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Enhancement of translational diffusion coefficient of a probe in a rotationally anisotropic fluid

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Enhancement of the translational diffusion coefficient of a probe molecule in a supercooled liquid over the value predicted by the traditional Stokes-Einstein equation has been interpreted as arising from dynamic heterogeneity. We show that the dynamic coupling of the translation to rotation can also lead to a strong enhancement in a rotationally anisotropic molecular fluid. For a dynamically heterogeneous fluid, the probe size may play an important role. We show that if the diffusion probe is large so as to encompass several regions of high and low mobility, the rotation-translation coupling parameter needs to be modified to reflect the averaging heterogeneity effect. We show that, while the averaging effect arising from dynamic heterogeneity may alter the final enhancement, the coupling of translation to rotational degrees of freedom must be taken into account to properly account for the experimental result.

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INTRODUCTION

The Stokes-Einstein (SE) equation for the translational self-diffusion coefficient of a spherical molecule is given by $D_{\mathrm{SE}}=k_bT/(6\pi\eta_sR)$, and the corresponding Debye-Stokes-Einstein (DSE) equation for the rotational diffusion coefficient is given by $D_r=3k_bT/(4\pi R^3\eta_s)$. Both equations show the temperature dependence to be T/η_s, where T and η_s are the absolute temperature and shear viscosity, respectively. Although the SE equation has been considered to be applicable only for diffusion of a large sphere in a hydrodynamic continuum [1], Zwanzig and Bixon have shown by simulation that Stokes' law may also be applicable for a particle in a fluid of the same kind or composed of particles having similar size [2].

A great deal of research has also been carried out in the last two decades dealing with translational and rotational diffusion of molecules in high-viscosity, supercooled liquids, with the objective of obtaining information about the liquid-glass transition process [3–5]. The viscous liquid-glass transition is generally characterized by a structure relaxation process with a mean relaxation time changing from about several 10^{-12} seconds above the melting temperature to several hundreds of seconds in the glass transition region of the material. Such an enormous change in the structural relaxation has stimulated the study of supercooled liquids using many experimental techniques.

Dynamic light scattering is one of the widely used techniques for the investigation of glass-forming liquids. Depolarized Rayleigh scattering (DRS) arises from the fluctuation of the off-diagonal elements of the dielectric tensor of the medium. The fluctuation of off-diagonal elements is due to the orientational motion of molecules. For a viscous liquid at high temperature, the DRS spectrum usually appears as a broad structureless component centered at the laser frequency. The width of the central component is proportional to the rate of molecular reorientation. However, as the liquid is brought to the supercooled state, the central component narrows greatly and a much weaker doublet, symmetrically shifted from the excitation laser frequency, also appear in the DRS spectrum [6]. The position of the doublet is very sensitive to the temperature variation and it merges with the central peak as the liquid is brought out of the supercooled state. The appearance of the doublet in the DRS spectrum is considered to be due to the collective transverse momentum of the liquid, which couples to the dielectric tensor through a rotation-translation (RT) coupling mechanism [7–9], ignoring the photoelastic coupling, which is unimportant in molecular liquids.

Combining the Fabry-Pérot interferometric [10] with a light beating [11] technique, it is possible to carry out DRS measurements of a glass-forming molecular liquid over a wide frequency range [12]. In *o*-terphenyl (OTP), the linewidth of the central peak, which is proportional to D_r, tracks the temperature dependence of T/η_s, as the liquid's viscosity η_s changes by over 12 orders of magnitude [10]. Similar results are also found from NMR [13] and photobleaching [14] measurements of rotational diffusion coefficients of probe molecules in OTP and in other glass-forming liquids. At present, it is generally agreed that the temperature dependence of D_r is well described by the DSE equation.

Translational diffusion coefficients D_t of various probes have been measured in supercooled molecular liquids using NMR [13] and photobleaching [14] and forced Rayleigh scattering [15] techniques. As the temperature is lowered toward T_g (the glass transition temperature), D_t of the probe molecule is found to be greater than the value predicted by the SE equation and in some cases an enhancement over two to three [16] orders of magnitude is observed. Similar enhancements of D_t have also been observed in polymeric glass-forming liquids [17,18].

Such a remarkable difference in the temperature dependence of translational and rotational diffusion coefficients in a supercooled liquid has recently been interpreted as due to the spatially heterogeneous dynamics in the supercooled glass-forming liquid. Enhancement of the translational diffusion coefficient has been considered as a signature of dynamic heterogeneity in the supercooled liquid [5,14].

By heterogeneous dynamics, it is mean that the dynamics in one region of the liquid is orders of magnitude faster (or slower) than that in another region a few nanometers away [5]. While the heterogeneous dynamics scenario is yet waiting for a direct experimental proof, various computer simulations supporting the dynamic heterogeneity scenario in supercooled liquids have appeared [19,20].

Hodgdon and Stillinger (HS) provided the first attempt to quantitatively relate the dynamically heterogeneity to translational diffusion. They modeled a dynamically heterogeneous fluid as a two-zone fluid [21]. A diffusing spherical particle having a radius R resides inside and is concentric with a spherical domain of radius L. Inside the domain, the viscosity is η^i, and outside, it is η^o. The Navier-Stokes equation and equation of continuity are assumed to hold in both zones, with appropriate viscosity η^i or η^o in the appropriate zone. The calculation shows that if ξ is less than 1, the drag force decreases monotonically with increasing ξ $(=\eta^o/\eta^i)$ and l $(=L/R)$ [22]. They obtained a fivefold drag force reduction (corresponding to a fivefold enhancement in the translational diffusion coefficient) when ξ and l are about equal to 10. On the other hand, the drag force is increased if the viscosity inside the domain is greater than that outside (i.e., for $\xi<1$).

The calculation has brought out the well-known fact that low viscosity enhances the diffusive flow whereas high viscosity retards it. The HS model did not include molecular orientation and was intended to account for a factor of 3 in the increase of D_t. However, the calculation shows that it needs a domain size about equal to 10 times the particle radius and a 10 times viscosity increase outside the domain to bring about a factor of 5 enhancement in D_t. Thus, it is unlikely that the HS model alone can account for a two to three orders of magnitude enhancement that has also been observed in several supercooled liquid systems.

In this paper, we show that another mechanism can also lead to the enhancement of D_t in an orientationally anisotropic fluid. The mechanism is the coupling of rotation and translational motion that one uses to account for the intensity distribution of the DRS spectrum in the supercooled liquid mentioned above. If the fluid is dynamically heterogeneous, the size of the diffusive particle may play an important role. For a probe size that is large enough to encompass several heterogeneous regions, the effect of coupling needs to be averaged over a range of heterogeneity. The averaging effect leads to a modification of the final enhancement factor; however, we show that, in addition to dynamical heterogeneity, the coupling to rotational degrees of freedom must be taken into account to properly account for the experimental result.

COUPLING OF TRANSLATION AND ROTATIONAL MOTIONS

The model that we consider here is a spherical particle undergoing translational diffusion in a viscoelastic fluid consisting of rotationally anisotropic molecules. Translational diffusion of a particle in a fluid is closely associated with the fluid's transverse linear momentum density, designated by $\vec{p}_T(\vec{q},t)$. Here $\vec{q}$ is the wave vector designating the propagation direction of the transverse momentum density. $\vec{p}_T(\vec{q},t)$ is the spatial Fourier transform of $\vec{p}_T(\vec{r},t)$. $\vec{p}_T(\vec{q},t)$ [or $\vec{p}_T(\vec{r},t)$] is a hydrodynamic variable. For rotational anisotropic molecules, such as *o*-terphenyl, $\vec{p}_T(\vec{q},t)$ is dynamically coupled to reorientation. The orientation variable involved in light scattering (and NMR) is a second-rank tensor designated as $\alpha_{jl}(\vec{q},t)$. For molecules of arbitrary shape, components of the orientational variable $\alpha_{jl}(\vec{q},t)$ are most conveniently given by rotation matrices. But it is not necessary to write them down explicitly in the present work. To decide on the component of $\alpha_{jl}(\vec{q},t)$ that is coupled to $\vec{p}_T(\vec{q},t)$, we take the direction of $\vec{q}$ to be along the z axis and consider specifically the transverse component of $\vec{p}_T(\vec{q},t)$ along the y axis; i.e.,

$$p_y(\vec{q},t)=\sum_j \pi_y^j \exp(i\vec{q}\cdot\vec{r}_j), \tag{1}$$

where π_y^j is the y component of the linear momentum of molecule j located at position $\vec{r}_j$. Both π_y^j and $\vec{r}_j$ are functions of time but this is not written out for brevity of notation. While rotation affects all component of $\alpha_{jl}(\vec{q},t)$, because of reflection and translation symmetry only $\alpha_{yz}(\vec{q},t)$ is coupled to $p_y(\vec{q},t)$. The equations that we shall need for the present work are the same set of generalized hydrodynamic equations previously derived for describing the DRS spectrum of a viscoelastic liquid [23]. In the small-wave-vector limit, these equations are [Eqs. (10) and (11) of Ref. [23]]

$$\frac{\partial\alpha_{yz}(\vec{q},t)}{\partial t}=-\int_0^t d\tau K_{11}(t-\tau)\alpha_{yz}(\vec{q},\tau) -iq\int_0^t d\tau K_{12}(t-\tau)p_y(\vec{q},\tau), \tag{2}$$

$$\frac{\partial p_y(\vec{q},t)}{\partial t}=iq\int_0^t d\tau K_{21}(t-\tau)\alpha_{yz}(\vec{q},\tau) -q^2\int_0^t d\tau K_{22}(t-\tau)p_y(\vec{q},\tau). \tag{3}$$

One can derive Eqs. (2) and (3) using the Zwanzig-Mori formalism [24] employing $p_y(\vec{q},t)$ and $\alpha_{yz}(\vec{q},t)$ as a *good set of variables*: random force terms are neglected in these equations. Here K_{ij} are memory function matrix elements, with K_{11} describing the correlation function associated with the rate of molecular reorientation, K_{22} describing the dynamic shear stress modulus, and K_{12} and K_{21} being associated with the coupling of translation to rotation. The explicit expressions for K_{ij} are given in Ref. [23] and will not be repeated here. If the various K_{ij} terms relax very rapidly compared with the dynamic variables $p_y(\vec{q},t)$ and $\alpha_{yz}(\vec{q},t)$, then one can invoke the Markov approximation to simplify Eqs. (2) and (3) to

$$\frac{\partial\alpha_{yz}(\vec{q},t)}{\partial t}=-\Gamma\alpha_{yz}(\vec{q},t)-iq\mu p_y(\vec{q},t), \tag{4}$$

$$\frac{\partial p_y(\vec{q},t)}{\partial t}=-\frac{q^2\eta_s}{\rho_m}p(\vec{q},t)+iq\mu'\alpha_{yz}(\vec{q},t), \tag{5}$$

where Γ is the orientational relaxation time and is equal to the integral of $K_{11}(t)$. ρ_m is the mass density of the fluid, and η_s is the shear viscosity and is proportional to the time integral of $K_{22}(t)$. μ and μ' are the rotation-translation coupling constants associated with the integrals of $K_{12}(t)$ and $K_{21}(t)$, respectively. Equations (4) and (5) are equivalent to the equations previously used by Anderson and Pecora for the calculation of the depolarized light scattering spectrum of a viscous molecular liquid [8,9]. We do not use the Markov approximation in this paper and hence the work presented here retains the viscoelastic effect of the fluid.

To proceed, we rewrite Eqs. (2) and (3) in vector form in the spatial coordinate system as

$$\frac{\partial\overleftrightarrow{\alpha}(\vec{r},t)}{\partial t} = -\int_0^t d\tau K_{11}(t-\tau)\overleftrightarrow{\alpha}(\vec{r},\tau) - \int_0^t d\tau K_{12}(t-\tau)\nabla\vec{p}_T(\vec{r},\tau), \tag{6}$$

$$\frac{\partial\vec{p}_T(\vec{r},t)}{\partial t} = \int_0^t d\tau K_{21}(t-\tau)\vec{\nabla}\cdot\overleftrightarrow{\alpha}(\vec{r},\tau) - \int_0^t d\tau K_{22}(t-\tau)\nabla^2\vec{p}_T(\vec{r},\tau). \tag{7}$$

From these equations we are interested in finding a solution for $\vec{p}_T(\vec{r},t)$ from which the frictional force that is exerted on the probe particle moving in the fluid is to be calculated. To accomplish this, we shall first combine Eqs. (6) and (7) to yield an equation for $\vec{p}_T(\vec{r},\omega)$. The combination of these two equations can be carried out in several steps. First, one converts the time variable t to frequency ω by taking Fourier transforms of both equations and simplifying the equations by the convolution theorem. One next takes the divergence of Eq. (6) and eliminates the orientational variable by solving for the orientational part and then substituting in Eq. (7) (in Fourier transformed form). The final result is a vector Helmhotz equation for $\vec{p}_T(\vec{r},\omega)$ given by

$$\nabla^2\vec{p}_T(\vec{r},\omega)+k(\omega)^2\vec{p}_T(\vec{r},\omega)=0 \tag{8}$$

where $k(\omega)$ is the complex propagation constant given by

$$k(\omega)=\pm\left(\frac{-i\omega}{G(\omega)/\rho_0-\zeta(\omega)/[i\omega+\Gamma(\omega)]}\right)^{1/2}$$

$$\text{with}\quad \zeta(\omega)=-\mu(\omega)\mu(\omega)'/\rho_0. \tag{9}$$

$\vec{p}_T(\vec{r},\omega)$ is the Fourier transform of $\vec{p}_T(\vec{r},t)$. $\Gamma(\omega)$, $\mu(\omega)$, and $\mu(\omega)'$ are the Fourier transforms of $k_{11}(t)$, $k_{12}(t)$, and $k_{21}(t)$, respectively. The dynamic shear viscosity $G(\omega)$ [the symbol $\eta(\omega)$ is often used in the literature] is proportional to the Fourier transform of $k_{22}(t)$. It has a real and an imaginary part. The real part is finite at all frequencies and is the shear viscosity η_s at $\omega=0$; whereas the imaginary part vanishes at $\omega=0$. $\vec{p}_T$ and $\overleftrightarrow{\alpha}$ have opposite time reversal symmetry; thus, the coupling moduli μ and μ' have opposite signs [9,25]. Hence, the quantity ζ defined above is a positive quantity, and it measures the strength of the RT coupling. The RT coupling has the effect of reducing the dynamic shear viscosity; furthermore, the propagation constant increases as Γ decreases or as the temperature of the fluid decreases. Therefore, the dynamics of $\vec{p}_T(\vec{r},\omega)$ at low temperature is significantly affected by reorientation and hence the RT coupling.

The solution to the vector Helmholtz equation can be expressed in terms of spherical Hankel functions as [26]

$$\vec{V}_T(\omega)=\nabla f(\vec{r},k)$$

$$\text{where}\quad f(\vec{r},k)=\sum_{n=0}^{\infty}A_n h_n(kr)P_n(\cos\theta), \tag{10}$$

where $\vec{p}_T=m\vec{V}_T$ and m is the mass of the particle. $h_n(kr)$ are spherical Hankel functions, and $P_n(\cos\theta)$ are Legendre polynomials. θ is the polar angle for the coordinate system with the z axis along the direction of the moving sphere; the azimuthal angle ϕ does not enter because $\vec{V}_T(\omega)$ is symmetrical about the z axis. Appropriate boundary conditions are needed to fix A_n. The boundary conditions have three parts. First, the fluid is at rest at infinity, and this involves choosing the sign of the propagation constant $k(\omega)$ such that velocity vanishes at an infinite distance from the sphere. Second, the normal component of the relative velocity of sphere and fluid vanishes on the surface of the sphere; i.e., $(\vec{V}-\vec{U})\cdot\hat{a}_R=0$, where $\hat{a}_R$ denotes a unit vector normal to the surface of the sphere. The third boundary condition is concerned with the degree of slip (or stick) on the surface. Zwanzig and Bixon considered a general case with an arbitrary degree of slip [2]; the stick boundary condition is, however, more appropriate for describing the motion of a sphere in the viscoelastic liquid. These three boundary conditions assure that only terms with $n=1$ in Eq. (10) contribute to the solution of Eq. (8).

After obtaining $\vec{V}_T$, one proceeds to the calculation of the force $\vec{F}(t)$ exerted on the spherical probe with radius R moving with a time dependent velocity $\vec{U}=U(t)\hat{z}$ in the fluid. The frequency dependent friction coefficient $\xi(\omega)$ is defined according to

$$\vec{F}(\omega)=-\xi(\omega)\vec{U}(\omega) \tag{11}$$

where $\vec{F}(\omega)$ and $\vec{U}(\omega)$ are the Fourier transforms of $\vec{F}(t)$ and $\vec{U}(t)$, respectively. The frequency dependent total force $\vec{F}(\omega)$ acting on the sphere is

$$\vec{F}(\omega)=\oint dS\,\overleftrightarrow{\sigma}(\omega)\cdot\hat{a}_R \tag{12}$$

where the integration is over the entire surface of the sphere; the stress tensor $\overleftrightarrow{\sigma}$ is given by

$$\overleftrightarrow{\sigma}(\omega)=[G(\omega)-\zeta(\omega)\rho_0/(i\omega+\Gamma)]\times[\nabla\vec{V}_T(\omega)+[\nabla\vec{V}_T(\omega)]^{+}] \tag{13}$$

where $(\nabla\vec{V}_T)^{+}$ is the transpose of $\nabla\vec{V}_T$. After carrying out considerable algebra needed for the evaluation of Eq. (13), we obtain a frequency dependent frictional coefficient as

$$\xi(\omega)=\frac{2\pi}{3}\rho_0[G(\omega)/\rho_0-\zeta(\omega)/(i\omega+\Gamma)]\times R(9-9X+X^2) \tag{14}$$

where $X=ik(\omega)R$. The dynamics of reorientation and relaxation of the shear modulus are expected to have significant effects on the frequency dependent frictional coefficient, and this topic is currently under investigation in our laboratory. For the present study, we consider translation diffusion.

The translational diffusion coefficient D_t is related to the zero-frequency friction coefficient $\xi(\omega=0)$ by the Einstein equation

$$D_t=\frac{k_BT}{\xi(\omega=0)}=\frac{D_{\mathrm{SE}}}{[1-\xi\rho_0/(\eta_s\Gamma)]}. \tag{15}$$

Here D_{SE} is the Stokes-Einstein expression for the translational diffusion coefficient given above. ξ is the value of $\xi(\omega)$ at $\omega=0$. The quantity $\xi\rho_0/(\eta_s\Gamma)$ is a positive number, and one notes immediately that D_t is enhanced over the value given by the simple SE equation. From the Schwartz inequality, it can be shown that $\xi\rho_0/(\eta_s\Gamma)$ does not exceed 1 [23]; hence, D_t is always positive.

EFFECT OF DYNAMIC HETEROGENEITY

Equation (15) is the result for a dynamically homogeneous fluid. Computer simulation of supercooled fluids has shown that regions of high and low mobility are distributed in the fluid. The molecular dynamics in these dynamically heterogeneous regions varies considerably. The heterogeneous dynamics scenario corresponds to a randomly distributed heterogeneity so that the RT coupling parameter ξ in mobile regions is high but is low in immobile regions. Thus, if the fluid is dynamically heterogeneous, and the size of the diffusive particle is large so as to encompass several regions of variable mobility, one expects the retardation effect in the low mobility region to cancel the enhancement effect in the high mobility region. Thus in this case, one needs to average the result obtained from the dynamically homogenous fluid calculation over a range of heterogeneity. Overall, the diffusive particle experiences an average RT coupling parameter $\langle\xi\rangle$ which may be considerably different from that of a dynamically homogeneous fluid. Thus, to compare with the diffusion data of a supercooled liquid, one needs the average D_t given in Eq. (15) for a homogeneous fluid over a distribution $f(\xi)$ to account for the dynamic heterogeneity; namely,

$$\overline{D_t}=\int_0^\infty d\xi\,\frac{D_{\mathrm{SE}}}{[1-\xi\rho_0/(\Gamma\eta_s)]}f(\xi). \tag{16}$$

In the above equation, the upper limit of the integral must have a cutoff so as not to have a ξ value that exceeds the physically allowed coupling parameter. The cutoff determines the allowable functional form of the distribution function. Although the information about the distribution function is unavailable at present, we consider two important distributions: (1) an exponential distribution given by $f(\omega)=\exp(-\xi/\langle\xi\rangle)/\langle\xi\rangle$ and 2) a Gaussian distribution given by $f(\omega)=[2/(\pi\langle\xi\rangle^2]^{1/2}\exp(-\xi^2/2\langle\xi\rangle^2)$. If the exponential distribution is assumed, then the evaluation of Eq. (16) gives

$$\overline{D_t}=\frac{D_{\mathrm{SE}}}{[1-\langle\xi\rangle\rho_0/(\eta_s\Gamma)]}. \tag{17}$$

In this case the final result is similar to the homogeneous fluid case [Eq. (15)], except that one replaces ξ by $\langle\xi\rangle$.

The evaluation of Eq. (16) using the Gaussian distribution yields

$$\overline{D_t}=\frac{D_{\mathrm{SE}}}{[1-[\langle\xi\rangle\rho_0/(\eta_s\Gamma)]^2]^{1/2}}. \tag{18}$$

In both cases the translational diffusion coefficient in the heterogeneous fluid is enhanced over the SE value, provided that $\langle\xi\rangle$ is finite.

Finally, it should be remarked that the RT coupling does not affect rotational diffusion. This can be shown by calculating the torque experienced by the particle in its motion. One contribution to the torque is due to the stress tensor associated with the translational motion, and the second is the stress tensor arising from the RT coupling. The contribution due to the RT coupling is through the $\vec{\nabla}\cdot\overleftrightarrow{\alpha}$ term [cf. Eq. (7)]. The torque due to this term vanishes when it is summed over the surface of the sphere.

RESULTS AND DISCUSSION

One notes that the system with the exponentially distributed heterogeneous dynamics yields essentially the same functional form as the homogeneous dynamic system, and one can interpret the result in the same way. The Gaussian distributed heterogeneity yields a slightly different result, but the effect of the RT coupling on the enhancement is clearly evident. For the remainder of this paper, we shall consider only the exponential distribution; the case of the Gaussian distribution can be similarly made.

We use the experimental results for OTP to compare with the predicted D_t value. Liquid OTP is a fragile liquid that can be readily supercooled. Liquid OTP has been extensively studied with several experimental techniques. The glass transition temperature ($T_g=243$ K) is only 86 K lower than the melting temperature ($T_m=329$ K). Translational and rotational motions of different probes in OTP and neat OTP have been studied using NMR, depolarized Rayleigh scattering

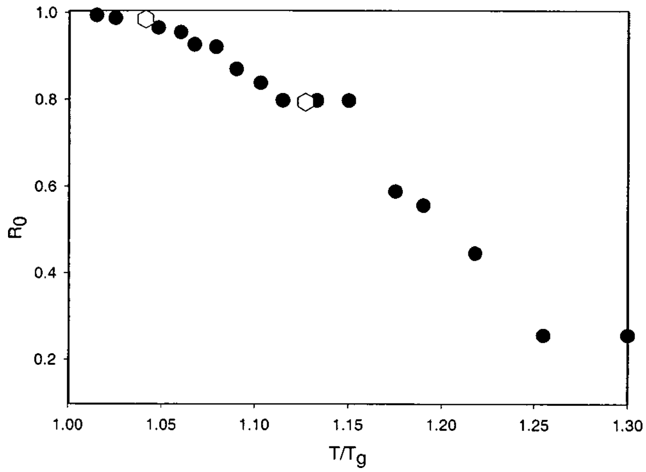

FIG. 1. R_0 $[=\zeta\rho_0/(\eta_s\Gamma)]$, extracted from the translational diffusion data (solid circles) in OTP is plotted versus temperature. The translational diffusion data were obtained from Ref. [14]. R_0 data derived from DRS (Ref. [27]) are presented as hexagons.

[11], and forced Rayleigh scattering [13,15]. Enhancement of D_t over the SE value for probes in OTP and also in neat OTP (self-diffusion) was observed. Cicerone and Ediger have also measured the translational and rotational diffusion coefficients of several probes in OTP using a photobleaching technique [14]. They confirmed the applicability of the DSE equation for rotational diffusion of all probes with various sizes in the temperature range over which OTP viscosity changes by 12 orders of magnitude. On the other hand, over the same temperature (viscosity) range, the measured translational diffusion coefficients for probes with size similar to OTP show a significant enhancement over the SE values.

Cicerone and Ediger introduced a quantity $(D_t\tau_r)/(D_t\tau_r)_{\mathrm{SE,DSE}}$, and plotted it verse T/T_g to compare the rotational and translational coefficients of different probes in different host supercooled liquids [14]. Here $\tau_r = D_r^{-1}$ and $(D_t\tau_r)_{\mathrm{SE,DSE}}$ indicates the value predicted by the SE and DSE equations. In accordance with Eq. (17), $(D_t\tau_r)/(D_t\tau_r)_{\mathrm{SE,DSE}}$ is the enhancement factor, equal either to $(1-\zeta\rho_0/\eta_s\Gamma)^{-1}$ or to $(1-\langle\zeta\rangle\rho_0/\eta_s\Gamma)^{-1}$, depending on whether OTP is considered to be a dynamically homogeneous or a dynamically heterogeneous liquid. Using high temperature D_t and D_r data for tetracene in OTP provided in Ref. [14], we have found R for tetracene to be equal to 0.27 nm. This value is similar to the hydrodynamic radius of OTP ($R=0.23$ nm) obtained by Sillescu and co-workers [13]; thus indicating that tetracene in OTP has about the same size as OTP. If we consider OTP to be dynamically heterogeneous with an exponential distribution, we can equate $(D_t\tau_r)/(D_t\tau_r)_{\mathrm{SE,DSE}}$ to $(1-\langle\zeta\rangle\rho_0/\eta_s\Gamma)^{-1}$. Using the diffusion data for tetracene in OTP given in Ref. [14], we have calculated the value of $\langle\zeta\rangle\rho_0/(\eta_s\Gamma)$ at different temperatures and show its temperature dependence (in terms of T/T_g) in Fig. 1. The data indicate that, as T is lowered toward T_g, the value of $\langle\zeta\rangle\rho_0/(\eta_s\Gamma)$ rapidly increases, approaching 1 in the vicinity of T_g.

This result is consistent with the shear wave data obtained by DRS. The DRS spectrum of OTP detected with a Fabry-Pérot interferometer has been determined by Wang *et al.* at various scattering angles in the temperature range of 253–388 K, covering the supercooled and viscous liquid regimes [27]. At high temperature (388 K), the spectrum has a broad Lorentzian line shape, with a shallow central dip. The width of the DRS spectrum narrows dramatically as the temperature is lowered and at 313 K the central dip disappears and a doublet shifted from the excitation laser frequency appears at lower temperatures. The spectral features, including the central dip at high temperature and the shifted doublet at lower temperature, have been analyzed using Eqs. (1) and (2), from which a RT coupling parameter $\Re(=\delta/\omega_s)$ is introduced [25]. Here $\delta=q^2\zeta(\omega)$ and $\omega_s=q^2\Gamma\eta(\omega)/\rho_0$, and hence $\Re(\omega)=\zeta(\omega)\rho_0/[\Gamma\eta(\omega)]$. One notes that the magnitude of the scattering vector q drops out from the $\Re$ expression. At $\omega=0$, we obtain $\Re(\omega=0)\equiv\Re_0=\zeta\rho_0/(\Gamma\eta_s)$. This quantity, originally introduced by Andersen and Pecora [8], is exactly equal to the coupling parameter introduced in Eq. (15). For dynamically inhomogeneous fluids, one replaces the quantity ζ with $\langle\zeta\rangle$.

The RT coupling parameter $\Re$ in general depends on frequency; however, from experiment one does not find a strong frequency dependence in $\Re$ [28]. Thus, we can estimate the $\Re_0$ value using the shear wave data of Ref. [27]. Extrapolating the results to zero scattering angle, we obtain an $\Re_0$ value equal to 0.793 at 274 K and 0.984 at 253 K. Unfortunately the $\Re$ values at other temperatures are not given in Ref. [27] and we are unable to make comparison at other temperatures. However, at these two temperatures, the $\Re_0$ data are in good agreement with the result of Cicerone and Ediger, as shown in Fig. 1 (inverted hexagons).

In summary, although an attempt has been made to relate dynamic heterogeneity in a supercooled liquid to enhancement of the translational diffusion coefficient, a calculation that does not include molecular orientation fails to account for the 2–4 orders of magnitude enhancement observed in orientationally anisotropic liquids. We have shown that the rotation-translation coupling mechanism that is responsible for the appearance of the shear wave doublet in the supercooled molecular liquid also leads to a translational diffusion coefficient enhancement. For a dynamically heterogeneous fluid, the probe size may play an important role. We have shown that, if the diffusion probe is large enough to encompass several regions of high and low mobility, the RT coupling parameter needs to be modified to reflect the averaging effect. We have shown that, while the averaging effect arising from dynamic heterogeneity may alter the final enhancement, the coupling to rotational degrees of freedom must be taken into account to properly account for the experimental result.

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