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KINEMATIC AND ELECTRODYNAMIC INTERPRETATIONS OF MOLECULAR MOTION IN GLASSES

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ABSTRACT

The development of a Smoluchowski equation for the evolution of the probability density of angular molecular motion in the condensed phase is considered in terms of kinematic and electrodynamic models. These are equivalent in some cases (i.e. two or more different interpretations may be assigned to the same equations of motion) so that wide ranges of environment and frequency are needed to distinguish between the different models. Therefore data over about ten or more decades of frequency have been used in the glassy and liquid environments of decalin solutions in order to illuminate the paths along which development of the basic formalism (due to Budo) should proceed.

The overall features of the experimental loss profile may be reproduced even in the glassy state but only by imposing severe constraints on the model parameters as they stand at present. These are more acceptable in a kinematic rather than electrodynamic interpretation of the Smoluchowski equation.

INTRODUCTION

The interaction of dipole moments affects the statistical auto-correlations and zero-THz absorption of molecules undergoing Brownian motion [1]. The dipole-dipole interactions, being long range, persist in dilute solution [2] and should be assessed in any theory of molecular motion in liquids and glasses. The most intractable problem is one of describing the fluctuations of the reaction field induced in its surroundings by a fluctuating dipole, and in general the equation of motion may be solved iteratively only as described by Scaife [3]. However, in the particular case where the interaction is considered pairwise, Coffey has shown recently [4] that the problem may be approached using in fresh ways the classical techniques developed by Budo, who considered the Brownian motion of a molecule with two interacting dipolar groups. In this paper we aim to take the simplest representation of Coffey's theory and compare it with data collected over a suitably wide range of frequency [5], in the different environments provided by the liquid state, and the glassy state. One of the consequences of Coffey's formalism is to underline the fact that an experimental picture of molecular relaxation processes over only a restricted range of low frequency can be misleading in the sense that short time details of the molecular motion cannot be assessed [6]. Often the far infra-red part of the loss curve is the only means available of distinguishing between the reality of such behaviour and models such as inertialess rotational diffusion and well-hopping (Ivanov) which 'wash out' the torsional oscillatory mode at THz frequencies [7]. This should always be considered as an integral part of the overall loss profile, i.e. of the overall dynamic evolution. Therefore, in a solution of dipoles in a non-dipolar glass such as decalin the Poley absorption survives as the newly characterised γ process [5], while its microwave frequency (Debye) adjunct has been shifted into the radio frequency region, evolving into the β loss process. A further cooperative α process persists at even lower frequencies in the viscous liquid above the glass transition point. Taken together, the β and γ peaks of the continuum profile in a glass such as CH_2Cl_2/decalin are separated by about ten decades. We aim in this paper to find what modifications are needed to the Coffey equations in order to achieve a simple representation of both liquid phase and glass phase molecular dynamics in a self-consistent fashion. This is a worthwhile exercise since the metamorphosis from liquid to glass has the most dramatic effect on the angular fluctuations of an individual dipole vector (as it evolves from the arbitrary t = o) without quite stopping the rotational diffusion altogether.

In this paper data in the frequency region up to the THz have been collected for dilute solutions of strongly dipolar molecules in non-dipolar solvents capable of being supercooled into the glass. The Coffey theory is then evaluated against this set of data and its statistical characteristics discussed in terms of auto-correlation functions and probability density functions designed to emphasize different aspects of the molecular dynamics as governed by a harmonic type of dipole-dipole potential. Firstly we develop some relevant points of the general theory.

Brownian motion with dipole-dipole interaction

The basis of Coffey's approach lies in the work of Budo [8] on the dielectric relaxation of molecules containing two rotating dipolar groups. The coordinate system, although applicable strictly to dipole-dipole interaction of dipolar groups within a single molecule, may be used as a frame of reference for dimer Brownian motion with the following provisos. Axes μ_1 and μ_2 refer to projections of the two separate dipole vectors μ_1 and μ_2 onto a common plane. In general, therefore, the perpendicular component μ_0 will not be zero when we speak of the dipole-dipole interaction of two separate molecules, each subjected to the influence of Brownian motion.

The restriction of μ_0 = o implies that the dipole moment vectors $\underset{\sim}{\mu}_1$ and $\underset{\sim}{\mu}_2$ of the molecules are undergoing libration or rotational diffusion either in the same plane or in parallel planes. Each dipole may be embedded in an asymmetric top molecular framework. In the case $\mu_0 \neq o$ the magnitude μ_0 is the sum of the components in a plane perpendicular to that defined by μ_1 and μ_2 of the interacting dipoles $\underline{\mu}_1$ and $\underline{\mu}_2$.

In order to obtain the simplest representation of the theory we assume inertialess dipoles and that $\mu_0 = o$. The Smoluchowski equation governing the evolution of the probability density function $f(\theta, \phi_1, \phi_2, t)$ is then:

$$\frac{\partial f(\theta,\phi_1,\phi_2,t)}{\partial t} = \frac{kT}{\zeta}\left[\frac{\partial^2 f}{\partial\theta^2} + \cot\theta\,\frac{\partial f}{\partial\theta} + \left(\cot^2\theta + \zeta/\zeta_1\right)\times\left(\frac{\partial^2 f}{\partial\phi_1^2} + \frac{\partial^2 f}{\partial\phi_2^2}\right) + 2\cot^2\theta\,\frac{\partial^2 f}{\partial\phi_1\partial\phi_2}\right] + \frac{\partial}{\partial\phi_1}\left(f\frac{\sin\theta}{\zeta_1}\frac{\partial V}{\partial\phi_1}\right) + \frac{\partial}{\partial\phi_2}\left(f\frac{\sin\theta}{\zeta_1}\frac{\partial V}{\partial\phi_2}\right) \quad (1)$$

In eqn.(1) ζ is a friction coefficient acting on the interacting pair considered as a unit - i.e. the friction acting on the molecule as a whole in the Budo theory. ζ_1 is that on an individual dipole. The probability density function f associated with the orientation of the molecule under the influence of a time varying electric field is governed by eqn.(1) after its sudden removal at t = o. In eqn.(1) the number of pairs of molecules with moments $\underline{\mu}_1$ and $\underline{\mu}_2$ having orientations between Ω and $\Omega + d\Omega$ is given by:

$$f\,d\Omega = f\sin\theta\,d\theta\,d\psi\,d\phi_1\,d\phi_2 \quad (2)$$

θ and ψ are the polar angles which specify the direction of the axis of μ_0 relative to that of $\underline{E}$, the measuring field vector, while ϕ_1 and ϕ_2 are the azimuthal angles of $\underline{\mu}_1$ and $\underline{\mu}_2$ measured from the plane containing $\underline{E}$ and the axis of μ_0. $V = V(\phi_1 - \phi_2)$ is the mutual potential energy of the dipoles $\underline{\mu}_1$ and $\underline{\mu}_2$ due to dipole-dipole interaction. In writing eqn.(1) we assume that the only portion of the interaction taken into account is that between the pair $\underline{\mu}_1$ and $\underline{\mu}_2$, i.e. pair interaction symmetry is assumed.

The mean dipole moment of the ensemble of interacting pairs is calculated from eqn.(1) as:

$$\langle \underline{m}\cdot\underline{e}\rangle = \frac{\beta E}{3}\sum_\lambda\left[e^{-t/\tau_\lambda}\int_{-\pi/2}^{\pi/2} e^{-\beta V(2\eta)}\xi_\lambda(\eta)\left[C_\lambda(\mu_1+\mu_2)^2\cos\eta + C'_\lambda(\mu_1-\mu_2)^2\sin\eta\right]d\eta \Big/ \int_{-\pi/2}^{\pi/2} e^{-\beta V(2\eta)}\,d\eta\right] \quad (3)$$

In eqn.(2), $\eta = (\phi_1 - \phi_2)/2$, $\beta = 1/kT$, and C_λ and C'_λ are constants defined through the orthogonality relations of the eigenfunctions $\xi_\lambda(\eta)$ of the equation:

$$\frac{d^2\xi_\lambda(\eta)}{d\eta^2} - 2\phi(\eta)\frac{d\xi_\lambda(\eta)}{d\eta} + \lambda\xi_\lambda(\eta) = 0 \quad (4)$$

i.e. $$\left.C_\lambda^{\lambda'}\right] = \int_{-\pi/2}^{\pi/2} \Phi(\eta)\,\xi_\lambda(\eta) \left.\begin{matrix}\sin\eta\\ \cos\eta\end{matrix}\right] d\eta \Big/ \int_{-\pi/2}^{\pi/2} \Phi(\eta)\,\xi_\lambda^2(\eta)\, d\eta \qquad (5)$$

with $$\Phi(\eta) = \exp\left(-2\int_0^\eta \phi(\eta')\,d\eta'\right)$$

and $$\phi(\eta) = \frac{1}{kT}\,\frac{dV'(2\eta)}{d(2\eta)}$$

Eqn.(4) is a Sturm-Liouville type of differential equation with eigenvalues λ. Eqn.(3) is the after-effect solution of eqn.(1) and shows that the polarisation is not a simple exponential decay with time but a superposition of a very large number of exponentials. The polarisability $\alpha_\mu^*(\omega)$ may now be calculated by means of the relation:

$$\alpha_\mu^*(\omega) = -\int_0^\infty \frac{d}{dt}\left(\langle \underset{\sim}{m}\cdot\underset{\sim}{e}\rangle_0\, e^{-i\omega t}\, dt\ \alpha_\mu'(0) - i\omega\int_0^\infty \langle \underset{\sim}{m}\cdot\underset{\sim}{e}\rangle e^{-i\omega t}\, dt \qquad (6)$$

where $\langle\ \rangle_0$ denotes ensemble averaging in the absence of $\underline{E}$ the measuring field. From eqns.(3) and (6):

$$\alpha_\mu^*(\omega) = \frac{\beta E}{2}\sum_\lambda I_\lambda \big/ (1 + i\omega\tau_\lambda) \qquad (7)$$

in the simplest case where inertia is neglected. Here I_λ is a weighted integral over the eigenfunctions appearing in eqn.(3). <u>There will therefore always be a distribution of relaxation times in the presence of dipole-dipole interaction</u>.

Inertial considerations are developed in this paper by making a simplification such that the vector $\underline{E}$ is always coplanar with the plance of rotation of the dipole components μ_1 and μ_2. The equations of motion of the system then reduce to ones formally identical with those governing the model [9] of planar itinerant libration of the asymmetric-top dipole, (developed recently by Coffey et al. [9,10]) provided the interaction potential takes on the harmonic form:

$$V = (\phi_1 - \phi_2)^2 V_0 \qquad (8)$$

The dielectric loss is now described by the following stochastic differential equations of motion:

$$I_1\ddot{\phi}_1(t) + \zeta_1\dot{\phi}_1(t) + V'(\phi_1 - \phi_2) + \mu_1 E\sin\phi_1(t) = g_1(t)$$
$$I_2\ddot{\phi}_2(t) + \zeta_2\dot{\phi}_2(t) - V'(\phi_1 - \phi_2) + \mu_2 E\sin\phi_2(t) = g_2(t) \qquad (9)$$

Here I_1 and I_2 are the moments of inertia of $\underset{\sim}{\mu}_1$ and $\underset{\sim}{\mu}_2$ respectively about a central axis $\perp$ to their own plane. $g_1(t)$ and $g_2(t)$ are random torques acting on $\underset{\sim}{\mu}_1$ and $\underset{\sim}{\mu}_2$ caused by the Brownian motion. ζ_1 and ζ_2 are the hydrodynamic friction coefficients acting on each dipole. We may now define $V_0 = \frac{1}{2} I_2 \omega_0^2$ where ω_0 is a harmonic frequency which we assume may be identified with the peak librational frequency of the far infra-red. In the liquid state it is reasonable to suppose that $\zeta_1 = \zeta_2 = \zeta_0$, which may be identified with the microwave loss peak frequency. Therefore there are no adjustable parameters within this framework of assumption, and the experimental loss is reproduced fairly accurately in the liquid solution at room temperature.

In a glassy environment however, we find that we are forced to set $\zeta_1 \gg \zeta_2$ in eqns.(9) in order to follow the split into two loss peaks of the continuum profile. In this case ζ_1 is identified with the radio frequency peak and ζ_2 serves as an adjustable parameter which broadens the THz loss peak (fig.(1)). This means that:

(a) Either the dynamical evolution of the molecular interactions in a glass or viscous liquid is not describable in terms of a simple model such as this, or

(b) Alternatively it might be possible to think of a process whereby the hydrodynamic friction coefficient ζ_1 acting on one dipole moment is very different from that on the other because the local environment is different at different instants t. A very small proportion of the molecules will be at the crest of a potential well at any one time (i.e. they are in the act of rotating through unusually large angles). The vast majority will be librating quasi-harmonically at the bottom against hugely different frictions represented by ζ_2 (say). The difficulty is that one would expect, <u>after an ensemble average</u>, that ζ_1 and ζ_2 should still be roughly similar, and in the glass, both very large. This implies immediately that the THz peak will be 'washed out' theoretically and replaced by a slowly decaying plateau in the absorption coefficient $\alpha(\omega)$ simply because a large ζ_2 broadens the THz resonance enormously). This would be true for any kind of dipole-dipole potential V. It seems therefore that the simple model is unrealistic in the glass. At the same time it is remarkable that if the same eqns (9) were to be interpreted in terms of the planar itinerant librator, the conceptual difficulty caused by $\zeta_1 \gg \zeta_2$ vanishes, since the former becomes the friction coefficient between an entire diffusing cage and its surroundings, and ζ_2 that between the inner molecule and the cage. This interpretation may however be objected to on the grounds that it is unlikely that a cage of nearest neighbours behaves as a rotationally diffusing entity. It is clear therefore that developments are needed in eqn.(1) or eqns.(9) before the glassy state spectrum can be interpreted in a manner consistent with that of the liquid state spectrum.

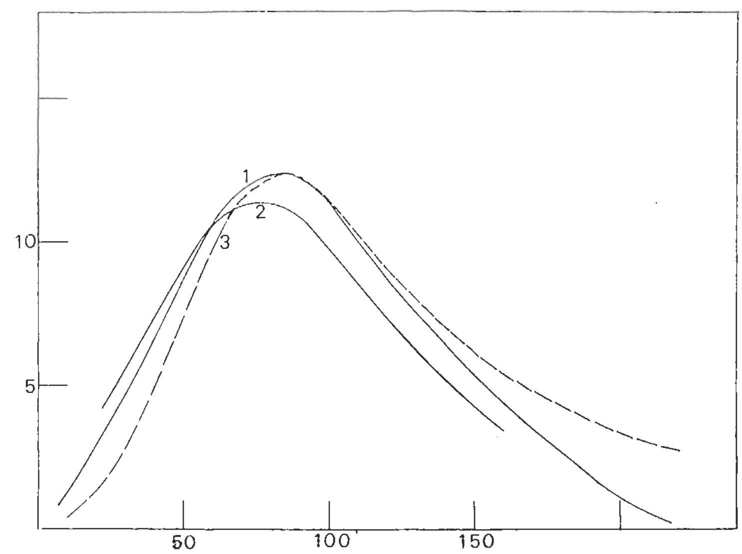
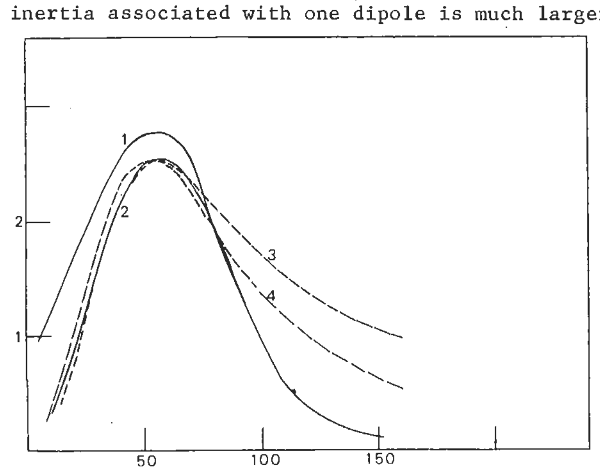


Figure 1 (a) Far infra-red absorption of tetrahydrofuran/decalin glass (10% v./
(1) Exptl. curve at 110 K; (2) Exptl. curve at 128 K; (3) Theoretical curve (normalised to $\alpha_{max}(\bar{\nu})$), with either of the following group of parameters:

$10^{39}\, I_1$ /gm cm^2	$10^{39}\, I_2$ /gm cm^2	ζ_1/THz	ζ_2/THz	T/K	ϵ_0	ϵ_∞
8	8	6040	20	110	3.5	2.4
2400	8	20.1	20	110	3.5	2.4

This means that the electrodynamic interpretation is valid provided the moment of inertia associated with one dipole is much larger than that associated with the ot



(b) Far infra-red absorption of fluorobenzene/decalin glass (10% v./v.)
(1) Exptl. curve at 128 K; (2) Exptl. curve at 110 K; (3), (4) Normalised theoretical curves showing the broadening effect of an increasing ζ_2:
(3) ζ_2 = 20 THz; (4) ζ_2 = 15 THz. The theoretical curves are normalised to the $\alpha_{max}(\bar{\nu})$ of curve (2).
Ordinate: $\alpha(\bar{\nu})$/neper cm^{-1}; Abscissa: $\bar{\nu}$/cm^{-1}

Statistical Considerations - Probability Density Functions

The molecular dynamics governed by eqns.(1) or (9) may be described statistically in terms of various autocorrelation functions associated with the mean dipole moment $\langle \underline{m}.\underline{e} \rangle$. These are derived by suitable integrations over their associated probability density functions [10].

These functions may be calculated from eqns.(1) or (9) and by Fourier transforming the orientational time auto-correlation function: in particular the loss is obtained as a function of frequency. By relating the angular velocity autocorrelation function to its memory function, evaluating thereby the conditional probability density function for angular velocity, and comparing the result with that from eqns.(9), an estimate may be made of the efficacy of the Kubo fluctuation-dissipation theorem [11]. This is an important link in generalising eqns. such as (1) to include inertial effects and non-Markov statistics. The probability density functions inherently contain more information than their autocorrelation functions and provide a more direct insight to the molecular dynamics. Using a variety of both types of functions the governing characteristics of a model may be elucidated.

Probability Density Functions of Angular Velocity

To evaluate this from eqns.(9) we use their matrix representation:

$$\dot{\underline{\underline{X}}}(t) = \underline{\underline{A}}_0 \underline{\underline{X}}(t) + \underline{\underline{B}} \dot{\underline{\underline{W}}}(t)$$

where:

$$\underline{\underline{X}} = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{bmatrix} \equiv \begin{bmatrix} \phi_1 \\ \phi_2 \\ \dot{\phi}_1 \\ \dot{\phi}_2 \end{bmatrix} ; \quad \underline{\underline{B}} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \tag{10}$$

Here $\underline{\underline{W}}$ is a matrix of Wiener processes, and

$$\Omega_0^2 = (I_1/I_2)\,\omega_0^2 .$$

Therefrom:

$$\langle \dot{\phi}_1(0)\,\dot{\phi}_1(t)\rangle_0 = \mathcal{L}^{-1}\left[\frac{kT}{I_1}\,\frac{s(s+\gamma_2)+\Omega_0^2}{F(s)}\right] \tag{11}$$

where:

$$F(s) = s^3 + s^2(\gamma_1+\gamma_2) + (\omega_0^2+\Omega_0^2+\gamma_1\gamma_2)s + \gamma_2\omega_0^2 + \gamma_1\Omega_0^2 \tag{12}$$

is the characteristic equation of the system (9). The angular velocity probability density function associated with eqn.(11) is that of $X_3(t)$ in eqn.(10), and since the random variables $\dot{W}_i(t)$ have a Gaussian probability distribution it follows that the probability density function is given by (in two dimensions):

$$f(X_3(t), t \mid X_1(0), X_2(0), X_3(0), X_4(0), 0)$$
$$= \left[\frac{3}{2\pi\langle Y_3^2(t)\rangle}\right]^{1/2} \exp\left[-\frac{3Y_3^2(t)}{2\langle Y_3^2(t)\rangle}\right] \tag{13}$$

where $Y_3(t) = X_3(t) - \langle X_3(t)\rangle$. This may be evaluated in terms of the roots of eqns.(12), and the resulting cumbersome expression is presented in appendix A. Integration of eqn.(13) over X_1, X_2 and X_4 gives the probability density function:

$$f(X_3(t), t \mid X_3(0), 0) \equiv f(\dot{\phi}_1(t), t \mid \dot{\phi}_1(0), 0) \tag{14}$$

A further integration of eqn.(14) produces eqn.(11).
The results, eqn.(14), may be obtained with the use of appendix A, giving:

$$f(\dot{\phi}_1(t), t \mid \dot{\phi}_1(0), 0) = \left[\frac{3}{2\pi y(t)}\right]^{1/2} \exp\left[-\frac{3\dot{\phi}_1(t)^2}{2y(t)}\right] \tag{15}$$

where:

$$y(t) = \frac{kT}{I_1}\left[1 - \frac{\langle\dot{\phi}_1(t)\dot{\phi}_1(0)\rangle^2}{\langle\dot{\phi}_1(0)\dot{\phi}_1(0)\rangle^2}\right]$$

This is identical with that obtained from the memory function representation of $\dot{\phi}_1(t)$, i.e.

$$\ddot{\phi}_1(t) + \int_0^t K(t-\tau)\dot{\phi}_1(\tau)\,d\tau = \Gamma(t) \tag{16}$$

Here, K(t) is the autocorrelation function of the non-Markovian, Gaussian angular acceleration $\Gamma(t)$ (Kubo's fluctuation-dissipation theorem). The Kubo theorem holds therefore for the angular velocity governed by eqn.(1). Given this equivalence it follows that the diffusion equation corresponding to eqns.(9) may be written in the form:

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \mathbf{A}}\cdot\left[\mathbf{C}_{\mathbf{A}}\mathbf{C}^{-1}_{\mathbf{A}}\mathbf{A}f\right] + \frac{1}{2}\frac{\partial}{\partial \mathbf{A}}\cdot\left[\mathbf{C}_{\mathbf{A}}\frac{d}{dt}\left(\mathbf{M}_0^{-1}\right)\mathbf{C}^{T}_{\mathbf{A}}\frac{df}{d\mathbf{A}}\right] \tag{17}$$

and possibly also the inertial corrected eqn.(1) which is as yet unknown. Here $\mathbf{A}(t)$ is a column vector of linearly independent dynamical variables chosen such that the angular velocity autocorrelation function is properly defined. $\mathbf{A}^{T}(t)$ is the corresponding row vector. In addition:

$$\mathbf{M}_0 \equiv \mathbf{C}^{T}_{\mathbf{A}}\mathbf{V}^{-1}\mathbf{C}_{\mathbf{A}},$$

$$\mathbf{V}(t) = \left\langle \mathbf{A}(o)\mathbf{A}^{T}(o)\right\rangle - \mathbf{C}_{\mathbf{A}}(t)\left\langle \mathbf{A}(o)\mathbf{A}^{T}(o)\right\rangle \mathbf{C}^{T}_{\mathbf{A}}(t),$$

$$\mathbf{C}_{\mathbf{A}}(t) = \left\langle \mathbf{A}(t)\mathbf{A}^{T}(o)\right\rangle\left\langle \mathbf{A}(o)\mathbf{A}^{T}(o)\right\rangle^{-1}.$$

Assuming that $\dot{\phi}_1(t)$ and $\dot{\phi}_2(t)$ are linearly independent, then eqn.(17) reduces to the Smoluchowski eqn. of the system (9) provided:

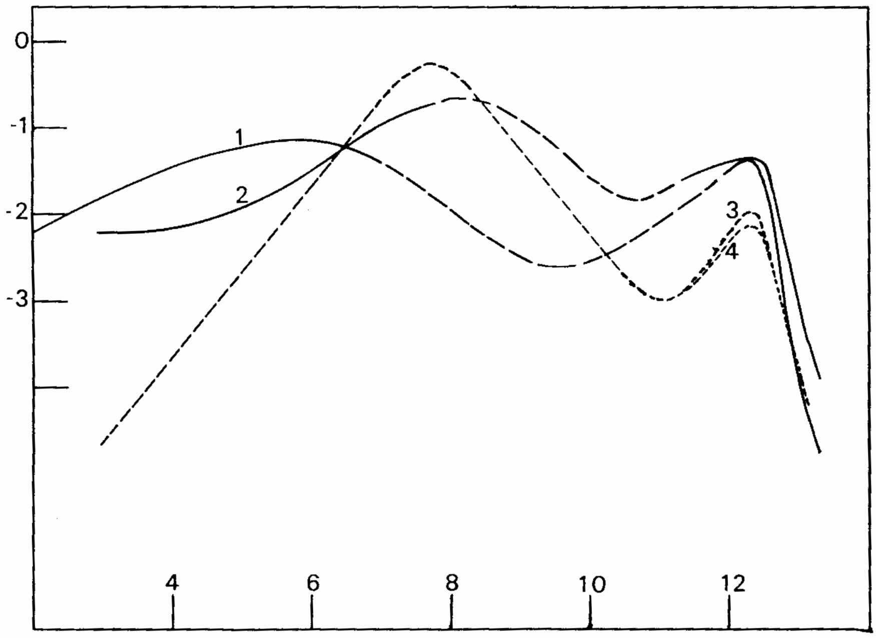
$$\mathbf{A}(t) = \begin{bmatrix}\dot{\phi}_1(t)\\ \dot{\phi}_2(t)\end{bmatrix}; \quad \phi_{\mathbf{A}}(t) = \begin{bmatrix}-\Omega_0^2 & \zeta_1\delta(t)+\Omega_0^2\\ \zeta_2\delta(t)+\omega_0^2 & -\omega_0^2\end{bmatrix}$$

$$F_{\dot{\mathbf{A}}}(t) = \begin{bmatrix}g_1(t)\\ g_2(t)\end{bmatrix}.$$

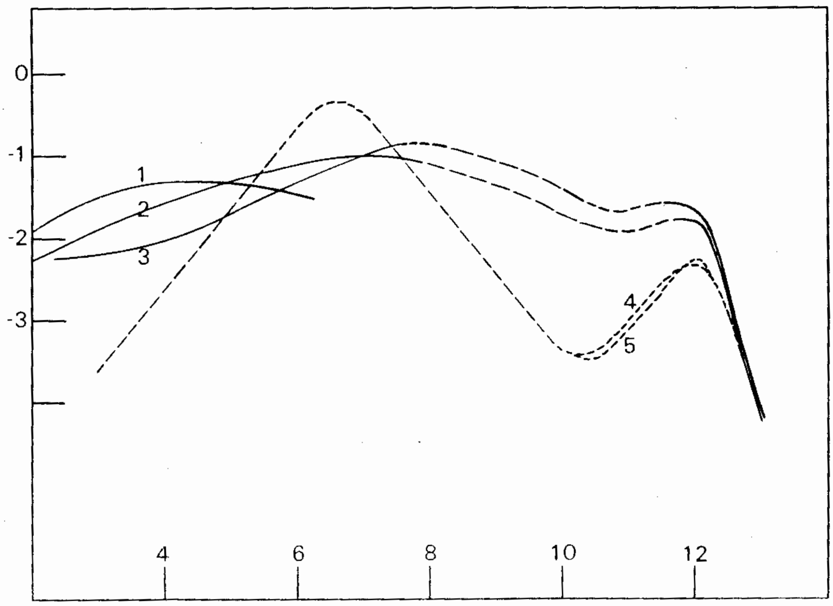
Here $\delta(t)$ is a Diraq delta function.

Results and Discussion

The parameters for best fit to some liquid and glassy solutions are shown in Table 1, and a typical frequency domain fitting in fig.1, where the loss has been converted into the conventional infra-red representation of power absorption coefficient $\alpha(\omega)$. A fit to glassy data is shown in fig.2, where the nature of the complete loss peak over fourteen decades is clearly delineated. It is clear from the extra peak at THz frequencies that no model of the molecular dyanmics in all environments can describe the complete loss profile without taking into consideration the inertial effects governing torsional oscillation at short times. These effects dominate the behaviour of various autocorrelation functions of $\phi_1(t)$ such as those (fig.3) of angular velocity, torque and rotational velocity $\left(\left\langle \frac{d}{dt}(\cos\theta(t))\left[\frac{d}{dt}(\cos\theta(t))\right]_0\right\rangle\right)$, the latter being the direct Fourier transform of the power absorption coefficient $\alpha(\omega)$. These are obtained from the model by adjusting ζ_1 and ω_0 to reproduce the loss and $\alpha(\omega)$ peaks of the liquid data. All three types of autocorrelation function oscillate about the



<u>Figure 2</u> (a) 'Complete' loss curve of 10% THF/decalin: (1) 77 K; (2) 110 K; (3) Theoretical curve, ζ_2 = 15 THz; (4) Theoretical curve, ζ_2 = 20 THz.



(b) 'Complete' loss curve of 10% fluorobenzene/decalin: (1) 77 K; (2) 110 K; (3) 127 K; (4) Theoretical curve, ζ_2 = 20 THz; (5) ζ_2 = 10 THz.

<u>Ordinate</u>: log $\epsilon''(\omega)$; <u>Abscissa</u>: log (ω/Hz)

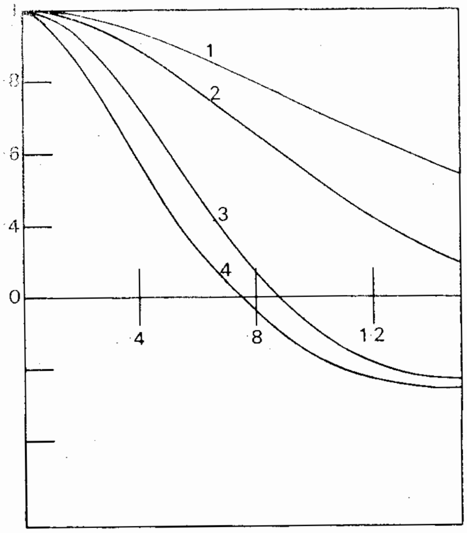
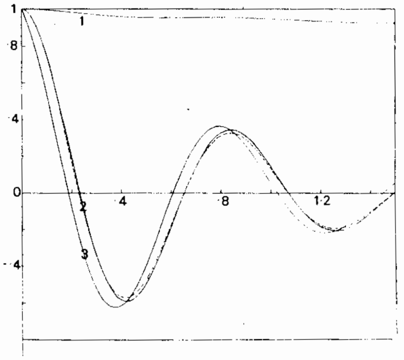


Figure 3 (a) Autocorrelation functions associated with ϕ_1 of eqns.(9), for CH_2Cl_2/decalin at room temperature.

(1) $\langle \cos\phi_1(t)\cos\phi_1(0)\rangle$; (2) $\langle \dot{\phi}_1(t)\dot{\phi}_1(0)\rangle$;

(3) $\left\langle \frac{d}{dt}\cos\phi_1(t)\left[\frac{d}{dt}\cos\phi_1(t)\right]_{t=0}\right\rangle$; (4) $\langle \ddot{\phi}_1(t)\ddot{\phi}_1(0)\rangle$

These illustrate average associated with (1) orientation; (2) angular velocity; (3) 'rotational' velocity (the Fourier transform of $\alpha(\bar{\nu})$); (4) torque.



(b) The same functions for the glass at 110 K. In this case the dotted curve (2) is that for 'rotational' velocity. Notice that all angular functions are now highly oscillatory except for function (1), the orientational a.c.f. (the Fourier transform of $\epsilon''(\omega)/\omega$).

Ordinate: f(t); Abscissa: $(\frac{kT}{I_1})^{1/2}t$.

Table 1

Parameters for Best Fit in Liquid and Glassy Decalin Solutions (0.1 mole fraction solute)

Sample in decalin solution	10^{39}xSolute moment of inertia (a) /gm cm^2	T/K	Far Infra-red(γ) Peak frequency /cm^{-1}	β peak Frequency /sec^{-1}	ϵ_0	ϵ_∞	$10^{-12}\zeta_1$ /sec^{-1}	$10^{-12}\zeta_2$ /sec^{-1}	Type of solution
CH_2Cl_2	2.37	300	58 ($1.1x10^{13}s^{-1}$)	$1.8x10^{11}$	2.56	2.19	30.9	20	Liquid
CH_2Cl_2	2.37	113	111 ($2.1x10^{13}s^{-1}$)	$2.0x10^4$	$\sim$ 3.4	2.41	$1.1x10^7$	20	Glass
CH_2Cl_2	2.37	110	112 ($2.1x10^{13}s^{-1}$)	$1.0x10^3$	$\sim$ 3.4	2.41	$2.0x10^8$	20	Glass
C_6H_5F	20.3	300	46 ($8.8x10^{12}s^{-1}$)	$2.0x10^{10}$	2.40	2.20			Liquid
C_6H_5F	20.3	110	58 ($1.1x10^{13}s^{-1}$)	$5.0x10^6$	$\sim$ 3.30	$\sim$ 2.41	$2.38x10^4$	20	Glass
C_6H_5F	20.3	77		$5.0x10^4$	$\sim$ 3.46	$\sim$ 2.44			Glass
Tetrahydro-furan	8	300	60 ($1.1x10^{13}s^{-1}$)		2.58	2.19			Liquid
		110	82 ($1.5x10^{13}s^{-1}$)	$\sim 10^8$	$\sim$ 3.50	$\sim$ 2.40	$6.04x10^3$	20	Glass
		77		$\sim 10^6$					Glass

(a) Reduced inertia I_2 = IxIy/(Ix + Iy).

Indicates a maximum uncertainty of $\pm$ 10%.

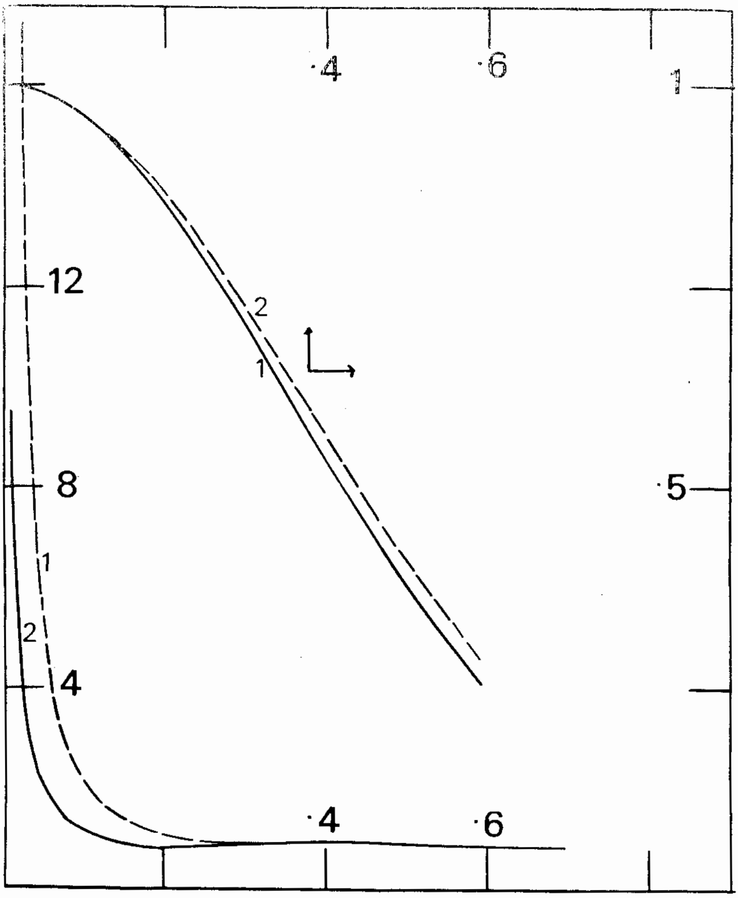


Figure 4   Probability density functions for fluorobenzene/decalin glass at 110 K.

Left hand curves: decay of peak height with time (bottom and left hand scales).

- - - (1) $f(X_3(t),t \mid X_1(o),X_2(o),X_3(o),X_4(o),o)$

—— (2) $f(X_3(t),t \mid X_3(o),o)$

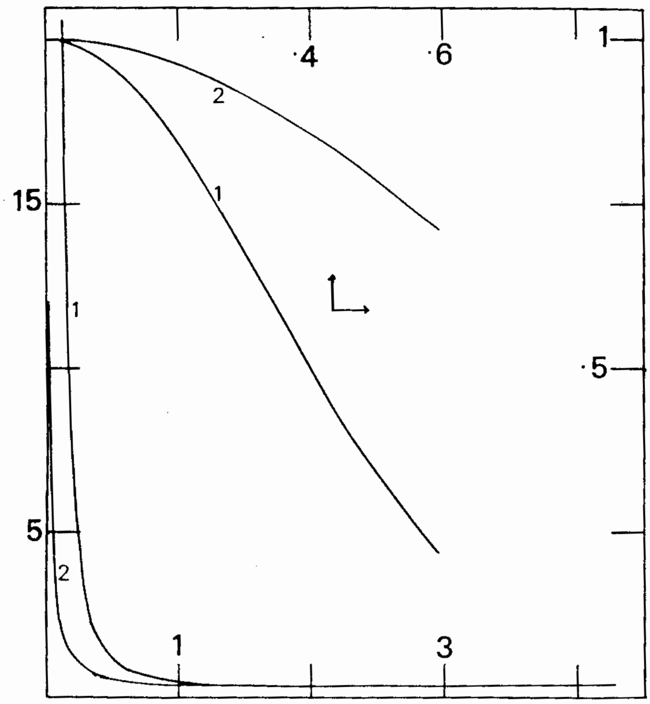
Right hand curves: p.d.f.'s for $t(kT/I_1)^{\frac{1}{2}} = 0.5$, angular velocity dependence (top and right hand scales).

—— (1) $f(X_3(t),t \mid X_1(o),X_2(o),X_3(o),X_4(o),o)$

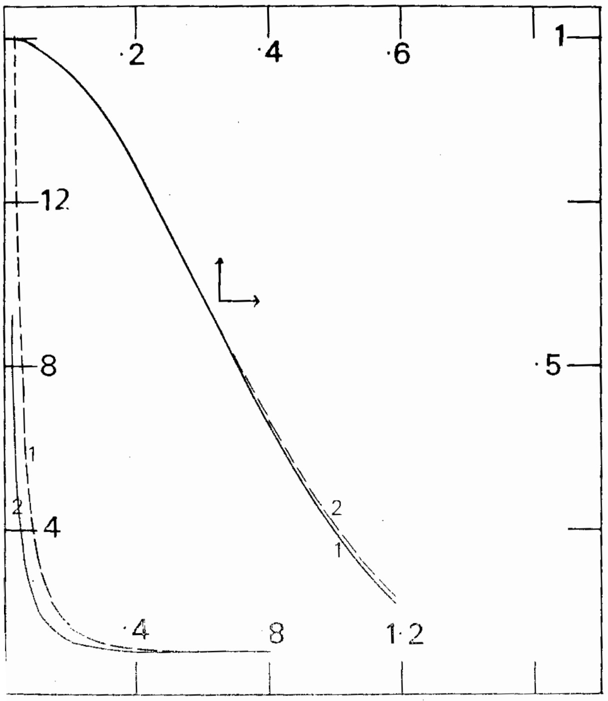
- - - (2) $f(X_3(t),t \mid X_3(o),o)$

Ordinate Scales: l.h.s. f(t);   r.h.s. $f(\phi_1)$.

Abscissae: top ϕ_1 $(I_1/kT)^{1/2}$;   bottom $t(kT/I_1)^{1/2}$.



Figures 5 and 6   As for figure 4, CH_2Cl_2/decalin, room temperature (300 K); THF/decalin at 110 K.



time axis reflecting the short time torsional oscillation. In some glassy solutions (figs.4 to 6) the oscillations are more pronounced than in the corresponding liquid solutions and are discernible in the related probability density functions $f(X_3(t), t \mid X_1(o), X_2(o), X_3(o), X_4(o), o)$ and $f(X_3(t), t \mid X_3(o), o)$. There is therefore periodically an increased probability of finding a molecule with a given angular velocity at times after the arbitrary, initial, t = o.

In other cases both types of probability density function rapidly fall to a constant value with time, indicating that correlation of angular velocity is rapidly lost. Another interesting feature is that the peak heights of the two functions decay to the same constant value at long enough times, but shortly after the initial t = o, it is, of course, more probable that $X_3(t)$ would be found given $X_1(o)$, $X_2(o)$, $X_3(o)$ and $X_4(o)$ than if given just $X_3(o)$ alone, so that f from eqn.(14) always decays the more rapidly.

Conclusions

(1) A very simple and straightforward model of molecular Brownian motion influenced by dipole-dipole interaction may be used to reproduce the main features of the loss profile up to THz frequencies in dilute liquid solutions, and with some unsatisfactory constraints, also in the glass.

(2) Consideration of dipole-dipole interaction leads to a broad distribution of relaxation times whatever the form of potential chosen.

(3) The aim of a simple molecular representation of the fluid state should be to reproduce, approximately, observable features in a wide range of environments and over a wide range of frequencies. In doing this it is of secondary importance only that some of the initial ideas are found to be at odds with the evidence (i.e. in the glass) since a formalism such as that of Coffey is flexible enough for considerable improvements to be made.

APPENDIX A

Denoting the roots of eqn.(12) by $-\alpha_1 \pm i\beta$ and α_2:

$$\langle y_3^2(t)\rangle = \frac{\omega_0^4 c^2}{(\alpha_1-\alpha_2)^2-\beta^2}\left[\frac{\beta^2+(\alpha_2-\alpha_1)^2}{2(\alpha_1^2+\beta^2)}\,\frac{(1-e^{-2\alpha_1 t})}{2\alpha_1}\right.$$

$$\left.+\frac{(1-e^{-2\alpha_2 t})}{2\alpha_2} - \frac{4\alpha_1}{(\alpha_1+\alpha_2)^2+\beta^2} + \frac{2\alpha_1-\alpha_2}{2(\alpha_1^2+\beta^2)}\right.$$

$$
+\frac{2e^{-(\alpha_1+\alpha_2)t}}{(\alpha_1+\alpha_2)^2+\beta^2}\left[(\alpha_1^2-\alpha_2^2-\beta^2)\frac{\sin\beta t}{\beta}+2\alpha_1\cos\beta t\right]
$$

$$
+\frac{e^{-2\alpha_1 t}}{2(\alpha_1^2+\beta^2)}\left[\frac{(\alpha_2-\alpha_1)}{\beta}(\alpha_1\sin 2\beta t+\beta\cos 2\beta t)\right.
$$

$$
+\beta\sin\beta t\cos\beta t\left(1-\frac{(\alpha_2-\alpha_1)}{\beta}\right)^2
$$

$$
\left.-\alpha_1\left(\cos^2\beta t+\left(\frac{\alpha_2-\alpha_1}{\beta}\right)^2\sin\beta t\right)\right]\Bigg\}.
$$

The constant c^2 is defined:

$$
\langle y_3^2(t)\rangle \xrightarrow[t\to\infty]{} \frac{kT}{I_1}.
$$

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