids.

3. Dependence of the Phenomena on Probes and Hosts

In the experimental studies of enhancement of translational diffusion of different probes in various glass-forming liquids, not only the enhancement parameters ξ and $\log[D_t\tau_c/(D_t\tau_c)_{\text{SE,DSE}}]$ but also other quantities change from system to system. The other quantities, which have been examined in conjunction with the enhancement parameters, include the KWW β for probe rotational diffusion and $\rho = r_{\text{vdW}}(\text{probe})/r_{\text{vdW}}(\text{host})$, the ratio of the van der Waals radii of the probe and the host. The former was considered by Ediger and co-workers,[5–11] which led them to discover that larger $\log[D_t\tau_c/(D_t\tau_c)_{\text{SE,DSE}}]$ is correlated with a smaller β. The latter was considered by Heuberger and Sillescu,[3] which led them to find that a smaller ξ correspond to a smaller ρ. Ediger and co-workers have also observed similar dependence of $\log[D_t\tau_c/(D_t\tau_c)_{\text{SE,DSE}}]$ on the increase of the size of the probe from tetracene and rubrene in various hosts.

Here we examine yet another quantity and that is τ_c/τ_α, the ratio of the probe rotation correlation time to the α-relaxation time of the host, τ_α. There are various experimental methods to measure τ_α. Examples include dielectric relaxation, photon correlation spectroscopy, mechanical relaxation, and various NMR techniques such as the ^{2}H NMR method on deuterated samples discussed earlier. For the same reasons offered for possible differences when considering translational diffusion, rotational diffusion, viscosity, and dielectric relaxation in the previous section, we should beware that τ_α may also depend on the dynamic variable measured.

(a) Case of $\tau_c/\tau_\alpha \gg 1$. If $\tau_c/\tau_\alpha \gg 1$, the rotation of the probe occurs at times much longer than the α-relaxation relaxation time of the host. Hence, for nonpolymeric hosts, the host molecules are already in steady-state flow when probe rotation takes place. The probe rotation has missed participation in the cooperative dynamics with the host molecules because the latter has already taken place at an earlier time of the order of τ_α. The consequence is that the probe rotation, as well as probe translation, is a simple motion in a hydrodynamic continuum with viscosity η. There is absence of cooperative molecular dynamics in any motion of the probe molecule. Therefore, the rotational correlation function is a linear exponential correlation function, $\exp(-t/\tau_c)$, i.e., $n_r = 0$, and its rotational correlation time obeys the DSE eq 1. Translational diffusion correlation function is also a linear exponential, i.e., $n_t = 0$, and its diffusion coefficient obeys the SE eq 2. The temperature dependences of various kinds of motion of the probe are all governed by that of the steady-state viscosity of the host. Hence D_t and $(\tau_c)^{-1}$ all have the same temperature dependence of T/η, a situation that is realized by rubrene in OTP. Among the nonpolymeric supercooled liquids studied by Ediger and co-workers, the condition $\tau_c/\tau_\alpha \gg 1$ is best met by rubrene in OTP[5–7] with $\tau_c/\tau_\alpha \approx 10$. Indeed in this case the enhancement factor $\log[D_t\tau_c/(D_t\tau_c)_{\text{SE,DSE}}]_{T=T_g}$ is small (see Figure 1, open circle labeled R/OTP). It is also in this system that they found[7,11] the smallest value of 0.11 ± 0.04 for n_r at T_g (see Figure 2, open circle labeled by R/OTP) and even smaller value of 0.04 ± 0.05 at higher temperatures[7,11] (see Table 2 of ref 7), in agreement with expectation.

The condition $\tau_c/\tau_\alpha \gg 1$ is certainly satisfied by diffusion in cresophthalatedimethyl-ether (CDE) and in phenolphthalate-dimethyl-ether (PDE) of very large spherical polystyrene micronetworks having hydrodynamic radii of 6 and 8 nm.[3] The
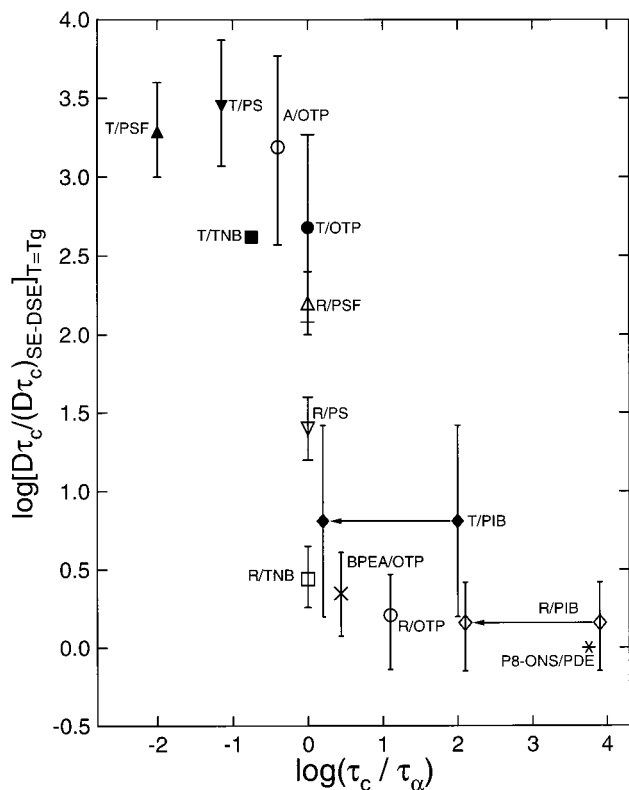
Figure 1. Correlation of enhanced translation $\log[D_t\tau_c/(D_t\tau_c)_{SE,DSE}]$ at T_g of the probes in various hosts with the extent of probe-host coupling measured by the ratio $\tau_c(T_g)/\tau_\alpha(T_g)$. Explanation of the horizontal arrows connected two data points of T/PIB and R/PIB can be found in the text.

ratio of the van der Waals radii of the tracer to the host is about 20. These gigantic size probes are not expected to move until the host molecules are in the steady-state flow regime, and hence, the temperature dependence of D_t is the same as T/η. In these cases, they found $\xi \approx 1$, consistent with the same temperature dependence for D_t and T/η. The rotational correlation function of the large tracer is a linear exponential (i.e., $\beta = 1$). The DSE and SE equations 1 and 2 are expected to hold. Therefore, $\log[D_t\tau_c/(D_t\tau_c)_{SE,DSE}]_{T=T_g}$ is equal to zero, and the third power of the ratio of the van der Waals radius of the tracer to the host is used to give an estimate of the ratio $\tau_c/\tau_\alpha \approx (20).$[3] The points represented by stars in Figures 1 and 2 and labeled by P8−ONS/PDE are obtained in the manner described.

There is another way that the condition $\tau_c/\tau_\alpha \gg 1$ can be satisfied without the size of the probe being large compared with the host. Consider the same probe but different hosts with a large spread in T_g's, but all having molecules of not too different sizes. It is possible that while in a host with higher T_g, the condition $\tau_c/\tau_\alpha \approx 1$ holds, but in a host with significantly lower T_g, the opposite condition $\tau_c/\tau_\alpha \gg 1$ becomes satisfied. The change occurs because τ_α is certainly drastically reduced in the host with lower T_g, but the corresponding alteration of τ_c of a probe may be significantly less. If this change from $\tau_c/\tau_\alpha \approx 1$ to $\tau_c/\tau_\alpha \gg 1$ can be realized, then we expect the enhancement of translational diffusion to decrease and even vanish in hosts of low T_g's. Examples of this behavior can be found[3] by comparing the tracer aberchrome 540 (ACR) in PDE ($T_g = 294$ K), glycerol ($T_g = 193$ K) and 1,2-propanediol (T_g=153 K). While $\xi = 0.71$ (or significant enhancement) for PDE that has a higher T_g, $\xi \approx 1$ (or no enhancement) for the other two with much lower glass temperatures. The ratio ρ changes from 0.93 to 1.43 by a mere 50%. The rotational
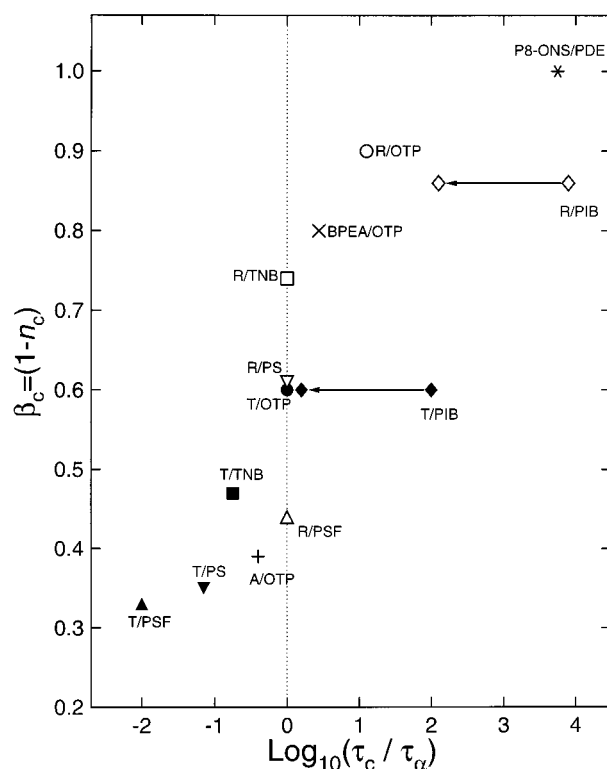

Figure 2. Correlation of the KWW β parameter for probe rotation at T_g in various hosts with the extent of probe-host coupling measured by the ratio $\tau_c(T_g)/\tau_\alpha(T_g)$. Explanation of the horizontal arrows connected two data points of T/PIB and R/PIB can be found in the text.

correlation function of ACR in these supercooled liquids has not been measured. Hence, the possibility that n_r is nonzero and $\tau_c/\tau_\alpha \approx 1$ for ACR in PDE but n_r goes to zero and $\tau_c/\tau_\alpha \gg 1$ for ACR in glycerol and 1,2-propanediol cannot be checked at this time.

Ediger and co-workers have studied so far only two non-polymeric supercooled liquids, OTP ($T_g = 243$ K) and TNB ($T_g = 343.5$ K). The difference in T_g of these two liquids may contribute possibly in part to the larger τ_c/τ_α value observed for the same probes, tetracene and rubrene, in OTP than in TNB. The larger τ_c/τ_α value of the same probe in OTP than in TNB and the accompanying changes in $\log[D_t\tau_c/(D_t\tau_c)_{SE,DSE}]_{T=T_g}$ and β can be seen by inspection of Figures 1 and 2 (filled circle T/OTP, open circle R/OTP, filled square T/TNB, open square R/TNB). This will be discussed further below. The results of their study of tetracene and rubrene in three polymeric hosts PSF ($T_g = 459$ K), PS ($T_g = 373$ K), and PIB ($T_g = 205$ K) also revealed that a larger τ_c/τ_α value is observed in a polymer with lower T_g (Figures 1 and 2).

(b) $\tau_c/\tau_\alpha \approx 1$ and $\tau_c/\tau_\alpha < 1$. If τ_c/τ_α is nearly 1, the rotational motion of the probe occurs at about the same time as the α-relaxation of the host, and the probe participates in the dynamically heterogeneous cooperative α-relaxation of the host molecules. The probe rotation may have its coupling parameter, n_r, of comparable value as n_α, the rotational coupling parameter of the α-relaxation of the host. This situation is realized for the host OTP and probes anthracene (Figures 1 and 2, A/OTP) and tetracene (Figures 1 and 2, filled circle, T/OTP), where $\tau_c/\tau_\alpha \approx$ 1. In fact, from the probe rotation data of Cicerone et al.[7] near T_g, the values $n_c = 0.4 \pm 0.06$ for tetracene and $n_c = 0.61 \pm 0.1$ for anthracene are not too different from $n_\alpha = 0.66 \pm 0.03$ found by deuterated OTP ^{2}H NMR data.[1,2] The condition $\tau_c/\tau_\alpha \approx 1$ is not the only factor that determines the degree of probe participation in the rotational motion of the host mol-

ecules. The degree still depends on how well the probe couples to the host molecules.

Starting from $\tau_c/\tau_\alpha \gg 1$, if we make $\tau_c(T)$ to become closer to $\tau_\alpha(T)$, the enhancement of translational diffusion and non-exponentiality of the probe rotational correlation function $r(t)$ will increase. For example, with the same probe rubrene, replacement of OTP by TNB[6] (which has a larger size similar to rubrene and also a higher T_g) makes $\tau_c(T)$ close to $\tau_\alpha(T)$. Correspondingly, $r(t)$ deviates more from a single exponential (KWW $\beta = 0.74$ for TNB compared with 0.9 for OTP, see Figure 2), and the difference between the T dependencies of D_t and $(\tau_c)^{-1}$ measured by the ratio $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ is larger at T_g (see Figure 1). The same is true on keeping the same host OTP but decreasing the probe size on replacing rubrene by a smaller molecule BPEA [see Figure 1 and 2 (○), R/OTP, and (×) BPEA/OTP].

For tetracene, experimentally, it was found that $\tau_c(T) \approx \tau_\alpha(T)$ in OTP and $\tau_c(T) < \tau_\alpha(T)$ in TNB, which indicates that the probe is participating fully in OTP and more than fully in TNB in the cooperative rotational motions with the host molecules. By "more than fully", we mean that since $\tau_c(T) < \tau_\alpha(T)$, the host molecules on the average are rotating slower than the probe, and consequently, they pose more severe intermolecular constraints on the rotation of the probe than when $\tau_c(T) \approx \tau_\alpha(T)$. Therefore, from the CM, a larger n_r is expected for tetracene in TNB than in OTP. This expected change of n_r is in accord with the KWW β found experimentally for T/TNB and T/OTP (Figure 2). In fact, the KWW function fit to $r(t)$ obtained $\beta \equiv (1 - n_r)$, equal to 0.60 and 0.47 for tetracene in OTP and TNB, respectively,[4-7] near T_g. These values of the stretch exponent are comparable to the value of $(1 - n_\alpha)$ near T_g. For neat OTP, it is 0.50 from dielectric relaxation and 0.35 from ^{2}H NMR. For neat TNB, it is 0.53 from ^{13}C NMR spectroscopy[42] and 0.55 from light scattering.[43] $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ at T_g is also larger for T/TNB than for T/OTP as shown in Figure 1.

(c) Temperature Dependencies of β and $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$. Experimental measurements of the KWW exponent $\beta_\alpha \equiv (1 - n_\alpha)$ of OTP as well as other small molecule glass-formers by light scattering,[44,45] dielectric relaxation,[46-48] and NMR[1,2] all show that it increases with temperature. The extensive light-scattering data show that $(1 - n_\alpha)$ is equal to 0.55 at 246 K, 0.60 at 268 K, and it increases rapidly to 0.80, 0.85, and 0.90 at 290, 295, and 300 K, respectively. Dielectric relaxation data of OTP show also a similar trend. Since n_r of tetracene in OTP and TNB is comparable to the respective n_α of the neat hosts because of its participation in the cooperative dynamics, one can expect that $(1 - n_r)$ has a similar temperature dependence, which indeed has been found[11] experimentally in T/OTP. When n_r becomes small at higher temperatures, n_t will be even smaller (eq 11). The ratio ξ given by eq 12 is then close to unity, and $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ approaches zero. For example, the minimum value that ξ can have is 0.9 if it is assumed that n_r of tetracene in OTP is equal to 0.1 at 295 K as suggested by the corresponding value of 0.15 for n_α from light-scattering measurement.[45] This explains the crossover from $\xi < 1$ and large $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ at lower temperatures to $\xi = 1$ and small $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ at higher temperatures compared to T_g. In the CM explanation of the effect, this crossover is driven from the decrease of n_r toward zero at temperature sufficiently high above T_g. For OTP, PDE, salol, and m-TCP, it turns out[47-49] that n_r is nearly zero above temperatures T_B, and it rapidly increases across T_B. Coincidentally, T_B is the temperature below which appears a discrepancy of the viscosity or the dielectric relaxation time, τ_α, from the

high-temperature Vogel–Fulcher–Tammann (VFT) fit found by Stickel et al. using a derivative plot.[47-49] For example, $T_B = 295$ K for OTP which is nearly the same as T_β, the temperature below which the α- and the β-relaxations bifurcate.[47-50] Recently, it was pointed out that T_B is also the temperature above which n_α is small and below which n_α increases rapidly.[50] These properties of T_B suggest that it is the onset temperature of significant intermolecular coupling or cooperativity. It is after this onset of intermolecular coupling that n_c can assume larger values and significant difference between n_r and n_t becomes possible to give rise to the effect.

An immediate consequence of this proposed origin of the effect is that glass-formers, which have a small n_α at T_g and a slow variation of n_α at T_B, will not exhibit significant difference between translation and rotation even for probe of the same size and when the optimal condition of coupling of probe to host, $\tau_c(T) \approx \tau_\alpha(T)$, holds. This is because, at all temperatures down to T_g, n_r like n_α is always small and the difference between n_r and n_t is insignificant. This expected behavior is realized experimentally in the study of diffusion of Aberchrome 540 (ACR) in glycerol and 1,2-propanediol.[3] These hosts compared with OTP and TNB have smaller n_α at T_g and exhibit no rapid change of n_α with temperature at their T_B's as shown in refs 47 and 48 and emphasized in ref 50. Another possible cause of the nonobservance of the effect of ACR in glycerol and 1,2-propanediol is that $\tau_c(T) \gg \tau_\alpha(T)$ because the tracer molecule being larger and the T_g's of these hosts are much lower than others, as discussed before.

On the other hand, it is known that amorphous polymers such as polystyrene has a larger n_α at T_g than OTP and TNB.[51,52] The same reasoning employed in the previous paragraph leads us to expect larger enhancement of probe translational diffusion in polystyrene than in OTP and TNB. This will be discussed next.

(d) Polymeric Glass-Formers, PS and PSF. The same line of reasoning to explain the difference between translational and diffusional motions of tetracene and rubrene in small molecule glass-formers can be applied to polymers. Ediger and co-workers have studied extensively these probes in polystyrene (PS),[7,8,11] bisphenol A polysulfone (PSF),[8,9] and polyisobutylene (PIB).[8,10] In PS and PSF, the D_t's have a significantly weaker T dependence than the τ_c's for these two probes. The enhancement parameter $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ of tetracene is even larger than the same probe in OTP and TNB, reaching the value of about 3.5–4.0 at the glass temperatures of these two polymers. The effects are again larger for tetracene than rubrene. In ref 8, the $\tau_\alpha(T)$'s of PS obtained by photon correlation spectroscopy, dielectric relaxation, and stress relaxation are compared with the $\tau_c(T)$'s of rubrene and tetracene in PS. I have added the NMR data of $\tau_\alpha(T)$ for PS,[53] which is more relevant when comparing with τ_c. The retardation time of local segmental motion determined from creep compliance measurement of Plazek and co-workers[51,54] on high molecular weight PS is in good agreement with the NMR relaxation time. The comparison shows that near and below T_g, the NMR $\tau_\alpha(T)$ is almost the same as $\tau_c(T)$ of rubrene and is between 1 and 1/2 decades *longer* than $\tau_c(T)$ of tetracene. We do not consider the so-called G component stress relaxation time $\tau_G(T)$ of PS shown in Figure 5 of ref 8 because its values depend on specific model used,[55] which may be problematic because it was assumed that stresses are additive.[56] Also, at T_g, $\tau_G(T_g) \approx 1$ s, which is more than 1 and 1/2 decades shorter than the retardation time[51,54] of PS determined directly from Plazek's recoverable compliance data.

The relation between $\tau_c(T)$ and $\tau_\alpha(T)$ is similar for the two probes in PSF. Because $\tau_\alpha(T_g)$ is either comparable and even longer than $\tau_c(T)$ for rubrene and tetracene, respectively, following the same reasoning given before, it follows the rotational motion of rubrene is well coupled and tetracene is more than fully coupled to the dynamics of the host macromolecules. Recall that $\tau_c(T) \gg \tau_\alpha(T)$ for rubrene and $\tau_c(T) \approx \tau_\alpha(T)$ for tetracene in OTP and $\tau_c(T) < \tau_\alpha(T)$ for tetracene in TNB. These conditions indicated before that rubrene is not participating at all in OTP, tetracene is participating fully in OTP, and tetracene is participating more than fully in TNB in the cooperative rotational motions with the host molecules. Therefore, similarly for either rubrene or tetracene, the probe rotational motion is more cooperative in PS and PSF than in OTP. These expectations are borne out by the smaller KWW exponents, $\beta \equiv (1 - n_r)$, or larger coupling parameter, n_r, of $r(t)$ for the same probe in PS and PSF than in OTP. Near the glass temperatures, n_r of rubrene in PS and PSF have the values of 0.39 ± 0.05 and 0.56 ± 0.07, respectively [see Figure 2, ($\triangledown$) R/PS, ($\triangle$) R/PSF]. These larger values are to be compared with 0.11 ± 0.04 for rubrene in OTP. Likewise, n_r of tetracene has the value of 0.65 ± 0.10 in PS and 0.67 ± 0.09 in PSF [see Figure 2, ($\blacktriangledown$) T/PS, ($\blacktriangle$) T/PSF]. These even larger values of n_r are to be compared with 0.40 ± 0.06 for tetracene in OTP [see Figure 2, ($\bullet$) T/OTP]. The larger values of n_r allow the possibility of a concomitant larger $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ of the same probe in PS and PSF than in OTP. This result is realized if an increase of n_r is followed by a proportionate or less than proportionate increase of n_t. In this manner, the difference between n_r and the corresponding n_t will be the same or even larger as n_r increases. Under this assumption, it is not difficult to show that eq 14 guarantees that $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ increases with n_r. Again, as we have discussed earlier that although this assumption is quite reasonable, it cannot be verified at this time because the values of n_t in various matrixes have not been determined by experiment. Experimentally, the enhancement factor $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ of the same probe is larger in PS and PSF than in OTP or TNB (see Figure 1).

Another difference between T/PS and T/OTP is $(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}$ of the former, unlike that of the latter, remains large even when T/T_g exceeds 1.2 (see Figure 5 of ref 11). n_α of amorphous polymers such as PS is not known to have the strong temperature dependence of small molecule glass-formers. For example, broad band dielectric spectroscopy performed on poly-(methylphenylsiloxane)[57] showed that n_α of this polymer is nearly temperature independent. If this temperature dependence of n_α is transferable also to n_r, then we can readily understand why $(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}$ of T/PS remains large at high temperatures.

(e) Polymeric Glass-Former, PIB. The dynamics of the probes in PS and PSF is totally different from that when they are in polyisobutylene (PIB). For rubrene in PIB,[8,10,11] D_t and $(\tau_c)^{-1}$ have essentially the same T dependence. Translational diffusion is only slightly enhanced for tetracene. These different behaviors of the probes in PIB compared with the same in PS and PSF arise from two factors. The first factor comes from the comparison between the magnitudes of $\tau_\alpha(T)$ and $\tau_c(T)$. The authors of ref 8 have found that the local segmental relaxation time, $\tau_\alpha(T)$, of PIB from stress relaxation data is about 2 orders of magnitude shorter than $\tau_c(T)$ of tetracene and about 4 orders of magnitude shorter than $\tau_c(T)$ of rubrene. This magnitude of $\tau_\alpha(T)$ of high molecular weight PIB is consistent with our own determination from recoverable creep compliance data,[58-60] which indicates[61] that $\tau_\alpha(T) \approx 1.3$ s at 205 K. Thus, for these

two probes in PIB, τ_c is much longer than τ_α. This condition, drastically different from the same probes in PS and PSF, may be unsurprising because the glass temperature of PIB is significantly lower than the other polymers. The reasoning given before in subsection (a) leads to the conclusion that the temperature dependences of the translational and rotational motions of the probe are both determined by the temperature dependence of $\tau_\alpha(T)$ of PIB. The latter is nearly the same as that of the viscosity for PIB.[58,59,62] This property of probe motion in PIB, $\tau_c \gg \tau_\alpha$, readily explains why the difference between the temperature dependences of translational and rotational motions of a probe is drastically reduced in PIB when compared with the data of the same probe in PS and PSF. This comparison is shown in Figure 1 where $\blacklozenge$ and $\lozenge$ near the tip of arrows are for T/PIB and R/PIB, respectively. In polymers there exist modes with length scale and time scale intermediate between the local segmental motion and the entropic Rouse modes. These "sub-Rouse" modes have been seen directly in PIB from mechanical relaxation and compliance data.[59-61] The "sub-Rouse" modes have retained some degree of cooperativity with a coupling parameter, n_{sR}, that is less than the coupling parameter, n_α, of local segmental motion in PIB.[61] The mean relaxation time of the sub-Rouse modes, τ_{sR} is about 100 time longer than τ_α in PIB. It is likely that the sub-Rouse modes having relaxation times comparable to $\tau_c(T)$ of tetracene can involve the probe in their cooperative motion and impart a finite coupling parameter, n_r, to $r(t)$ of tetracene in PIB. This may account for the not so small observed value of 0.4 of n_r (see Figure 2) as well as the nonzero $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ value (see Figure 1) of tetracene in PIB. The contribution of the sub-Rouse modes to n_r is brought out in Figures 1 and 2 by re-plotting the data labeled T/PIB and R/PIB against τ_c/τ_{sR}. Since $\tau_{sR}/\tau_\alpha \approx 10^2$ in PIB, the replotting is equivalent to horizontal shifts of two decades of the PIB data in Figures 1 and 2 to the corresponding points near the heads of the arrows. One may notice that neat OTP and neat PIB have the same $n_\alpha = 0.45$, and yet $(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}$ at T_g is larger for tetracene in OTP than tetracene in PIB.[8,10,11] This difference can be explained by the first factor that, for tetracene in PIB, τ_c is much longer than τ_α, while in OTP its τ_c is comparable to τ_α.

The second factor is the larger coupling parameter, n_α, of neat PS and PSF than PIB and OTP. PS[52] has $n_\alpha = 0.64$ while PIB[58,59,61] has $n_\alpha = 0.45$. The difference of n_α can be understood from the more flexible and compact repeat units of PIB which minimize the intermolecular constraints and hence a smaller n_α. In contrast, the bulkier rings attached either to the backbone of the repeat units such as in PS or residing in the backbone like in PSF cause stronger intermolecular coupling and a larger n_α and n_r for these polymers. As argued before, larger n_r for PS and PSF allows for the possibility of a bigger difference between n_r and n_t and, consequently, a more enhanced translation or larger $(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}$ at T_g.

(f) Correlation of $(D_t\tau_c)$ and β with τ_c/τ_α. The results of different probes in various hosts discussed above are summarized in Figures 1 and 2. When considered all together, clear patterns that the enhanced translation $(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}$ at T_g as well as β are correlated with τ_c/τ_α. It is clear from Figure 2 that $\beta \equiv (1 - n_r)$ increases with $\log(\tau_c/\tau_\alpha)$. This pattern is particularly clear after the data of T/PIB and R/PIB is corrected for the sub-Rouse modes contribution by the horizontal shifts. Figure 1 shows that the enhanced translation $\log[(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}]$ at T_g is also strongly correlated with $\log(\tau_c/\tau_\alpha)$. Of course, on combining Figures 1 and 2, we recapture the correlation of $(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}$ with β found by Ediger and
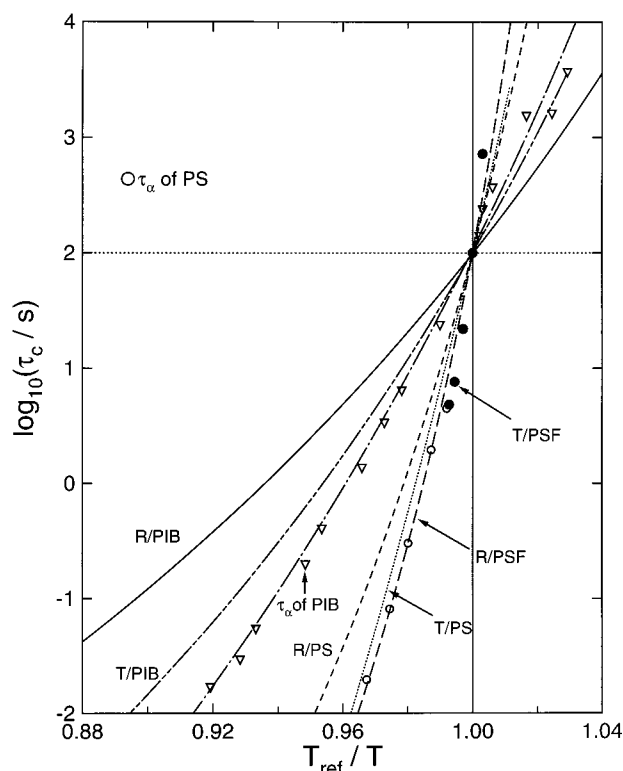
Translational Diffusion and Rotational Diffusion

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Figure 3. A plot of tetracene and rubrene rotation relaxation time τ_c in various polymeric hosts against scaled reciprocal temperature, T_{ref}/T. For each probe/host system, T_{ref} is the temperature at which $\tau_c(T_{ref})$ = 10^2 s. The α-relaxation times τ_α of neat PIB ($\triangledown$) and neat PS ($\bigcirc$) are also shown for comparison.

Figure 4. Correlation of the steepness index $m_p = d(\log \tau_c)/d(T_{ref}/T)$, evaluated at $T_{ref}/T = 1$ with the KWW β parameter for tetracene and rubrene rotation at $T = T_g$ in three polymeric hosts. Included are results from tetracene in OTP and TNB, and rubrene in TNB. Data of rubrene in OTP is excluded for reason stated in the text.

co-workers[4–11] at the glass temperature. According to the CM interpretation, the enhanced translation originates from the properties (eqs 8 and 11) of many-body molecular dynamics. The enhanced translation $(D_t\tau_c)/(D_t\tau_c)_{SE,DSE}$ is proportional to the nonexponentiality parameter, n_r, which in turn depends on the probe-host coupling condition described by the ratio τ_c/τ_α.

4. Comparing the Different Temperature Dependences of τ_c

The temperature dependences of the α-relaxation times in neat glass-formers have been compared with one another by plotting log τ_α against the T_g-scaled reciprocal temperature, T_g/T, where T_g is operationally defined as the temperature at which τ_α reaches an arbitrarily chosen long time[52] like 10^2 s. Different glass-formers exhibit large differences in their T_g-scaled temperature dependences of log τ_α. These differences are conveniently characterized by the steepness or "fragility" index, m = d(log τ_α)/d(T_g/T), evaluated at $T_g/T = 1$. It was later found that a correlation between m and the Kohlrausch exponent β_α exists. Within the same class, a glass-former with a larger m usually has a smaller β_α. Naturally, when considering the probe rotation in glass-formers, we are led to ask the following question. Does a similar correlation exist between m_p = d(log τ_c)/d(T_{ref}/T), evaluated at $T_{ref}/T = 1$ where T_{ref} is defined[52] as the temperature at which τ_c attains 10^2 s. To answer this question, the dependence of log τ_c on T_{ref}/T of different probes in various hosts are examined. The results of tetracene and rubrene in polymers are shown in Figure 3 together with the data of neat PIB and PS (i.e., log τ_α against T_g/T). Large variations are found, with R/PIB and T/PSF being the extremes. From the scaled temperature dependences, the steepness indices m_p are evaluated and plotted against the KWW β of the probe
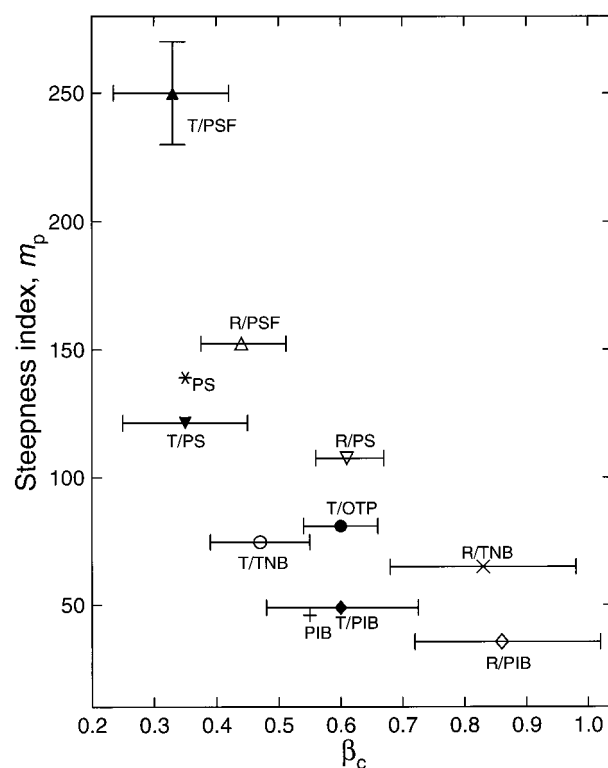
rotational correlation function in Figure 4. The appreciable errors involved in the determination of β by Ediger and co-workers are indicated. Due to the sparse amount of available data of τ_c for T/PSF, there are large errors in the determination of m_p of T/PSF, which are also shown in Figure 4. Included in this plot are the fragility indices m of neat PIB (+) and PS (*) plotted against their corresponding β_α. A correlation between m_p and β is evident particularly for polymer hosts in Figure 4. Although the data of tetracene and rubrene in OTP and TNB are also included in Figure 4, they may be distinguished from those of polymer hosts. This is because even in neat glass-formers, the correlation between the steepness index and β exists separately for polymers and small molecule liquids, but in mixing them together, the overall correlation is worsened.[52] Also, as explained in section 4a, the physics of rotational and translational diffusion of rubrene in OTP is simple. Rubrene in OTP satisfies the condition $\tau_c/\tau_\alpha \gg 1$ and moves such as in a hydrodynamic continuum. Hence, τ_c of rubrene in OTP has the temperature dependence of the viscosity and τ_α of neat OTP and yet it does not participate in any cooperative molecular dynamics and has $\beta \approx 1$. The difference in physics between R/OTP and T/OTP makes the comparison between their m_p's and β's in a figure like Figure 4 meaningless and hence not included.

5. Discussion

It is the many-body aspects of the molecular dynamics of systems with interaction that different dynamic variables of the *same* molecule weigh the slowing down effects of intermolecular interactions differently. Theoretically, this difference can be understood from a constraint entropy formulation of the coupling model (CM) based on the Dirac constraint dynamics.[38] In the CM, this result leads to the following conclusion. First, for a

neat glass-former (i.e., the tracer is identical to the host), the coupling parameters for rotational diffusion, n_r, and for shear viscosity, n_η in the KWW functions, $\exp[-(t/\tau_c)^{1-n_r}]$ and $\exp[-(t/\tau_\eta)^{1-n_\eta}]$, are larger than n_t, the coupling parameter in $\exp[-(t/\tau_t)^{1-n_t}]$ for translational self-diffusion. Experimentally, difference of the KWW exponents for different dynamic variables all related to the structural α-relaxation are often found. In glass-formers, such differences have been pointed out for various physical quantities by Moynihan[63] and by Ngai et al.[26] Molecular dynamics simulations of the α-relaxation in polyethylene by Roe[31] have obtained the time correlation functions, $M_1(t) = \langle \mathbf{u}(0)\mathbf{u}(t) \rangle$ and $M_2(t) = (1/2)\langle 3[\mathbf{u}(0)\mathbf{u}(t)]^2 - 1 \rangle$, where $\mathbf{u}$ is a unit vector embedded in a certain direction. It was found that the KWW β of the two correlation functions are not the same. The one with a smaller β has a stronger temperature dependence,[31] similar to what we propose here for rotational and self-translational diffusion in supercooled liquids. Thus, the occurrence of these differences in relaxation properties seems general for two different dynamic variables that are related to the structural α-relaxation of a neat glass-former. The recent findings of Chang and Sillescu,[17] that the dielectric relaxation, like translational self-diffusion, is also enhanced compared with shear viscosity, provide further evidence that this general phenomenon is not restricted to just translational and rotational diffusions.

When considering a tracer which is different from the host and making similar statements such as in the last paragraph, we have to be careful to separate two possible cases, $\tau_c/\tau_\alpha \gg 1$ and $\tau_c/\tau_\alpha \approx 1$ or $\tau_c/\tau_\alpha < 1$, discussed in sections 3a and 3b. If either $\tau_c/\tau_\alpha \approx 1$ or $\tau_c/\tau_\alpha < 1$ holds, the coupling parameter for rotational diffusion of the tracer, n_r, is larger than n_t, the coupling parameter for translational tracer diffusion. From $n_r > n_t$, we are led via the CM eqs 8 and 12–14 to a stronger temperature dependence for τ_c than $(D_t)^{-1}$ as found experimentally. However, if $\tau_c/\tau_\alpha \gg 1$, both probe rotation and probe translation now are simple motions in a hydrodynamic continuum (i.e., the host). As emphasized in section 3a, this is a special and rather trivial case, where the coupling parameters n_r and n_t are both zero and the temperature dependencies of τ_c and $(D_t)^{-1}$ are both governed by the viscosity η of the host. The physics is already clear in this case (e.g., R/OTP) and there is no need to enlist the help of any theory or model related to the glass transition phenomenon including the CM.

It is important to further clarify the result for two different dynamic variables having different coupling parameters. The prediction of stronger temperature dependence of the correlation time being associated with the dynamic variable that has a larger coupling parameter is made and it is applicable only for two different dynamic variables of the *same* tracer molecule. There is a danger that some reader may mistakenly extend this prediction to either the same dynamic variable or two different dynamic variables to two *different* tracers. For example, that reader may compare the rotational diffusions of tetracene and rubrene in OTP to test their n_r's correlation with the temperature dependencies of their τ_c's. This comparison is uncalled for or inappropriate for two reasons. The first is that we have not proposed any prediction for two *different* tracers, and the second is the simpler physics in R/OTP that does not even need the CM as explained above.

The consideration of the participation of the probe with the host in cooperative motion based on the ratio τ_c/τ_α is similar to earlier applications of the CM to binary blends of polymers[64] and supercooled liquids.[65] There we successfully explained the component dynamics of the mixtures. In blends, we have

concentration fluctuation which broadens the dispersion of each component and complicates the interpretation. The advantage here in the study of rotational diffusion of probe or tracer in supercooled liquids is the absence of concentration fluctuation because of the extremely low concentration. Without concentration fluctuation, the KWW β parameter of the rotational correlation function can be immediately identified with the coupling parameter of the probe n_r via the relation $n_r \equiv (1 - \beta)$. The probe participation in the cooperative dynamics with the host can be considered from the ratio of the independent relaxation times $\tau_{oc}/\tau_{o\alpha}$ like that done before in blends.[64,65] Such consideration has been done, and the conclusions are consistent with those obtained here from τ_c/τ_α.

The property is more general than just supercooled liquids. There is an analogous problem in glassy ionic conductors where the measured conductivity (σ) relaxation is quite different from nuclear spin lattice (SLR) relaxation of the diffusing ions. The SLR correlation time, τ_{SLR}, is much longer than[66] its conductivity relaxation time, τ_σ. Also the Arrhenius activation energy, E_{SLR}, of τ_{SLR} is larger than E_σ of τ_σ. The CM explained these from the difference between the correlation functions measured for conductivity and SLR.[66] The frequency dependent conductivity, $\sigma(\omega)$, is given by the Fourier transform of the current−current correlation function $(e/VkT)\int_0^\infty \langle J_x(0)J_x(t) \rangle \exp(i\omega t)\,dt$, where $J_x = \sum_i v_{ix}$ is the sum of the x-component of the velocity of the number N of ions. On the other hand, the SLR rate, T_1^{-1} is given in terms of another correlation function, $(1/N)\sum_{i\neq j}(1/N)\sum_{i\neq j}\langle F_{ij}^{(q)}(t)F_{ij}^{(q)}(0) \rangle$, where $F_{ij}^{(q)}(t) = (q\sqrt{8\pi/15}Y_2^q(\Omega_{ij}(t))/r_{ij}^3$, Y_2^q are the spherical harmonics, r_{ij} is the distance between two ions, Ω_{ij} is the spherical coordinates of the vector $\mathbf{r}_{ij}$, and $q = 1, 2$. The $(r_{ij})^{-3}$ factor in the SLR correlation function emphasizes the contribution at shorter distances, where the ion−ion interaction is larger. Consequently, the effects of ion−ion interactions are stronger for SLR than in $\sigma(\omega)$, and the coupling parameter of relaxation of ions in SLR, n_{SLR}, is larger than n_σ of conductivity relaxation. The CM calculates neither n_{SLR} nor n_σ. Fortunately, they are determined by the experiments which found the SLR correlation function to have the KWW form $\exp[-(t/\tau_{SLR})^{1-n_{SLR}}]$ and the ion hopping correlation function in conductivity relaxation also has the KWW form $\exp[-(t/\tau_\sigma)^{1-n_\sigma}]$, and indeed $n_{SLR} > n_\sigma$ as expected. Since the independent relaxation of the ion and its relaxation time, τ_o, as well as t_c are the same for both SLR and $\sigma(\omega)$, applying eq 8 separately to SLR and $\sigma(\omega)$, one obtains the following relation between their relaxation times,

$$\tau_\sigma \approx [\tau_{SLR}]^\xi, \quad \xi = [(1 - n_{SLR})/(1 - n_\sigma)] < 1. \quad (16)$$

The corresponding activation energies are related by $(E_\sigma/E_{SLR}) = \xi$. With the known values of n_{SLR} and n_σ from experiment, the last relation provides a critical test of the prediction of the CM, which turned out to be valid in general for glassy ionic conductors.[66] The analogy between eq 16 of dynamics of ions in glasses and eqs 3 and 12 that describe enhanced translation in supercooled liquids is rather obvious.

6. Comparison with Explanation Based on Spatial Heterogeneity

It is instructive to compare our explanation with that proposed by Ediger and co-workers[39] based on spatially heterogeneous dynamics. They assume that dynamics in some regions of the sample are orders of magnitude faster than in other regions perhaps 5 nm away. They further assume that a region in which molecules rotate faster, so is the local translation. With these

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assumptions, they show by simulation that translation diffusion is enhanced because translation and rotation experiments each average over the heterogeneity in their own way.[6,14] Specifically, rotational correlation time weights regions of slower mobility to a much greater extent, while long-time translational diffusion coefficient emphasizes regions of high mobility. This explanation is appealing because there is experimental evidence for dynamic heterogeneity,[67-69] i.e., there are fast and slow relaxing molecules, and they reverse their role within a time approximately equal to $2\tau_{\mu}$. However, it is neither clear nor certain that the spatially heterogeneous model of translational diffusion envisaged by Ediger and co-workers is compatible with the dynamically heterogeneous relaxation seen experimentally.

The CM interpretation of enhanced translation diffusion does not contradict outright the proposed explanations that are based on spatially heterogeneous dynamic of the molecules and, particularly, dynamic heterogeneity. As was mentioned before, the molecular dynamics in the coupling model is consistent with dynamic heterogeneity. In fact, one earlier formulation of the CM based on the "Dining Philosophers Problem" in computer science[70] gave a vivid demonstration that the cooperative relaxation has to be dynamically heterogeneous and is the source of the nonexponential KWW function (eq 5). This paper[70] was published in 1990, 1 year before the seminal experimental work of Schmidt-Rohr and Spiess,[67] which proves that the dynamic is heterogeneous. Thus, the results of the CM are not only eqs 5, 6, and 8 but also include dynamic heterogeneous nature of the KWW function. The latter means that there is no total contradiction between Ediger's explanation and the CM. However, our explanation differs in approach from that of Ediger. Both explanations agree that translational diffusion and rotational diffusion can be different. In the CM, this difference comes from these two processes weighting the molecular interactions and constraints differently, as discussed in section 2. Our explanation starts at a more fundamental level of comparing *the microscopic translational diffusion correlation function* (i.e., for length scale of the order of r_s, the spherical radius of the molecule, as in eq 2) with the microscopic orientation correlation function. In contrast, Ediger compares the microscopic orientation correlation function with the *long time-translational diffusion coefficient*.[39] Both translation and rotation of molecules originate from microscopic motions, and they should be treated on equal footing, i.e., at the microscopic correlation functions level as in the CM explanation. By considering the long-time translational diffusion coefficient and not the microscopic translational diffusion correlation function, some information of the dynamics is lost.

In the framework of the CM, the difference between the two correlation functions is characterized by the differences of their KWW exponents $(1 - n_{\mu})$ and of their correlation times τ_{μ} (eq 5), where $\mu = t$ and r for translation and rotation, respectively. From the constraint entropy formulation of the CM, we have shown that $n_t \leq n_r$ (eq 11). This inequality, together with the relation between the cooperative correlation times τ_{μ} and their primitive relaxation times $\tau_{o\mu}$ given by eq 8, leads to the quantitative predictions given by eqs 12−15. Throughout this explanation, the dynamic heterogeneous nature of KWW function is not emphasized, although the CM has this property for its KWW correlation function (eq 5). This is not surprising because dynamic heterogeneity is the property of the KWW correlation function (eq 5), which is just one consequence among others (eqs 6 and 8) of the many-body dynamics of supercooled liquids caused by intermolecular interactions. In the CM, the cooperative relaxation time τ_{μ} of the dynamically heterogeneous

KWW correlation function $\langle u(0)u(t) \rangle$ (eq 5) is related to the primitive correlation time $\tau_{o\mu}$ (eq 6) by the important eq 8. The origin of this relation is microscopic because it involves a crossover time t_c approximately equal[27-36] to 10^{-12} s. This relation, together with $n_r \geq n_t$ (eq 11), which comes from rotational diffusion weighting intermolecular interaction and constraint more than translational diffusion, is used to explain the enhanced translational diffusion. Thus, our explanation has molecular dynamics underpinning, all the way from microscopic times to macroscopic times. In contrast, Ediger's explanation, being confined to the comparison of the KWW rotational correlation function and the long-time translational diffusion coefficient, is less fundamental. Hence, it is expected not to be general.

There are evidences showing that the current explanation is in fact more generally applicable than that offered by Ediger. The translation diffusion in the heterogeneous lattice model of Ediger yields enhanced long-time translational diffusion coefficient from molecules "percolating" in space through the easier paths, as likened to the flow of current in a network of resistors following the paths of lower than average resistance.[39] Obviously, this spatially heterogeneous dynamics explanation cannot work for two relaxation processes, both of which are *local*, but they have different relaxation times and temperature dependences, similar to translational and rotational diffusions. Examples of these differences of *local* processes in glass-forming substances have been found by dielectric relaxation spectroscopy, depolarized light scattering and mechanical relaxation more than 10 years ago.[26] More recent findings of similar effects include the enhancement of dielectric relaxation compared with viscosity or rotational diffusion by Chang and Sillescu[17] in the same supercooled liquids where enhanced translational diffusion has been found. A study of the α-relaxation of diglycidyl ether of bisphenol A using a combination of dielectric relaxation, depolarized light scattering, and mechanical relaxation by Comez et al.[71] has found the same effect. The Debye−Stokes−Einstein relation (eq 1) works for dielectric relaxation, i.e., $\tau_{\text{diel}} \propto (T/\eta)$. However, it breaks down for depolarized light scattering (DLS) because a fractional power dependence of the relaxation time $\tau_{\text{DLS}} \propto T/(\eta)^{0.89}$ has been found, like in translational diffusion (eq 3), over 7 decades. While the spatially heterogeneous dynamics of Ediger cannot explain these similar experimental facts, the CM explanation still works. Moreover, the CM results are in quantitative agreement with the data as demonstrated for polymeric glass-formers in ref 26, for diglycidyl ether of bisphenol A in ref 72, and in here for the findings of Chang and Sillescu (see section 2, near the end).

7. Conclusion

The results discussed in this work do show that the CM can rationalize all the experimental facts on the translational and rotational motions in various glass-forming liquids. In particular, one can understand from the CM the impressive correlation between $(D_t\tau_c)/(D_t\tau_c)_{\text{SE,DSE}}$ and the KWW β found by Ediger and co-workers at the glass temperature and the dependence of ξ on the ratio of the van der Waals radii shown by Heuberger and Sillescu. Thus, the CM can offer an explanation of the difference between translation and rotation. The strength of this explanation is that it follows the same line (i.e., a physical principle) that explains other similar features found in the studies of the structural relaxation of glass-forming liquids using different probes, in blends and in other fields. The weakness of the explanation is that it does not provide a detailed description of molecular motion in the cooperative translational and rotational diffusions.

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