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An interpretation of the bifurcation of orientational relaxation processes in a supercooled liquid

Biman Bagchi and Amalendu Chandra

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012 India

Stuart A. Rice

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

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The orientational relaxation of molecules in a supercooled liquid is known to exhibit interesting dynamical behavior. As the temperature of the liquid is lowered towards its glass transition temperature, there is a bifurcation of the relaxation dynamics into primary (α) and secondary (β) processes; the former is associated with the collective motion responsible for the glass transition, while the latter is associated with single particle motion. In this paper we present a theory of orientational relaxation in a supercooled liquid. This theory provides both qualitative and quantitative descriptions of the ($\alpha\beta$) bifurcation phenomenon at a molecular level. The theory exploits the properties of a time dependent free energy functional which explicitly includes the effects of the collective motions in the liquid on the orientational motion of a solute (or a tagged) molecule. In the overdamped limit, this analysis leads to two coupled Smoluchowski equations for the orientation distribution function. These equations, when solved, reveal the essential features of the ($\alpha\beta$) bifurcation phenomenon. Explicit calculations are presented for orientational relaxation in a liquid of dipolar hard spheres, a liquid of nonpolar ellipsoids, and an orientationally disordered solid. Our calculations demonstrate the ubiquity of the ($\alpha\beta$) bifurcation phenomenon and they reveal many of its aspects. The relevance of the present work to current theories of glass transition is discussed briefly.

I. INTRODUCTION

Despite decades of study, the molecular dynamics underlying the mechanism of glass formation remains poorly understood.¹ Although it is clear that whether or not a glass is formed is determined by kinetic processes, there is not yet consensus as to whether the glass transition is to be interpreted as a purely kinetic phenomenon or if there is an associated underlying structural transition which would occur at non-zero temperature if the system could be cooled infinitely slowly in a fashion that bypasses crystallization. From a qualitative point of view, the key observations motivating these very different interpretations are the following.

In support of the kinetic process interpretation, it is found that in all systems the approach to the glass transition through the supercooled liquid is characterized by rapid increases, as the temperature is decreased, of the relaxation times associated with different kinds of molecular motions; at the glass transition temperature some relaxation times, e.g., for the viscosity, "diverge." Moreover, the temperature at which the glass transition occurs, and some of the properties of the glass, e.g., the density, depend on the rate of cooling. In this interpretation, a system does not have a unique glassy state but, rather, a range of nonequilibrium states in which the structure is arrested in configurations intermediate between the structures of the liquid and solid states.

In support of the associated underlying structural transition interpretation, it is found that the glass transition is characterized by rounded discontinuities in the several thermodynamic susceptibilities of the system, analogous to those predicted for second order transitions in the Ehrenfest clas-

sification. Moreover, some, but not all, of the conventional thermodynamic relationships between the changes in susceptibilities, temperature, etc., at the transition are found to hold. Although the observed glass transition temperature and the bulk properties of the glass are functions of the cooling rate, it is assumed that well defined limits for each exist as the rate of cooling approaches zero. In this interpretation there is an implicit separation of time scales assumption. It is acknowledged that the crystalline state is the one that is globally stable for the given external constraints of temperature and pressure, but that the existence of the crystalline state is irrelevant to the glass transition because the system can be trapped for a very long time in a restricted region of phase space which has multiple relative minima in the local free energy surface, each minimum corresponding to a dense but disordered atomic configuration. In the restricted region of phase space the multiple minima in the free energy surface imply the existence of a configurational entropy which renders the globally stable crystalline state locally unstable with respect to the range of states which characterize the glass.²

The most recent kinetic descriptions of the glass transition are based on mode coupling models.^{1d,3-7} In these models the Fourier components of the fluctuating density satisfy the equation of motion of a nonlinear damped oscillator with memory; the nonlinear memory term represents the influence of structural rearrangement in the liquid on the amplitudes of the Fourier components of the density beyond that characterized by linear damping. It is shown that the viscosity of the fluid can diverge due to its coupling to long-lived, small wave vector density fluctuations whose rate of decay is

dominated by coupling of modes with wave vector near the first peak in the static structure factor; the divergence is accompanied by a sharp transition to a state with arrested density fluctuations. This transition in the system dynamics resembles the underlying structural transition, referred to above, in that it can only be reached asymptotically as the rate of cooling approaches zero.

The most recent ideal structural transition descriptions of the ideal glass transition imply that it has random first order character.² In this picture the supercooled liquid is composed of “glassy clusters,” which are continually created and destroyed; the clusters are identified with spatially separated sets of configurations in the restricted system phase space. These configurations are internally connected in the sense that there are easy transitions between them, hence there is an associated configurational entropy. As the temperature is decreased the size of a cluster grows and, eventually, diverges at the ideal glass transition temperature. The definition of the cluster states implies that the configuration space of the system is sampled only over a limited time domain, and thereby introduces the above referred-to separation of time scales into the analysis. Moreover, transitions between the group of configurations that define a metastable cluster have a characteristic relaxation time which determines, say, the viscosity of the supercooled liquid. Kirkpatrick, Thirumalai, and Wolynes² find that relaxation in the supercooled liquid state associated with such transitions follows the Vogel–Fulcher form,⁸ while the long time dynamics of the system is controlled by the creation and destruction of the clusters, and this latter relaxation process is activated.

The theories of the glass transition briefly sketched above focus attention on the translational degrees of freedom of the system and give no specific information about relaxation of other degrees of freedom of the constituent molecules. It has been known for a long time that local molecular rearrangements, associated with internal degrees of freedom of the molecules in the system, still occur in the glass.¹ For example, the rotational relaxation of a solute molecule in a glass forming host is observed to have the following features in a vast variety of systems⁹: Above some temperature T^* , which is itself above the glass transition temperature T_g , there is apparently a single (β) relaxation process, whereas between T^* and T_g there are apparently two (β and α) relaxation processes, where the word “apparently” means that the interpretation cited is the simplest available and does not, for example, account for the possible existence of different distributions of relaxation times corresponding to these two processes. The spectra of the coexisting β and α relaxation processes have comparable integrated intensities over the range of temperature for which observations exist, which suggests that they are independent and sequential rather than competitive and parallel. As suggested by the notation, the faster of the two relaxation processes active below T^* , namely the β process, appears to be a continuation of the process active above T^* ; the activation energy for this process is sensibly independent of temperature, with the same value above and below the glass transition temperature. The slower of the two relaxation processes active below T^* , namely the α process, has a relaxation time proportional to

the viscosity. This relaxation time, like the viscosity, “diverges” at the glass transition temperature. In the region between T^* and the glass transition temperature, the apparent activation energy for the viscosity is strongly temperature dependent. Kivelson and Kivelson¹⁰ argue that both below T_g and above T^* only the β process is active because below the glass transition the α process is frozen out and above T^* the β process dominates the molecular dynamics. They assign the β process to rapid rotational relaxation (angular diffusion) within a long-lived torsional potential well, and the α process to restructuring of the torsional potential well.

We consider the development of an understanding, at the molecular level, of the continuity and bifurcation of the relaxation rate as the temperature of the supercooled liquid passes through T^* towards T_g to be a key step in improving our understanding of the glass transition. This paper describes a theory of the orientational relaxation of a solute molecule in a dense host supercooled liquid. Our approach, which is based on an application of density functional theory, leads to a kinetic equation for the orientational distribution function of a solute molecule in a supercooled liquid. This kinetic equation explicitly exhibits the coupling of the orientational motion of the solute to translational motions of the host liquid molecules and to density fluctuations in the host liquid. Using the known temperature dependences of the viscosity and the translational and rotational diffusion coefficients near T_g , qualitative arguments suggest that the solution of the kinetic equation displays the characteristic branching of relaxation times for $T^* < T < T_g$ mentioned above. Numerical solution of the kinetic equation provides quantitative verification of the predicted bifurcation of the orientational relaxation of a solute molecule in a host supercooled liquid.

The preceding analysis can be applied to orientational relaxation in a pure liquid, in which case we follow the motion of a nominally tagged molecule and approximate the time dependence of the dipolar correlation function by the time dependence of the single particle orientational correlation function. This approximation is satisfactory if the influence of collective motions in the liquid on single particle orientational relaxation is accounted for.

The formalism we have developed to analyze orientational relaxation in a supercooled liquid can also be used to describe orientational relaxation in a disordered solid; the latter subject is discussed briefly in Sec. VI.

II. THE KINETIC EQUATION

Let $\rho_B(\omega, t)$ be the orientation distribution function of a solute molecule of species B in a liquid of species A, and $\rho_A(\mathbf{r}, \omega, t)$ be the joint position-orientation distribution function of the host liquid molecules. In all that follows we shall assume that the host remains liquid at all temperatures of interest. Indeed, we shall be particularly interested in the low temperature behavior of the system, in which region it is assumed that the host liquid is in a metastable supercooled state. To obtain the equation of motion of $\rho_B(\omega, t)$ we start with the equation of continuity,

$$\frac{\partial \rho_B(\omega, t)}{\partial t} = -\nabla_\omega \cdot g_B(\omega, t), \quad (2.1)$$

where $g_B(\omega, t)$ denotes the angular momentum flux. We assume that the rate of relaxation of the angular momentum is sufficiently great that $g_B(\omega, t)$ is determined by the instantaneous effective force acting on the molecule. Then the angular momentum flux is given by

$$g_B(\omega, t) = -D_R^B \cdot \rho_B(\omega, t) \times \nabla_\omega \left\{ \beta \frac{\delta F[\rho_B(\omega, t), \rho_A(\mathbf{r}, \omega, t)]}{\delta \rho_B(\omega, t)} \right\}, \quad (2.2)$$

where D_R^B is the "bare" rotational diffusion tensor of the solute molecule, which describes the orientational motion of the solute molecule in the force field of stationary solvent molecules. As usual, $\beta \equiv (k_B T)^{-1}$. The free energy functional can now be expressed in terms of the solute–host and host–host direct correlation functions of the system¹¹:

$$\begin{aligned} \beta F[\rho_B(\omega, t), \rho_A(\mathbf{r}, \omega, t)] &= \int d\omega \rho_B(\omega, t) [\ln \rho_B(\omega, t) - 1] + \int d\omega d\mathbf{r} \rho_A(\mathbf{r}, \omega, t) [\ln \rho_A(\mathbf{r}, \omega, t) - 1] \\ &\quad - \frac{1}{2} \int d\omega d\mathbf{r} d\omega' d\mathbf{r}' C_{AA}(\mathbf{r} - \mathbf{r}', \omega, \omega') \delta \rho_A(\mathbf{r}, \omega) \delta \rho_A(\mathbf{r}', \omega') \\ &\quad - \frac{1}{2} \int d\omega d\mathbf{r} d\omega' C_{AB}(\mathbf{r}, \omega, \omega') \delta \rho_A(\mathbf{r}, \omega) \delta \rho_B(\omega') \end{aligned} \quad (2.3)$$

with

$$\begin{aligned} \delta \rho_A &= \rho_A(\mathbf{r}, \omega, t) - \frac{\rho_A^0}{4\pi}, \\ \delta \rho_B &= \rho_B(\omega, t) - \frac{1}{4\pi}, \end{aligned} \quad (2.4)$$

where ρ_A^0 is the number density of the host liquid, $C_{AA}(\mathbf{r} - \mathbf{r}', \omega, \omega')$ is the host liquid two particle direct correlation function and, taking the origin of the coordinate system at the center of a solute molecule, $C_{AB}(\mathbf{r}, \omega, \omega')$ is the solute–host two particle direct correlation function. Substitution of Eqs. (2.2) and (2.3) in Eq. (2.1) leads to the equation of motion of the solute orientational density distribution^{12,13}:

$$\begin{aligned} \frac{\partial \rho_B(\omega, t)}{\partial t} &= \nabla_\omega \cdot D_R^B \cdot \nabla_\omega \rho_B(\omega, t) - \nabla_\omega \cdot D_R^B \\ &\quad \cdot \left[\rho_B(\omega, t) \nabla_\omega \int d\omega' d\mathbf{r}' C_{AB}(\mathbf{r}', \omega, \omega') \delta \rho_A(\mathbf{r}', \omega') \right]. \end{aligned} \quad (2.5)$$

Equation (2.5) includes the coupling of the solvent reorientation to the solvent density fluctuations. The second term in Eq. (2.5) describes the collective component of the orienta-

tional relaxation dynamics. As the glass transition is approached from the supercooled liquid side, the density fluctuations in the host liquid are damped, which leads to a slowdown in the rate of orientational relaxation of the solute molecule.

For simplicity, in this section and in Sec. III we shall assume that the solute molecule can be represented as a dipolar sphere. We now rewrite the second term on the right-hand side of Eq. (2.5) in Fourier space (with \mathbf{k} the wave vector conjugate to \mathbf{r}). The result is

$$\begin{aligned} \frac{\partial \rho_B(\omega, t)}{\partial t} &= D_R^B \nabla_\omega^2 \rho_B(\omega, t) - \frac{D_R^B}{(2\pi)^3} \nabla_\omega \\ &\quad \cdot \left[\rho_B(\omega, t) \nabla_\omega \int d\mathbf{k} d\omega' C_{AB}(\mathbf{k}, \omega, \omega') \delta \rho_A(\mathbf{k}, \omega', t) \right]. \end{aligned} \quad (2.6)$$

Of course, neither Eq. (2.5) or Eq. (2.6) are complete without specification of $\delta \rho_A$. The same method as used to derive Eq. (2.5), with inclusion of the translational motion of the solvent molecule, leads to

$$\begin{aligned} \frac{\partial}{\partial t} \delta \rho_A(\mathbf{k}, \omega, t) &= D_R^A \nabla_\omega^2 \delta \rho_A(\mathbf{k}, \omega, t) - D_T^A k^2 \delta \rho_A(\mathbf{k}, \omega, t) \\ &\quad - D_R^A \nabla_\omega \int d\mathbf{k}' \rho_A(\mathbf{k} - \mathbf{k}', \omega, t) \cdot \nabla_\omega \int d\omega' C_{AA}(\mathbf{k}', \omega, \omega') \delta \rho_A(\mathbf{k}', \omega', t) \\ &\quad - D_R^A \nabla_\omega \rho_A(\mathbf{k}, \omega, t) \cdot \nabla_\omega \int d\omega' C_{AB}(\mathbf{k} = 0, \omega, \omega') \delta \rho_B(\omega', t) \\ &\quad + D_T^A \int d\mathbf{k}' \rho_A(\mathbf{k} - \mathbf{k}', \omega, t) \mathbf{k} \cdot \mathbf{k}' \int d\omega' C_{AA}(\mathbf{k}', \omega, \omega') \delta \rho_A(\mathbf{k}', \omega', t) \\ &\quad + D_T^A k^2 \rho_A(\mathbf{k}, \omega, t) \int d\omega' C_{AB}(\mathbf{k} = 0, \omega, \omega') \delta \rho_B(\omega', t), \end{aligned} \quad (2.7)$$

where, for simplicity, we have assumed that the translational and rotational motions of the host liquid molecules are completely characterized by the isotropic diffusion coefficients D_T^A and D_R^A , which are functions of the viscosity. As the glass transition is approached from the supercooled liquid side these diffusion coefficients decrease in magnitude and, because of the coupling of translational and rotational motions, said decreases affect the rate of rotational relaxation of the solute molecules.

III. THE ROTATIONAL CORRELATION FUNCTION

The first step in obtaining the solution to Eq. (2.6) is to expand the densities $\delta\rho_B$ and $\delta\rho_A$, and the direct correlation functions C_{AA} and C_{AB} , in spherical harmonics¹⁴:

$$\delta\rho_B(\omega, t) = \sum_{lm} B_{lm}(t) Y_{lm}(\omega), \quad (3.1)$$

$$\delta\rho_A(\mathbf{k}, \omega, t) = \sum_{lm} A_{lm}(\mathbf{k}, t) Y_{lm}(\omega), \quad (3.2)$$

$$C_{AB}(\mathbf{k}, \omega, \omega') = \sum_{l_1 l_2 m_1} C_{AB}(l_1 l_2 m_1; \mathbf{k}) \times Y_{l_1 m_1}(\omega) Y_{-l_2, -m_1}(\omega'), \quad (3.3)$$

$$C_{AA}(\mathbf{k}, \omega, \omega') = \sum_{l_1 l_2 m_1} C_{AA}(l_1 l_2 m_1; \mathbf{k}) \times Y_{l_1 m_1}(\omega) Y_{-l_2, -m_1}(\omega'). \quad (3.4)$$

We shall also have use for the correlation functions

$$\phi_{lm}^A(\mathbf{k}, t) = \langle A_{lm}(\mathbf{k}, 0) A_{lm}(-\mathbf{k}, t) \rangle, \quad (3.5)$$

$$\phi_{lm}^B(t) = \langle B_{lm}(0) B_{lm}(t) \rangle. \quad (3.6)$$

Substitution of Eqs. (3.1)–(3.4) into Eq. (2.6) and linearization with respect to the density fluctuations leads to the following equation of motion for the coefficients $B_{lm}(t)$:

$$\begin{aligned} \frac{\partial B_{lm}(t)}{\partial t} = & -l(l+1)D_R^B B_{lm}(t) \\ & + \frac{(-)^m}{(2\pi)^4} D_R^B l(l+1) \int d\mathbf{k} \\ & \times \sum_{l_2 m_2} C_{AB}(l l_2 m; \mathbf{k}) A_{l_2 m}(\mathbf{k}, t). \end{aligned} \quad (3.7)$$

The corresponding equation of motion for the correlation function (3.6) is

$$\begin{aligned} \frac{\partial \phi_{lm}^B(t)}{\partial t} = & -l(l+1)D_R^B \phi_{lm}^B(t) + \frac{(-)^m}{(2\pi)^4} D_R^B \\ & \times \int d\mathbf{k} C_{AB}(l l_2 m; \mathbf{k}) \phi_{l_2 m}^{AB}(\mathbf{k}, t), \end{aligned} \quad (3.8)$$

where

$$\phi_{lm}^{AB}(\mathbf{k}, t) = \langle B_{lm}(0) A_{lm}(\mathbf{k}, t) \rangle \quad (3.9)$$

and we have assumed that

$$\langle B_{l_1 m_1}(0) A_{l_2 m_2}(\mathbf{k}, t) \rangle = \phi_{l_1 m_1}^{AB}(\mathbf{k}, t) \delta_{l_1 l_2} \delta_{m_1 m_2}. \quad (3.10)$$

To obtain the equation of motion of the solute–host molecule direct correlation function we linearize Eq. (2.7) with respect to the density fluctuation $\delta\rho_A$. Equation (2.7) then simplifies to

$$\begin{aligned} \frac{\partial}{\partial t} \delta\rho_A(\mathbf{k}, \omega, t) = & D_R^A \nabla_\omega^2 \delta\rho_A(\mathbf{k}, \omega, t) - D_T^A k^2 \delta\rho_A(\mathbf{k}, \omega, t) - D_R^A \nabla_\omega^2 \frac{\rho_A^0}{4\pi} \int d\omega' C_{AA}(\mathbf{k}, \omega, \omega') \delta\rho_A(\mathbf{k}, \omega', t) \\ & + D_T^A k^2 \frac{\rho_A^0}{4\pi} \int d\omega' C_{AA}(\mathbf{k}, \omega, \omega') \delta\rho_A(\mathbf{k}, \omega', t) \\ & - D_R^A \nabla_\omega^2 \frac{\rho_A^0}{4\pi} \int d\omega' C_{AB}(\mathbf{k} = 0, \omega, \omega') \delta\rho_B(\omega', t) (2\pi)^3 \delta(\mathbf{k}) \\ & + D_T^A k^2 \frac{\rho_A^0}{4\pi} \int d\omega' C_{AB}(\mathbf{k} = 0, \omega, \omega') \delta\rho_B(\omega', t) (2\pi)^3 \delta(\mathbf{k}). \end{aligned} \quad (3.11)$$

Equation (3.11) has an interesting structure in that it shows, to terms linear in the density fluctuations, that only the $\mathbf{k} = 0$ mode of the solvent molecule relaxation spectrum is influenced by the coupling to the solute molecule. In contrast, recent computer simulations by Zhu and Robinson¹⁵ imply that both translational and rotational relaxation of the nonpolar solvent molecules in the first shell surrounding a solute molecule are faster than in the bulk liquid. If Eq. (3.11) is accepted, such behavior arises from a nonlinear dependence of the relaxation on the density fluctuations.

If we neglect the influence of the solute molecule on the relaxation dynamics of the host liquid molecules Eq. (3.11) can be solved to yield

$$\phi_{lm}^{AB}(\mathbf{k}, t) = \phi_{lm}^{AB}(\mathbf{k}, t=0) e^{-t/\tau_{lm}(\mathbf{k})}. \quad (3.12)$$

$\phi_{lm}^{AB}(\mathbf{k}, t=0)$ is determined by the solute–solvent equilibri-

um correlation function, which is given by

$$\phi_{lm}^{AB}(\mathbf{k}, t=0) = \frac{(-)^m}{(4\pi)^2} h^{AB}(l l_2 m; \mathbf{k}), \quad (3.13)$$

with $h(l l_2 m; \mathbf{k})$ the coefficients in the expansion in spherical harmonics of the host liquid total pair correlation function, i.e.,

$$\begin{aligned} h^{AB}(\mathbf{k}, \omega, \omega') = & \sum_{l_1 l_2 m} h^{AB}(l_1 l_2 m; \mathbf{k}) \\ & \times Y_{l_1 m}(\omega) Y_{-l_2, -m}(\omega'). \end{aligned} \quad (3.14)$$

The relaxation times corresponding to the various spherical harmonics, $\tau_{lm}(\mathbf{k})$, are given by

$$\begin{aligned} \tau_{lm}^{-1}(\mathbf{k}) = & [l(l+1)D_R^A + k^2 D_T^A] \\ & \times \left[1 - \frac{\rho_A^0}{4\pi} (-)^m C(l l_2 m; \mathbf{k}) \right]. \end{aligned} \quad (3.15)$$

Within this model of the relaxation dynamics, every term in Eq. (3.8) is now determined. Equation (3.8), with Eq. (3.15), has the solution

$$\begin{aligned} \phi_{lm}^B(t) = & \phi_{lm}^B(0)e^{-l(l+1)D_R^B t} + \frac{(-)^m}{2(2\pi)^4} \\ & \times \int d\mathbf{k} \frac{C_{AB}(llm;\mathbf{k})\phi_{lm}^{AB}(\mathbf{k},0)e^{-t/\tau_{lm}(\mathbf{k})}}{1 - [l(l+1)D_R^B \tau_{lm}(\mathbf{k})]^{-1}} \\ & - \frac{(-)^m}{2(2\pi)^4} \\ & \times \int d\mathbf{k} \frac{C_{AB}(llm;\mathbf{k})\phi_{lm}^{AB}(\mathbf{k},0)e^{-l(l+1)D_R^B t}}{1 - [l(l+1)D_R^B \tau_{lm}(\mathbf{k})]^{-1}}, \quad (3.16) \end{aligned}$$

where $\phi_{lm}^B(t=0) = (4\pi)^{-1}$, and $\tau_{lm}(\mathbf{k})$ and $\phi_{lm}^{AB}(\mathbf{k},t=0)$ are given by Eqs. (3.15) and (3.16), respectively.

Equation (3.16), which is the principal result of our analysis, implies that the orientational relaxation of a solute molecule in a dense liquid is, in general, nonexponential; in addition to the obvious orientational diffusion of the solute molecule there is a contribution to the dynamical behavior arising from the density fluctuations of the host liquid. We note that in the limit that the host liquid relaxation is very fast, the solute and host molecule relaxation times are not very different and the overall rotational relaxation rate will vary as $l(l+1)D_R^B$. In the other limit, when the host liquid relaxation is very slow, although all the relaxation times $\tau_{lm}(\mathbf{k})$ are large the solute bare rotational diffusion coefficient need not be small, since the short ranged interactions that dominate the motion of the solute in the frozen field of the solvent are not very different in the normal liquid and the supercooled liquid states. Accepting this picture, in this limit the correlation function $\phi_{lm}^B(t)$ will decay as $\exp[-l(l+1)D_R^B t]$. In the intermediate regime, where the $\tau_{lm}(\mathbf{k})$ are quite different from $[l(l+1)D_R^B]^{-1}$, the two classes of relaxation times will generate two peaks in the dielectric dispersion spectrum. To generate a correspondence with the observed behavior described in Sec. I we identify the terms decaying with rates $l(l+1)D_R^B$ as those responsible for the β relaxation and the terms controlled by the solvent relaxation rates $\tau_{lm}^{-1}(\mathbf{k})$ as those responsible for the α relaxation. And, as noted by Kivelson and Kivelson, the short ranged part of D_R^B has the $l(l+1)$ dependence expected for diffusional motion, whereas the host liquid controlled relaxation has a more complicated dependence on l because the $\phi_{lm}^B(t)$ depend on l in a nontrivial way. In terms of the observed spectrum, the β relaxation process is diffusional whereas the α relaxation process involves collective motions of the host liquid molecules.

IV. QUALITATIVE ASPECTS OF RELAXATION IN THE SUPERCOOLED LIQUID

Our representation for the rotational autocorrelation function of a spherical solute in a host liquid, Eq. (3.16), clearly displays the dependence of the rate of rotational relaxation on the dynamical properties of the host liquid [the terms $\tau_{lm}(\mathbf{k})$] and on the thermodynamic state of the sol-

ute–host system (the terms $C_{AB}(llm;\mathbf{k})$ and $C_{AA}(llm;\mathbf{k})$). We now examine the qualitative behavior of the rate of orientational relaxation predicted by Eq. (3.16) for the region of state space where the solute–host liquid mixture is supercooled.

The relaxation rate predicted by Eq. (3.16) depends on the various D 's. Our discussion of the temperature dependence of these is guided by use of the Stokes–Einstein relation which, when extrapolated to the molecular domain, predicts that the product of the viscosity and the translational diffusion coefficient is a temperature independent constant. There is a considerable body of information available concerning the temperature dependence of the viscosity of a glass forming liquid. The temperature dependences of the viscosities of many such liquids have been fitted to the Vogel–Fulcher relation

$$\eta(T) = A \exp\left(-\frac{B}{T - T_0}\right), \quad (4.1)$$

with A , B , and T_0 empirical constants. It is usually the case that T_0 is close to but slightly smaller than T_g . A rationale for Eq. (4.1) has been provided by Adam and Gibbs,¹⁶ who argued that the relaxation time for the transitions between the configurations that define a metastable cluster is proportional to $\exp[\text{constant}/TS_c]$, so that Eq. (4.1) is a consequence of the decrease to zero of the configurational entropy as the glass temperature is approached from above. More recent attempts^{1–7} to describe $\eta(T)$ near T_g have focused attention on the slowing down of density fluctuations as $T \rightarrow T_g$; these theories predict that near T_g the viscosity is of the form

$$\eta(T) = \eta_0(T - T_g)^{-\gamma}, \quad (4.2)$$

with $\gamma \approx 1.8$. The mode coupling theories that lead to Eq. (4.2) also predict that the temperature dependence of the translational diffusion coefficient is of the form

$$D(T) = D_0(T - T_g)^{\gamma'}, \quad (4.3)$$

with γ' close to but not identical with γ .

A careful analysis of the available experimental data shows that both Eqs. (4.1) and (4.2) fail very close to T_g . Indeed, very close to T_g the viscosities of many liquids are apparently best fit with an Arrhenius function.¹⁷ As to the solute rotational diffusion coefficient, current theory¹⁸ suggests that

$$D_R \propto L + \frac{K}{\eta}, \quad (4.4)$$

where L is determined by the local structural and dynamical properties of the host liquid, and K by the host liquid hydrodynamic properties.

If our qualitative analysis of the solute rotational relaxation rate in a supercooled liquid mixture is combined with the results of mode coupling theory, it is predicted that for temperatures close to but immediately below T^* one should find

$$\langle \tau_\alpha \rangle \propto (T - T^*)^{-\gamma}, \quad (4.5)$$

where $\langle \tau_\alpha \rangle$ is the average value of the $\tau_{lm}(\mathbf{k})$.

Consider, now, a spherical solute in a supercooled host liquid. When T is very far from T_g (high temperature) the

single particle relaxation times $[l(l+1)D_R]^{-1}$ and the solvent relaxation times $\tau_{lm}(\mathbf{k})$ are of comparable magnitude, hence no clear cut distinction can be made between orientational relaxation due to single particle rotational diffusion and that due to density fluctuations in the host liquid. However, as $T \rightarrow T_g$ both D_T^A and D_R^A decrease in magnitude, and the second term on the right-hand side of Eq. (3.16) becomes rather different from the other two terms, leading to a new peak in the relaxation spectrum.

V. ORIENTATIONAL RELAXATION OF ELLIPSOIDAL MOLECULES

The existing data base for orientational relaxation in supercooled liquids and glasses is dominated by the results obtained from studies of dielectric relaxation. Such studies determine the value of the first rank ($l=1$) coefficient in the spherical harmonic expansion of the inhomogeneous density distribution. It is natural to inquire whether the higher rank terms in the density expansion display temperature dependencies which are similar to that of the first rank term, in particular whether they display a bifurcation of relaxation processes as the glass transition is approached. Beyond satisfying our curiosity concerning the structure of the models of the relaxation processes in a supercooled liquid, it is possible to test the predictions of various theories concerning the behavior of the term $l=2$ since the correlation function $\langle A_{2m}(-k)A_{2m}(k,t) \rangle$ can be obtained from light scattering and Raman spectroscopy measurements.¹⁹

If the molecules of the liquid can be represented as smooth dipolar spheres it can be shown that, within the

framework of the linearized equilibrium theory of dipolar liquids, all the coefficients in the spherical harmonic expansion of the two particle direct correlation function with rank greater than one are zero.²⁰ In this case collective effects in the dipolar dynamics are not expected to affect the correlation functions $\phi_{lm}(t)$ when $l > 1$. However, it is rarely the case that a dipolar molecule is well represented as a smooth sphere with an embedded point dipole.

The next simplest model of a dipolar molecule is a smooth ellipsoid with an embedded point dipole. Both the equilibrium properties and the dynamical properties of a liquid of ellipsoids are richer and more complex than those of a liquid of spherical particles. In a liquid of ellipsoidal molecules the extent of orientational and positional correlation depends strongly on the axial ratio; for large enough axial ratio there is a phase transition generating coexistence between an orientationally disordered isotropic liquid and an orientationally ordered nematic liquid crystal.²¹ It is almost a tautology to expect that the orientational ordering in a liquid of ellipsoidal particles will influence the rates of orientational relaxation processes in that liquid, in particular those processes which involve the collective motion of many particles. In the following text we describe briefly a calculation of the rate of relaxation of the correlation function $\phi_{2m}(t)$ for a liquid of ellipsoidal particles.

We shall examine the motion of a tagged prolate ellipsoid solute (B) in a liquid of prolate ellipsoid host molecules (A). We assume that the axial ratios of the A and B ellipsoids are the same. In this case we expect the correlation function $\phi_{20}^{AB}(\mathbf{k}, t)$ to be affected most by the existence of a collective relaxation process. The function $\phi_{20}^B(t)$, for the tagged ellipsoidal solute particles, has the form

$$\begin{aligned} \phi_{20}^B(t) = & \phi_{20}^B(0) \exp(-6D_R^B t) + \frac{1}{(2\pi)^4} \int d\mathbf{k} \frac{C_{AB}(220; \mathbf{k}) \phi_{20}^{AB}(\mathbf{k}, t=0) \exp[-t/\tau_{20}(\mathbf{k})]}{1 - [6D_R^B \tau_{20}(\mathbf{k})]^{-1}} \\ & - \frac{1}{(2\pi)^4} \int d\mathbf{k} \frac{C_{AB}(220; \mathbf{k}) \phi_{20}^{AB}(\mathbf{k}, t=0) \exp(-6D_R^B t)}{1 - [6D_R^B \tau_{20}(\mathbf{k})]^{-1}}, \end{aligned} \quad (5.1)$$

where D_R^B is the rotational diffusion constant for motion about the minor axes and $\tau_{20}(\mathbf{k})$, the relaxation time for the solvent, can be written in the form

$$\begin{aligned} [\tau_{20}(\mathbf{k})]^{-1} = & (6D_R^A + D_T^A k^2) \left[1 - \frac{\rho_0}{4\pi} C(220; \mathbf{k}) \right] \\ = & (6D_R^A + D_T^A k^2) \\ & \times \left\{ 1 - \frac{\rho_0}{4\pi} \left[\frac{h(220; \mathbf{k})}{1 + (\rho_0/4\pi)h(220; \mathbf{k})} \right] \right\}. \end{aligned} \quad (5.2)$$

The second line in Eq. (5.2) follows from use of the Ornstein-Zernike equation for the Fourier components of the direct and total pair correlation functions, namely

$$h(lm; \mathbf{k}) = C(lm; \mathbf{k}) + \frac{\rho_0}{4\pi} (-)^m C(lm; \mathbf{k}) h(lm; \mathbf{k}). \quad (5.3)$$

In a dense liquid of prolate ellipsoids with axial ratio greater than 2, $h_{220}(\mathbf{k})$ increases considerably as $\mathbf{k} \rightarrow 0$, which then implies that $\tau_{20}(\mathbf{k})$ becomes very large as $\mathbf{k} \rightarrow 0$. This behavior is a precursor signal of the isotropic-to-nematic liquid crystal phase transition in such a system.²¹ To a lesser extent, the same behavior is found in liquids of prolate ellipsoids with axial ratio less than 2.

The lifetime corresponding to the relaxation of $\phi_{20}^B(t)$ also increases near the glass transition of the liquid of ellipsoids. Indeed, Eq. (5.2) implies that $\phi_{20}^B(t)$ can support a bifurcation of the lifetimes for the relaxation processes at some temperature above the glass temperature. We note that in a liquid of nonpolar ellipsoidal particles the dipolar correlation functions $\phi_{lm}(t)$ will not display any collective relaxation effects since all of the odd harmonic coefficients in the expansion of the two particle direct correlation function vanish by virtue of the inversion symmetry of the ellipsoids.

VI. ORIENTATIONAL RELAXATION IN DISORDERED SOLIDS

Many molecular liquids freeze into orientationally disordered solids. It is observed that these solids exhibit interesting orientational relaxation behavior, which behavior has both similarities to and differences with the orientational relaxation behavior in the parent isotropic liquid.^{9,22,23} In particular, it is found that orientational relaxation in a disordered solid can exhibit a bifurcation of the orientational relaxation lifetimes at a temperature above the orientational glass transition. A well studied example of such behavior is provided by the orientational relaxation dynamics of neohexanol.⁹ Solid neohexanol undergoes an orientational glass transition at 163 K. For a temperature range above this glass transition there are two relaxation processes, both of which have Arrhenius-type temperature dependences with, of course, different activation energies. Solid cyclohexanol also undergoes an orientational glass transition, and also supports two relaxation processes for a temperature range above the glass transition temperature.⁹ In this latter case, however, the α relaxation has a non-Arrhenius-type temperature dependence while the β relaxation has an Arrhenius-type temperature dependence.

In this section we show that the density functional formulation of orientational relaxation in a liquid can be extended to the description of orientational relaxation in a disordered solid. We assume, for simplicity, that for the purpose of describing the orientational relaxation of the solid it is sufficient to represent the molecules as spheres with embedded point dipoles, one at each lattice site. Each point dipole is assumed to undergo Brownian rotational diffusion in the force field generated by all of its neighbors. As in the description of orientational relaxation in the liquid phase, the force field is obtained from the density functional representation of the free energy of the system, but in this case using a density expansion that reflects the symmetry of the

lattice on which the dipoles reside. That density expansion reads

$$\rho(\mathbf{r}, \Omega, t) = \frac{\rho_0}{4\pi} \left[1 + \sum_{l,m,\{\mathbf{G}\}} a_{lm}(\mathbf{G}, t) e^{i\mathbf{G} \cdot \mathbf{r}} Y_{lm}(\Omega) \right], \quad (6.1)$$

where the $\{\mathbf{G}\}$ are the reciprocal lattice vectors of the solid. The equation of motion for the wavevector dependent coefficients in Eq. (6.1) is

$$\frac{\partial a_{lm}(\mathbf{G}, t)}{\partial t} = -2D_R^A a_{lm}(\mathbf{G}, t) + \frac{(-)^m D_R^A \rho_A}{2\pi} C(lm; \mathbf{G}) a_{lm}(\mathbf{G}, t), \quad (6.2)$$

so that the relaxation of $a_{lm}(\mathbf{G}, t)$ has a simple exponential form with relaxation time $\tau_{lm}(\mathbf{G})$ given by

$$[\tau_{lm}(\mathbf{G})]^{-1} = 2D_R^A - \frac{(-)^m D_R^A \rho_A}{2\pi} C(lm; \mathbf{G}). \quad (6.3)$$

The orientational distribution function for the tagged particles can be expanded in the same fashion as for the liquid since they are randomly placed in the lattice. It is found that the equation of motion for the coefficients $A_{lm}(t)$ is

$$\begin{aligned} \frac{\partial A_{lm}(t)}{\partial t} &= -2D_R^B A_{lm}(t) \\ &+ \frac{(-)^m D_R^B}{(2\pi)^4} \int d\mathbf{k} C_{AB}(lm; \mathbf{k}) a_{lm}(\mathbf{k}, t) \\ &= -2D_R^B A_{lm}(t) \\ &+ \frac{(-)^m D_R^B}{2\pi} \sum_{\{\mathbf{G}\}} C_{AB}(lm; \mathbf{G}) a_{lm}(\mathbf{G}, t). \end{aligned} \quad (6.4)$$

We now follow the procedure outlined in Sec. III to obtain an expression for the correlation function $\phi_{lm}(t)$. The result is

$$\begin{aligned} \phi_{lm}^B(t) &= \phi_{lm}^B(0) \exp[2D_R^B t] + \frac{(-)^m}{2\pi} \sum_{\{\mathbf{G}\}} \frac{C_{AB}(lm; \mathbf{G}) \phi_{lm}^{AB}(\mathbf{G}, t=0) \exp[-t/\tau_{lm}(\mathbf{G})]}{1 - [2D_R^B \tau_{lm}(\mathbf{G})]^{-1}} \\ &- \frac{(-)^m}{2\pi} \sum_{\{\mathbf{G}\}} \frac{C_{AB}(lm; \mathbf{G}) \phi_{lm}^{AB}(\mathbf{G}, t=0) \exp(-2D_R^B t)}{1 - [2D_R^B \tau_{lm}(\mathbf{G})]^{-1}}. \end{aligned} \quad (6.5)$$

Comparing Eqs. (6.5) and (3.16), it is clear that the arguments already advanced to describe the qualitative features of orientational relaxation in the liquid also apply to orientational relaxation in the disordered solid. In particular, Eq. (6.5) supports a bifurcation of relaxation times at some temperature above the orientational glass transition temperature.

As expected, there are also some differences between the orientational relaxation processes in a disordered solid and in a liquid. The following implications can be drawn from an examination of Eq. (6.5).

(1) Within the density functional representation, the rates of orientational relaxation in different lattices differ

because the reciprocal lattice vectors of different lattices are not the same and because the Fourier coefficients $C(lmn; \mathbf{G})$ for different lattices are not the same. For example, the lowest order reciprocal lattice vectors of a body centered cubic lattice are $(\pm 1, \pm 1, 0)(2\pi/a)$, $(\pm 1, 0, \pm 1)(2\pi/a)$, $(0, \pm 1, \pm 1)(2\pi/a)$, whereas those for a face centered cubic lattice are $(\pm 1, \pm 1, \pm 1)(2\pi/a)$, where a is the lattice parameter. If only the lowest order reciprocal lattice vector terms in the description of the time dependence of $\phi_{lm}(t)$ are retained, that time dependence is biexponential. Of course, the inclusion of higher order reciprocal lattice vector terms in the time dependence of $\phi_{lm}(t)$, which may be required for adequate representation of the density distribution, will lead

to a multiexponential description of the time evolution. The relative importance of the terms in such a multiexponential representation of the time dependence of $\phi_{lm}(t)$ will depend on the magnitudes of the Fourier components of the direct correlation function evaluated at the wave vectors corresponding to the reciprocal lattice vectors.

(2) If we assume that the absence of translation-rotation coupling which is inherent in our density functional representation of relaxation in a disordered solid is correct, the value of the relaxation time $\tau_{lm}(G)$ is very likely different from the value of its counterpart in the liquid. We expect that both $\tau_{11}(G)$ and $\tau_{10}(G)$ have values close to $(2D_R^A)^{-1}$ at sufficiently high temperature. Then, as the orientational glass transition temperature is approached, collective orientational relaxation slows down and the lifetimes for the relaxation processes as a function of temperature exhibit the $\alpha\beta$ bifurcation.

(3) Equation (6.5) can be used to describe dielectric relaxation in a disordered solid. For that case our model predicts that dielectric relaxation in a disordered solid is simpler than in the corresponding liquid. Zwanzig²⁴ has examined the motion of a Brownian rotor in the force field of neighboring rotors arranged on a simple cubic lattice for the purpose of demonstrating the source of non-Debye terms in the orientational relaxation. The model we have described can be considered an extension of the Zwanzig model in that Eq. (6.5) shows the multiple exponential character of the orientational relaxation emerging from solute-solvent interactions.

VII. RESULTS AND NUMERICAL CALCULATIONS

We consider first the results obtained from numerical calculation of the rate of orientational relaxation in a model liquid of spherical dipolar particles, which we examine via the frequency dependence of the imaginary part of the dielectric function. The unpolarizable solute and solvent dipolar particles, which are taken to have the same diameter and dipole moment, are allowed to have different rotational diffusion constants. The two particle direct correlation function for this model liquid was approximated by the result obtained from the mean spherical approximation (MSA), which is known to be reasonably accurate when the liquid dielectric constant is not large. The reduced ratio of the translational and rotational diffusion constants, $p' = D_T^A/2D_R^A\sigma^2$ where σ is the particle diameter, is taken to be zero near the glass transition temperature and 0.2 at high temperature. The static dielectric constant of the liquid, as calculated from the MSA, is 38.

We show in Fig. 1 the high temperature frequency dependence of the imaginary part of the dielectric function for the model liquid for the case that the bare rotational diffusion constant of the solute and the coupled rotational diffusion constant of the solvent molecules are equal and there is modest coupling of the translational and rotational motion ($p' = 0.2$). We find only one peak in the imaginary part of the dielectric function, hence there is only one important time scale for orientational relaxation, which we identify with the β relaxation. The behavior displayed in Fig. 1 is that expected when the solute and solvent diffusion occur at com-

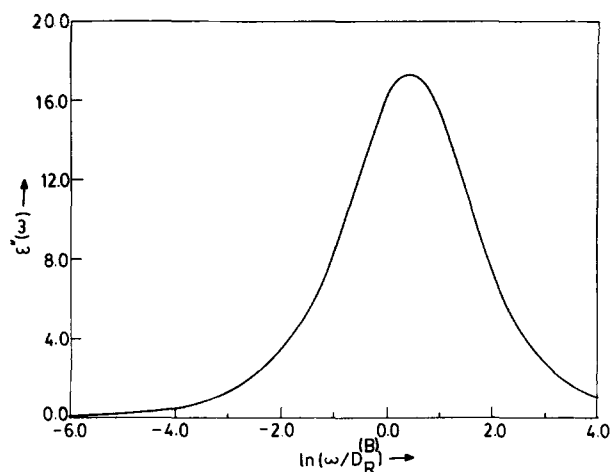


FIG. 1. The dependence of the imaginary part of the dielectric function on the reduced frequency for a spherical dipolar solute (B) in a liquid of dipolar host spheres (A) with the same diameter and dipole moment. For this calculation it was assumed that $D_R^A = D_R^B$ and that $p' = D_T^A/2D_R^A\sigma^2 = 0.2$, with σ the particle diameter. The static dielectric constant of the liquid with reduced density 0.8 is, from the MSA, 38.0.

parable rates, as is the case in the "high temperature" normal liquid range.

Figure 2 displays the frequency dependence of the imaginary part of the dielectric function for the case that the bare rotational diffusion constant of the solute is very much larger than that of the solvent ($D_R^B/D_R^A = 50$), such as occurs near the glass transition temperature. There is, in this case, clear evidence for two relaxation processes. We note that the separation of these two relaxation processes increases as the solute to solvent rotational diffusion constant ratio increases. We identify the lower frequency peak in the imaginary part of the dielectric function with the α -relaxation process and the higher frequency peak with the β -relaxation process.

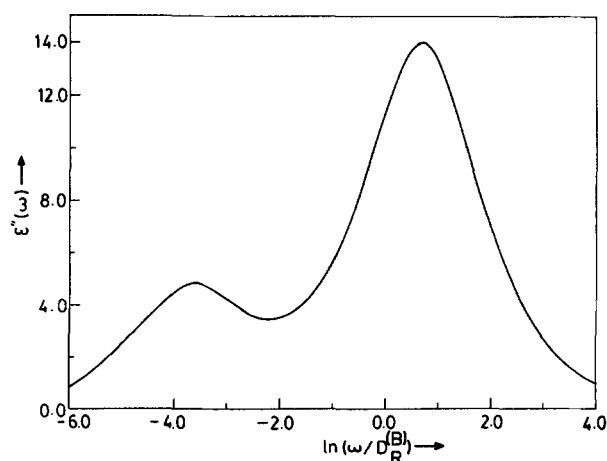


FIG. 2. The frequency dependence of the imaginary part of the dielectric function for the liquid system described in the caption to Fig. 1 near the glass transition temperature. The temperature is determined implicitly by the ratio of the rotational diffusion constants of the solute and solvent molecules, which for this calculation was taken to be $D_R^B/D_R^A = 50$, and by the relationship between the translational and rotational diffusion constants of the solvent molecules, which for this calculation was taken to be represented by $p' = 0$. The reduced density and the static dielectric constant of the liquid are the same as for the case depicted in Fig. 1.

The behavior displayed in Fig. 2 is very much like that observed experimentally except that the amplitudes of the α and β relaxation processes are reversed. We attribute this discrepancy to two approximations used in our reduction of the analysis for numerical calculation. First, we have represented the solvent molecules as dipolar hard spheres and, second, we have used the MSA result for the pair direct correlation function. Both of these approximations underestimate the orientational correlations in the liquid at the $l = 1$ level. The removal of these approximations should increase the amplitude of the α -relaxation process relative to that of the β process, as is observed for real liquids.

We now consider the rate of orientational relaxation of an ellipsoidal solute molecule in a dense host liquid of ellipsoidal molecules. In contrast with the situation for a liquid of spherical molecules, there is no model of a liquid of ellipsoidal molecules for which there is an analytic expression for the direct correlation function. We have, therefore, adopted the approximation introduced by Colot *et al.*²⁵ This approximation assumes it is sufficiently accurate to write the direct correlation function as the product of a density dependent function of the particle positions and a density independent function of the particle orientations, namely

$$C(\mathbf{r} - \mathbf{r}', \omega - \omega') = C_0(|\mathbf{r} - \mathbf{r}'|)f(\omega, \omega'). \quad (7.1)$$

To use Eq. (7.1) we have further assumed that C_0 is adequately approximated by the Percus-Yevick form for the direct correlation function of a liquid of hard spheres with the same density,²⁶ and that the angular function $f(\omega, \omega')$ is adequately approximated by the intrinsically anisotropic excluded volume of two ellipsoids. Adopting the expression of Berne and Pechukas²⁷ for the angle dependent contact distance of two ellipsoids of revolution we have

$$f(\omega, \omega') = \left[\frac{1 - X^2(\mathbf{e} \cdot \mathbf{e}')^2}{1 - X^2} \right]^{1/2}, \quad (7.2)$$

where $X = [(a/b)^2 - 1]/[(a/b)^2 + 1]$ with (a/b) the common axial ratio of the solvent and solute ellipsoidal molecules, and \mathbf{e} and \mathbf{e}' unit vectors along the major axes of the solvent and solute ellipsoidal molecules. Figure 3 displays the time dependence of $\phi_{20}(t)$ when $D_R^B/D_R^A = 1$, corresponding to a temperature in the normal liquid range and when $D_R^B/D_R^A = 50$ corresponding to a temperature near the glass transition temperature. The temporal evolution of $\phi_{20}(t)$ is clearly not of simple exponential form, but is representable as occurring in two time regimes. The fast relaxation processes which occurs for small t arises from single molecule reorientation and the slow relaxation process which persists at large t arises from collective relaxation of the solvent molecules. We note that near the glass transition temperature the solvent relaxation rate becomes very small and, because of the coupling of solute and solvent molecule motions, this leads to a slowdown of the long time relaxation of the solute molecules (see curve 4 in Fig. 3). The large difference between the time scales of the two different relaxation processes near the glass transition temperature implies the existence of a bimodal structure in the relaxation of the second rank correlation functions of a liquid of ellipsoidal molecules.

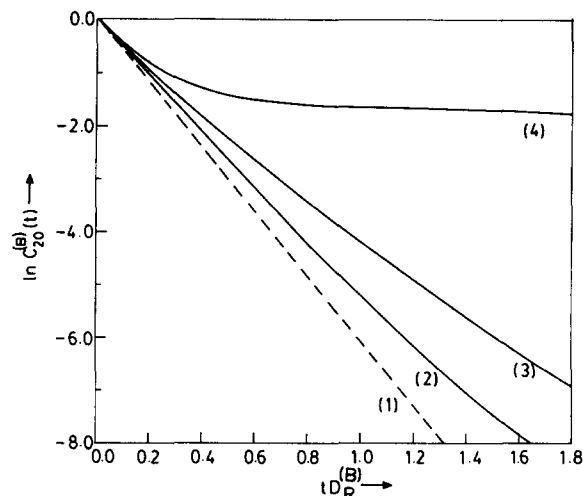


FIG. 3. The time dependence of the correlation function of an ellipsoidal solute particle in a dense fluid of host ellipsoidal particles. The several curves correspond to the correlation functions for the following different conditions: (1) Single particle rotational diffusion in the absence of all intermolecular interactions, for which $\phi_{20}^B(t) = \exp(-6D_R^B t)$. So as to be able to compare this ideal behavior with the behavior in other situations, such as displayed in curves 2, 3, and 4, the density is taken to be the same as in those cases, namely 0.8. (2) $D_R^B/D_R^A = 1.0$ and $p = 2.0$; (3) $D_R^B/D_R^A = 1.0$ and $p = 0$; (4) $D_R^B/D_R^A = 50$ and $p = 0$. For this system $p = D_T^A/D_R^A b^2$, where b is the length of the minor axis of the ellipsoidal solvent particle and D_R is the rotational diffusion constant about that axis. The shape and size of the solute and solvent molecules are taken to be the same, and the axial ratio was taken to be 2.0.

VIII. DISCUSSION

This paper has dealt with the interpretation of the divergence of the rates corresponding to different mechanisms of rotational relaxation in the supercooled liquid state just above the glass transition temperature, as signalled by a bifurcation at some temperature $T^* > T_g$ of the relaxation times as a function of temperature. We have shown that explicit inclusion of the coupling of the orientational motion of the solute molecule to translational motions of the solvent molecules and to density fluctuations in the host liquid in a Smoluchowski-type kinetic equation for the orientational distribution function of the solute molecule provides a sound basis for understanding the observed behavior. The solution to the kinetic equation implies that the two relaxation processes are, respectively, solute molecule reorientation in the field of stationary neighboring solvent molecules and collective relaxation of the solvent molecules, just as suggested by Kivelson and Kivelson.¹⁰

In describing the orientational relaxation of a solute in a supercooled liquid as $T \rightarrow T_g$ we have represented the relative importance of the single particle and collective relaxation processes parametrically via the ratios D_R^B/D_R^A and p' . To complete our arguments it will be necessary to calculate the various D 's directly from the microscopic properties of the supercooled liquid, which is a formidable task. In the absence of such calculations we seek confirmation of the qualitative features imposed on the system by our parametrization from general analyses of the glass transition.

The basic problem faced in constructing a theory of the glass transition is understanding how a transformation from

ergodic to nonergodic behavior of a system can occur, and how that transformation affects particular properties of the system. One of the key ideas concerning this transformation was mentioned in Sec. I, namely, formal partitioning of the system phase space to remove those portions corresponding to crystalline states. The most systematic development of this partitioning is derived from the work of Stillinger and Weber,²⁸ who have shown that it can be convenient to analyze the many body dynamics of a liquid by separating consideration of the stable packing configurations which correspond to the local minima in the potential energy hypersurface from consideration of the thermally excited molecular motion on that potential energy hypersurface. The local minima in the potential energy hypersurface can be located by following suitably chosen trajectories in the multidimensional configuration space; these trajectories can also be used to define mutually exclusive basins surrounding each of the relative minima. At low temperature the system dynamics is dominated by vibrations which remain bounded in the basins, but as the temperature is increased large amplitude motions can be excited, and these can generate transitions which carry the system from one basin to another. The complete set of local minima includes those configurations of the system which are global minima, e.g., which correspond to crystalline packings of the molecules. A glass state can be defined by enforcing nonergodicity of the system dynamics, formally, by projecting out of the set of local minima of the potential energy hypersurface those that represent crystalline packings of the entire system and those that represent microcrystalline domains equal to or larger than that required to nucleate the freezing transition; the residual set defines the glass. The interbasin kinetics in the residual set is then described by a master equation. Mohanty²⁹ and Stillinger³⁰ have exploited this formulation to provide a qualitative explanation of the Kohlrausch–Williams–Watts form of the spectrum of relaxation times, which is the form observed for many system properties near the glass transition.³¹ Mohanty³² has also shown how this formulation can be used, with the Green–Kubo time correlation function representation of transport coefficients, to obtain the single particle (noncollective) contribution to the diffusion coefficient and viscosity of a supercooled liquid.

To understand the origin of the collective relaxation term we recognize that the Stillinger–Weber^{28,30} construction of the topology of the potential energy hypersurface and the motion it supports, and the cluster structure interpretation of the glass transition and glass properties^{2,16} both imply that the viscosity of a supercooled liquid will display spatial dispersion near T_g , i.e., a dependence of the magnitude of the viscosity on the scale length of the measurement process. An interesting experiment that is pertinent to this theoretical inference has been reported by Kiyachenko and Litvinov.³³ These investigators have determined the viscosity of supercooled glycerol near T_g directly by measuring the rate of flow of the liquid through a capillary, and indirectly by using the Stokes–Einstein relationship to invert values of the diffusion constant obtained from light scattering from polystyrene spheres suspended in the liquid. The values so obtained agree when the temperature is well above T_g , but

increasingly differ as T_g is approached, which Kiyachenko and Litvinov interpret as evidence for spatial dispersion with a scale length that increases as T_g is approached.

A different view of the growth in scale length associated with the dynamical processes in a supercooled liquid as T_g is approached is reported by Sidebottom and Sorenson.³⁴ These investigators have carried out measurements of the lifetimes of density fluctuations in normal and supercooled liquid phenyl salicylate. They find a temperature independent hydrodynamic mode, which they ascribe to density fluctuations driven by entropy fluctuations, and a strongly temperature dependent nonhydrodynamic mode which they ascribe to internal structural relaxation in the liquid. The internal relaxation suppresses the hydrodynamic mode when the relaxation time of the latter is comparable or less than the relaxation time of the former. Since this suppression is observed to occur in the same temperature range near T_g as the failure of Eq. (4.2), it is argued to be the driving force for the glass transition.

These experimental observations, and the qualitative implications of the inherent structure and cluster pictures of the glass transition, are consistent with our interpretation of the temperature dependence of the relative importance of single particle and collective relaxation processes in the orientational relaxation of a solute in a supercooled liquid.

ACKNOWLEDGMENT

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