

# Use of the Memory Function to Simulate the Debye and Poley Absorptions in Liquids

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*Received 17th July, 1975*

A single, simple equation is derived to describe the molecular rotational processes giving rise to the microwave and far infrared absorption bands of dipolar molecules in the liquid phase. The absorption spectrum over  $\sim 3$  decades of frequency is deduced by approximating the associated orientational correlation function with a hierarchy of response functions (or memory functions). These and the correlation function form a set of integro-differential equations called the Mori series. By truncating this at a certain level, with an empirical function such as a single exponential of correlation time  $1/\gamma$ , a spectrum can be calculated which contains equilibrium averages proportional to the intermolecular mean square torque,  $\langle o(v)^2 \rangle$ , its derivative  $\langle \dot{o}(v)^2 \rangle$ , etc., depending on the level at which the Mori series is truncated. The formalism is tested with the liquids  $\text{CHF}_3$ ,  $\text{CClF}_3$ ,  $\text{CBrF}_3$ ,  $\text{HC}\equiv\text{CCH}_3$ , and the nematogen MBBA, a series chosen to cover the extremes of molecular isotropy and anisotropy.

## INTRODUCTION AND THEORETICAL CONSIDERATIONS

This paper aims to treat the microwave and far infrared absorption of dipolar liquids and mesophases as a dynamical entity encompassing the peaks known as the Debye and Poley absorptions. A spectrum is calculated by considering a simple approximation to the orientational autocorrelation function  $C_m(t)$  in the classical limit ( $\hbar \rightarrow 0$ ). In this condition  $C_m(t)$  has a Maclaurin expansion in time which contains no odd powers, which explains why the Debye representation, with its exponential  $C_m(t)$ , is badly behaved at short times (*i.e.*, at far infrared frequencies) and fails to predict a return to transparency of the power absorption coefficient,  $\alpha(\omega)$ , (*cf.* the Beer-Lambert law) on the high frequency side.

By considering a hierarchy of memory functions <sup>1, 2</sup> ( $K_0, \dots, K_n$ ), and terminating this series at a high enough order, a correlation function  $C_m(t)$  is generated which is Fourier-transformed to its associated spectrum  $C_m(-i\omega)$ , where  $\omega$  is the angular velocity. The expression for  $C_m(-i\omega)$  contains two equilibrium averages,  $K_0(0)$  and  $K_1(0)$ , having the units of  $\text{s}^{-2}$ , the former being a single molecule property, and the latter being proportional to a mean intermolecular squared torque  $\langle o(v)^2 \rangle$ . In addition it contains a correlation time  $\gamma^{-1}$  which is phenomenological. The averages  $K_0(0)$ ,  $K_1(0)$ ,  $\dots$ ,  $K_n(0)$ ,  $n$  being the order of truncation, are related to the spectral moments:

$$\int_0^\infty \omega^n \alpha(\omega) d\omega$$

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of the absorption and are not independent variables. Their behaviour is restricted by the fact that the total integrated intensity of all rotational type motions over frequencies from static to  $\sim 250 \text{ cm}^{-1}$  produced by any formalism must be the same as that observed for each molecule (Gordon's sum rule<sup>3</sup>).

The effect of truncating at second order, and of taking a Gaussian form for the first order memory function  $K_1(t)$  is studied in relation to systems where the torques are not Markovian, *i.e.*, where states other than the last occupied by a process are relevant in determining its future behaviour.

#### FORMALISM

The equation proposed by Langevin to account for translational Brownian motion can be extended to describe the rotational (or trochilic) counterpart :

$$\dot{\omega} + \beta\omega = \Gamma(t), \quad (1)$$

where  $\Gamma(t)$  in this equation has the dimensions of angular acceleration, so that  $F(t) = m\Gamma(t)$  is the stochastic or random, torque on a molecule of mass  $m$  due to its neighbours.  $\beta$  is a friction tensor with the units of frequency, with  $\omega$  as the angular velocity in  $\text{rad s}^{-1}$ . In this representation  $F(t)$  has the following properties :

- (i) It is stationary in time,<sup>2</sup> with a Gaussian probability distribution.
- (ii) It has an infinitely short correlation time, so that :

$$\langle F(0) \cdot F(t) \rangle = D\delta(t)$$

where  $\delta(t)$  is a delta function and  $D$  is the classical<sup>1</sup> diffusion tensor.

- (iii) No correlation exists between the kinetic moment of the molecule and the random angular acceleration, so that :

$$\langle \omega(0) \cdot \Gamma(t) \rangle = 0.$$

The autocorrelation function which eqn (1) yields upon direct integration is :

$$C_\omega(t) = \langle \omega(0) \cdot \omega(t) \rangle = \exp(-\beta t) \langle \omega(0) \cdot \omega(0) \rangle, \quad (2)$$

a pure exponential. Fourier inversion of eqn (2) leads to the Debye equations for the complex spectral density  $S(\omega)$ , given by :

$$S(\omega) = D/(\beta + i\omega)^2. \quad (3)$$

By Doob's theorem,<sup>1, 2</sup> the angular velocity probability distribution is rigorously Markovian, so that it is unaffected by past events in the ensemble. This is the classical treatment of Debye for liquid phase microwave absorption in liquids due to vestigial molecular rotation of viscously damped molecules taking place by infinitely fast, infinitesimally small, changes of angular velocity, so that all dynamical coherence (including molecular inertia) is neglected.<sup>4</sup> The general theory of random processes shows that the derivative  $|\dot{C}_\omega(t)|_{t=0}$  must be well defined. This is not the case for eqn (2), showing that the random variable  $F(t)$ , of infinitely short correlation time, has no physical reality. These flaws manifest themselves experimentally<sup>4</sup> in the far infrared (upwards from the microwave to  $\sim 250 \text{ cm}^{-1}$ ), where eqn (3) produces the Debye plateau in  $\alpha(\omega)$ , an asymptote that appears at about  $20\text{-}50 \text{ cm}^{-1}$  and does not return to spectral transparency. The observed absorptions in liquids are characterised<sup>4</sup> by the Poley band of dipolar molecules (see figures) which rises well above this plateau, transparency being regained at  $\sim 100$  or  $200 \text{ cm}^{-1}$ .

In this paper we link the microwave to the Poley absorption by considering a more realistic model for the behaviour of  $F(t)$ . In general, it is required that : (i)  $F(t)$  be not necessarily Gaussian, and have a finite correlation time ; (ii) the friction tensor  $\beta$  be dependent on time.

These conditions are fulfilled by a more general form of the Langevin eqn (1), proposed by Kubo and others:<sup>2</sup>

$$\dot{\omega}(t) + \int_0^t K_{\omega}(t-\tau')\omega(\tau') d\tau' = \Gamma(t) \quad (4)$$

where  $K_{\omega}(t)$  is a time-dependent friction tensor, known as the memory function. As for the simple eqn (1):

$$\langle \Gamma(t) \rangle = 0; \quad \langle \omega(0) \cdot \Gamma(t) \rangle = 0.$$

Starting from the modified Langevin equation, it is possible to show that:

$$\frac{d}{dt} \langle \omega(0) \cdot \omega(t) \rangle = - \int_0^t K_{\omega}(t-\tau') \langle \omega(0) \cdot \omega(\tau') \rangle d\tau' + \langle \omega(0) \cdot \Gamma(t) \rangle. \quad (5)$$

The memory function is the correlation function of the random torque, a result known as the second fluctuation-dissipation theorem:

$$\langle \omega(0) \cdot \omega(t) \rangle K_{\omega}(t) = \langle \Gamma(0) \cdot \Gamma(t) \rangle. \quad (6)$$

Rotational type<sup>5,7</sup> far infrared and microwave bands of dipolar molecules have their associated time auto-correlation functions defined by:<sup>7</sup>

$$C_m(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \int_{-\infty}^{\infty} \exp(i\omega t) \frac{3\hbar c}{4\pi^2} \frac{\sigma(\omega) d\omega}{\omega [1 - \exp(-\hbar\omega/kT)]} \quad (7)$$

where  $\sigma(\omega)$  is the absorption cross-section per molecule and  $\mathbf{u}$  is a unit vector in the dipolar axis. Using the classical limit of  $C_m(t)$  in eqn (5) gives:

$$\dot{C}_m(t) = - \int_0^t K_0(t-\tau') C_m(\tau') d\tau' \quad (8)$$

with  $K_0(t-\tau')$  as the associated response function whose Fourier transform would be the frequency dependent friction coefficient.

It can be shown<sup>2</sup> that the set of memory functions  $K_0(t), \dots, K_n(t)$  obey the set of coupled Volterra equations such that:

$$\frac{\partial}{\partial t} K_{n-1}(t) = - \int_0^t K_n(t-\tau') K_{n-1}(\tau') d\tau'.$$

Taking Laplace transforms:

$$\tilde{C}_m(p) = \frac{C_m(0)}{p + \tilde{K}_0(p)} = \frac{C_m(0)}{p + \tilde{K}_0(0)} = \dots \quad (9)$$

This is Mori's continued fraction representation of the correlation function  $C_m(t)$ ,  $p$  being the Laplace variable. The associated complex spectral density is  $C_m(-i\omega)$ , the Fourier-Laplace transform of  $\tilde{C}_m(p)$ , and can be obtained by truncating the series of eqn (9) using a suitable form for  $K_n(t)$ . It is shown below how the equilibrium averages  $K_0(0), \dots, K_{n-1}(0)$  are related to the terms in the even time expansion of  $C_m(t)$ , so that, for a linear molecule or a symmetric top,  $K_0(0) = 2kT/I_B$  (where  $I_B$  is the moment of inertia perpendicular to the dipole axis) *i.e.*, is a single molecule property, and  $K_1(0)$  is related to the intermolecular mean square torque  $\langle o(v)^2 \rangle$ . Any truncation of the series (9) that leaves out  $\tilde{K}_1(p)$  and higher functions cannot account for this torque without inbuilt singularities. Such is the termination  $K_0(t) = K_0(0) \exp(-\gamma t)$ , which corresponds to the  $M$ -diffusion model of instantaneous

molecular collisions where the torque becomes infinite at the instant of impact, and where the molecular angular velocity vector is randomised in direction. The  $J$ -diffusion model,<sup>2</sup> in which  $\omega$  is randomised in magnitude as well, is easily derived<sup>16</sup> using the truncation :

$$K_0(t) = {}^{(\text{FR})}K_0(0) \exp(-\gamma|t|)$$

where  ${}^{(\text{FR})}K_0(0)$  refers to the function  $K_0(0)$  for a Gaussian ensemble of free rotors.

One of the simplest ways of introducing a finite  $\langle o(v)^2 \rangle$  is to use the truncation :<sup>1</sup>

$$K_1(t) = K_1(0) \exp(-\gamma t) \quad (10)$$

*i.e.*, to truncate the series (9) at 1st order. In this work we investigate also the spectral consequences of the 2nd order truncation :

$$K_2(t) = K_2(0) \exp(-\gamma t) \quad (11)$$

and of taking the Gaussian function :

$$K_1(t) = \frac{2}{\sqrt{\pi}} K_1(0) \exp(-\gamma^2 t^2). \quad (12)$$

#### FIRST ORDER TRUNCATION

(a) If  $K_1(t) = K_1(0) \exp(-\gamma t)$ , then

$$\tilde{K}_1(p) = \frac{K_1(0)}{p + \gamma}$$

so that

$$\tilde{C}_m(p) = \frac{p^2 + p\gamma + K_1(0)}{p^3 + p^2\gamma + p[K_0(0) + K_1(0)] + \gamma K_0(0)}. \quad (13)$$

The absorption coefficient (neper  $\text{cm}^{-1}$ ) is given<sup>6</sup> by :

$$\alpha(\omega) \propto \omega^2 \text{Re}[\tilde{C}_m(-i\omega)]$$

*i.e.*, is related to the real part of the Fourier-Laplace transform of  $\tilde{C}_m(p)$ . Thus :

$$\alpha_1(\omega) \propto \frac{\omega^2 K_0(0) K_1(0) \gamma}{\gamma^2 [K_0(0) - \omega^2]^2 + \{\omega^3 - [K_0(0) + K_1(0)]\omega\}^2}. \quad (14)$$

When  $\omega^4$  [with  $\omega$  normalised in units of  $(2kT/I_B)^{1/2}$ ] is very small compared with  $\omega^2$  (normalised), which for common values of the parameters involved will occur for frequencies  $\omega < 10^{11} \text{ rad s}^{-1}$ , then eqn (14) reduces to the Debye-type spectrum of eqn (3), *i.e.* :

$$\alpha_1(\omega) \rightarrow \frac{\omega^2 K_0(0) K_1(0) \gamma}{\gamma^2 K_0^2(0) + \{K_0^2(0) + K_1^2(0) + 2K_0(0)[K_1(0) - \gamma^2]\}\omega^2} \quad (15)$$

if, and only if :

$$[K_0(0) + K_1(0)]^2 > 2K_0(0)\gamma^2. \quad (16)$$

This inequality imposes a restriction on the quantities  $K_0(0)$ ,  $K_1(0)$  and  $\gamma$  of eqn(14).

The overall memory function  $[K_m(t)]$  corresponding to  $C_m(t)$  is defined by :

$$\tilde{K}_m(p) = p + \tilde{C}_m^{-1}(p) \quad (17)$$

so that eqn (10) implies that :

$$\begin{aligned}
 K_m(t) &= K_0(0) e^{-\gamma t/2} \left[ \cos at + \frac{\gamma}{2a} \sin at \right] \quad \text{if } K_1(0) > \gamma^2/4 \\
 &= K_0(0) e^{-\gamma t/2} \left[ \cosh bt + \frac{\gamma}{2b} \sinh bt \right] \quad \text{if } K_1(0) < \gamma^2/4 \\
 &= K_0(0) e^{-\gamma t/2} [1 + \gamma t/2] \quad \text{if } K_1(0) = \gamma^2/4
 \end{aligned} \quad (18)$$

with  $a^2 = -b^2 = [K_1(0) - \gamma^2/4]$ .

For the purpose of physical interpretation of the truncation at first order, it is relevant to note that this form for  $K_m(t)$  is the same as that <sup>6</sup> for the angular velocity correlation function derived from the  $M$ -diffusion model of a vibrator perturbed by a Poisson distribution of collisions randomising the angular velocity vector in direction. Using the second fluctuation-dissipation theorem, it is clear that  $K_m(t)$ , the time autocorrelation function of the random external torque, is  $M$ -diffuse in character.

This implies that we now have a well defined torque, but that its derivative  $\langle \dot{\delta}(v)^2 \rangle$  is singular at the instant of collision. This is linked with the fact that the Maclaurin expansion of our  $C_m(t)$  is even up to  $t^4$ , but contains a term in  $t^5$ , whereas classically <sup>2</sup> there is no  $t^5$  term and  $\langle \dot{\delta}(v)^2 \rangle$  appears only in the  $t^6$  coefficient. The Debye model [ $\tilde{K}_0(p) = \gamma$ ] corresponds to a randomisation of molecular position at every collision (no dynamical coherence— inertia being neglected <sup>4</sup>): the  $M$ -diffusion model [ $\tilde{K}_0(p) = K_0(0)/(p + \gamma)$ ] is a randomisation of the direction of the angular velocity at every collision; and the 1st order truncation is a randomisation of the direction of the molecular angular acceleration vector. The torque correlation function  $K_m(t)$  is no longer exponential [eqn (18)] so the statistical behaviour of the torque is no longer Markovian, *i.e.*, the system at any future instant is influenced by past events.

(b) If  $K_1(t) = \frac{2}{\sqrt{\pi}} K_1(0) \exp(-\gamma^2 t^2)$ , then:

$$\tilde{K}_1(p) = \frac{K_1(0)}{\gamma} \exp(p^2/4\gamma^2) \operatorname{erfc}(p/2\gamma) \quad (19)$$

$$\text{where } \operatorname{erfc}(p/2\gamma) = 1 - \frac{2}{\sqrt{\pi}} \exp\left(-\frac{p^2}{4\gamma^2}\right) \sum_{n=0}^{\infty} \left[ \frac{2^n}{1.3 \dots (2n+1)} \left(\frac{p}{2\gamma}\right)^{2n+1} \right].$$

Thus, substitution into eqn (12) gives, eventually:

$$\alpha_2(\omega) = \frac{\omega^2 K_0(0) K_1(0) \gamma^{-1} \exp(-\omega^2/4\gamma^2)}{\left\{ B \omega \sum_{n=0}^{\infty} \left[ \frac{2^n}{1.3 \dots (2n+1)} \left(\frac{\omega}{2\gamma}\right)^{2n+1} \right] - \omega^2 + K_0(0) \right\}^2 + A^2 \omega^2} \quad (20)$$

$$\text{with } A = \frac{K_1(0)}{\gamma} \exp(-\omega^2/4\gamma^2) \text{ and } B = \frac{2K_1(0)}{\sqrt{\pi}\gamma}.$$

At low frequencies [cf eqn (14) and (15)]:

$$\begin{aligned}
 \alpha_2(\omega) &\rightarrow \frac{1 - \omega^2/4\gamma^2}{[B\omega^2/2\gamma - \omega^2 + K_0(0)]^2 + A^2\omega^2} \\
 &\div \left[ K_0(0)^2 + \omega^2 \left( \frac{K_0^2(0)}{4\gamma^2} + 2K_0(0) \left( \frac{B}{2\gamma} - 1 \right) + A^2 \right) \right]^{-1}
 \end{aligned}$$

which is Debye-type behaviour if, and only if,

$$\left[ \frac{K_0^2(0)}{4} + K_1^2(0) + \frac{2}{\sqrt{\pi}} K_0(0) K_1(0) \right] > 2K_0(0)\gamma^2.$$

## SECOND ORDER TRUNCATION

In this case :

$$K_2(t) = K_2(0) \exp(-\gamma t)$$

giving

$$\alpha_3(\omega) \propto \frac{\omega^2 \gamma K_0(0) K_1(0) K_2(0)}{\left\{ \gamma^2 \{ \omega^3 - \omega [K_0(0) + K_1(0)] \}^2 + \{ \omega^4 - \omega^2 [K_0(0) + K_1(0) + K_2(0)] + K_0(0) K_2(0) \}^2 \right\}} \quad (21)$$

which reduces to the Debye-type equation :

$$\alpha_3(\omega) \rightarrow \frac{\omega^2 K_0(0) K_1(0) K_2(0) \gamma}{\left\{ \gamma^2 [K_0(0) + K_1(0)]^2 - 2 K_0(0) K_2(0) [K_0(0) + K_1(0) + K_2(0)] \omega^2 + K_0^2(0) K_2^2(0) \right\}} \quad (22)$$

giving for this  $\gamma$  a lower bound :

$$[K_0(0) + K_1(0)]^2 \gamma^2 > 2 K_0(0) K_2(0) [K_0(0) + K_1(0) + K_2(0)].$$

It can be seen from eqn (14) and (21) that  $\alpha(\omega)$  falls off more steeply on the high frequency side as the hierarchy is truncated at higher order. This means a narrower half width to the  $\alpha(\omega)$  curve and thus a less damped oscillation in the time correlation function  $C_m(t)$ . For the sake of completeness, and in order to demonstrate the overall form of equations for  $\alpha(\omega)$  derived from yet higher order truncation, we give  $\alpha(\omega)$  from the third order memory function below :

$$\alpha(\omega) \propto \omega^2 \gamma K_0(0) K_1(0) K_2(0) K_3(0) / D \quad (23)$$

where :

$$D = \gamma^2 \{ \omega^4 - \omega^2 [K_0(0) + K_1(0) + K_2(0)] + K_0(0) K_2(0) \}^2 + \{ \omega^5 - \omega^3 [K_0(0) + K_1(0) + K_2(0) + K_3(0)] + \omega [K_1(0) K_3(0) + K_0(0) K_3(0) + K_0(0) K_2(0)] \}^2.$$

## SERIES EXPANSION OF THE CORRELATION FUNCTION

Gordon <sup>7</sup> has shown that  $C_m(t)$  has the form :

$$C_m(t) = \sum_{n=0}^{\infty} a_n \frac{t^{2n}}{(2n)!} \quad (24)$$

where  $a_0 = 1$  by definition, and successive  $a_n$  are alternatively negative and positive. From eqn (9) it can be shown (appendix 1) that the memory functions  $K_0, K_1, K_2, \dots$  must also take the form of eqn (24). Therefore :

$$\left. \begin{aligned} K_0(t) &= \sum_{n=0}^{\infty} {}^0k_n \frac{t^{2n}}{(2n)!} \\ K_1(t) &= \sum_{n=0}^{\infty} {}^1k_n \frac{t^{2n}}{(2n)!} \\ K_2(t) &= \sum_{n=0}^{\infty} {}^2k_n \frac{t^{2n}}{(2n)!} \end{aligned} \right\} \quad (25)$$

Solving the first eqn (9) for  ${}^0k_n$  in terms of  $a_N$  gives, for  $N \geq 1$ :

$${}^0k_N = -a_{N+1} - \sum_{n=1}^N k_{N-n} a_n \quad (26)$$

so that the coefficients  ${}^0k_N$  are known in terms of  $a_N$  and their precursors. The first two coefficients are given by:

$${}^0k_0 = -a_1 = K_0(0) = 2kT/I_B \quad (27)$$

$${}^0k_1 = -a_2 - {}^0k_0 a_1 = a_1^2 - a_2 \quad (28)$$

so that  $K_0(t)$ ,  $K_1(t)$  and  $K_2(t)$  are determined analytically by the coefficients of  $C(t)$  in even powers of time through the use of the eqn (25). Thus:

$${}^1k_0 = K_1(0) = a_1 - a_2/a_1 \quad (29)$$

$${}^2k_0 = K_2(0) = (a_1^2 - a_1 a_3)/[a_1(a_2 - a_1^2)]. \quad (30)$$

Darmon, Gerschel and Brot<sup>8</sup> have shown that  $a_1$ ,  $a_2$  and  $a_3$  are given in terms of the experimental spectral moments  $\int_0^\infty \omega^n \alpha(\omega) d\omega/N_1$ ,  $n = 0, \dots, m$ , with  $N_1$  as the molecular number density as follows:

$$a_1 = -\Xi \int_0^\infty \alpha(\bar{\nu}) d\bar{\nu} \quad (31a)$$

$$a_2 = 4\pi^2 c^2 \Xi \int_0^\infty \bar{\nu}^2 \alpha(\bar{\nu}) d\bar{\nu} \quad (31b)$$

$$a_3 = -16\pi^4 c^4 \Xi \int_0^\infty \bar{\nu}^4 \alpha(\bar{\nu}) d\bar{\nu} \quad (31c)$$

*etc.*, where  $\omega = 2\pi\bar{\nu}c$ , and:

$$\Xi = \frac{3kTc^2}{\pi N_1 \mu^2} [9n_\infty/(n_\infty^2 + 2)^2]$$

with  $\mu$  as the dipole moment,  $n_\infty$  the D-line refractive index,  $c$  the velocity of light,  $k$  the Boltzmann constant, and  $T$  the absolute temperature.

Thus eqn (14), (20) and (21) yield the power spectrum  $\alpha(\omega)$  at all frequencies from static to  $\sim 250 \text{ cm}^{-1}$  with two unknown variables  $\gamma$  and  $K_1(0)$ , together with  $K_2(0)$  for second order termination of the series (9). Eqn (31) are used to ensure that the observed and calculated integrated intensity per molecule agree, *i.e.*, if Gordon's sum rule holds, the number of unknown parameters drops to one, the correlation time  $\gamma^{-1}$ . However, there always remains the phenomenon of induced dipolar absorption, which gives rise to absorption in non-dipolar liquids and gases<sup>10</sup> in the far infrared, and which is present in the spectra of dipolar liquids as well. Ideally, this ought to be subtracted from  $\alpha(\bar{\nu})$  before calculating  $a_2$  or  $a_3$ , but since the dependence of  $\bar{\nu}$  on  $\alpha$  is unknown for induced dipolar absorption in general, this subtraction is in practice possible only for  $a_1$ , the single molecule property.

## DISCUSSION

Sum rules for the permanent dipolar contribution to  $K_1(0)$  and  $K_2(0)$  have not been developed, and it is known<sup>4,9</sup> that in dense liquids, the integrals in eqn (31b) and (31c) will contain a 50 % or more contribution from induced dipoles. However, eqn (27) and (28) give

$$|a_3| > \frac{I_B a_2^2}{2kT} > \left( \frac{I_B}{2kT} \right)^{-3} \quad (32)$$

for positive  $K_1(0)$  and  $K_2(0)$ . Therefore, in calculating  $\alpha(\omega)$  with eqn (14), (20) or (21) we use eqn (31) and (32) as guidelines to  $K_1(0)$  [and, when necessary,  $K_2(0)$ ] and regard  $\gamma^{-1}$  as a free variable. The final fit to the experimental data is then carried out by a least mean squares iteration.

The proportionality constant in eqn (14), (20) and (21) is given by :

$$\frac{4\pi N\mu^2}{3kTcV} = \frac{(\epsilon_0 - \epsilon_\infty)}{n(\bar{\nu})c} \quad (33)$$

which is corrected for internal field effects<sup>8</sup> by the factor  $[(n_\infty^2 + 2)^2/9n_\infty]$ . In eqn (33)  $n(\bar{\nu})$  is the frequency dependent refractive index, and  $(\epsilon_0 - \epsilon_\infty)$  the dispersion over the

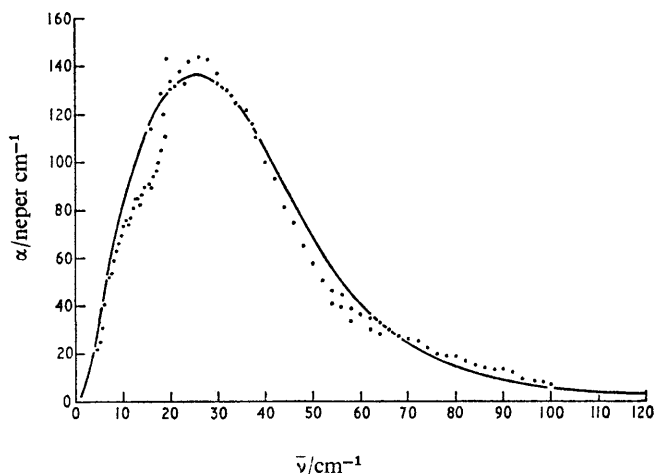


FIG. 1.—Observed and calculated [eqn (14)] power spectrum for liquid  $\text{HCF}_3$  at 296 K. ● Exp. (Baize<sup>11</sup>); — eqn (14) with  $\gamma$ ,  $K_0(0)$  and  $K_1(0)$  as in table 1.

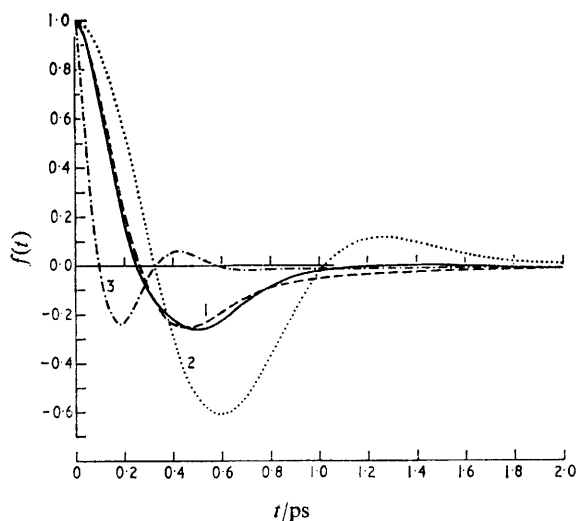


FIG. 2. — Fourier transform<sup>14</sup> of  $\alpha(\bar{\nu})$ <sup>11</sup> normalised to unity at  $t = 0$  for  $\text{CHF}_3(\text{l})$  at 296 K. --- (1)  $f(t)$  from eqn (35); (2) gas phase free rotor<sup>18</sup> at 296 K; (3) Larkin-Brot model<sup>5, 18</sup> at 296 K.



complete frequency span of absorption.<sup>4</sup> Eqn (33) is strictly valid where the molecule under consideration is not strongly dipolar, since Brot *et al.*<sup>8</sup> have shown that the internal field correction is, in general, frequency dependent, and the loss factor  $\varepsilon''(\omega)$  is sensitive to the particular expression used (*e.g.*, Lorentz or Onsager). However,  $\alpha(\omega)$  is much less affected by this correction when the original Lorentz or Onsager expressions are applied to the case where not merely a single molecule, but rather a group of intercorrelated molecules is constrained in the cavity for which the internal field has been computed. Since we deal with autocorrelation functions, cross correlations such as this can be represented only by a Kirkwood factor ( $g$ ) in the numerator of eqn (33).

Eqn (14) has been compared with the experimental absorptions observed in the far infrared for liquid  $\text{CHF}_3$ ,  $\text{CClF}_3$  and  $\text{CBrF}_3$ , pseudo-spherical species<sup>11, 19</sup> (fig. 1, 3, 5), and for liquid propyne<sup>12</sup> a less isotropic, almost linear molecule (fig. 7). The microwave data of Maurel and Price<sup>13</sup> for the nematogen *N*-(*p*-methoxybenzylidene)-*p*'-n-butylaniline (MBBA), a very anisotropic molecule, have been fitted (fig. 9 and 11) using eqn (14), and the theoretical far infrared curve (fig. 9) generated therefrom. The comparison has been extended to the time domain (fig. 2, 4, 6, 8 and 10) using the function:<sup>18</sup>

$$f(t) = \frac{\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle}{\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(0) \rangle} = \int_0^\infty \alpha_1(\omega) \cos \omega t \, d\omega / \int_0^\infty \alpha_1(\omega) \, d\omega \quad (34)$$

[derived from  $\alpha_1(\omega)$  of eqn (14)] in comparison<sup>8</sup> with the direct Fourier transform of the experimental  $\alpha(\omega)$  curves. In eqn (34)  $\mathbf{u}$  is the unit dipole vector, and the

TABLE 1.—PARAMETERS OF EQN (14) FOR THE CURVES OF FIG. 1-11

molecule	$T/\text{K}$	$\gamma$	$K_1(0)$	$K_0(0)$	$10^{-12} \omega_0 \equiv (2kT/gI)^{1/2} / \text{rad s}^{-1}$
$\text{CHF}_3$	296	4	8	1	2.25
$\text{CClF}_3$	288	5.5	10	1	1.79
$\text{CBrF}_3$	295	5.0	10.5	1	1.43
propyne	296	4	25	1	2.89
MBBA	340	2	200	0.78 <sup>13</sup>	1.44

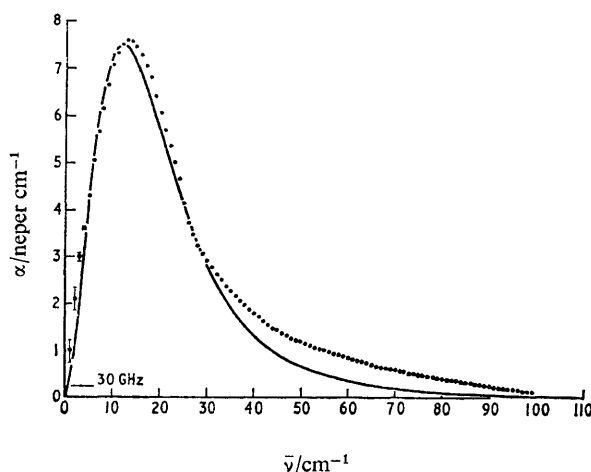


FIG. 3.—As for fig. 1 for  $\text{CClF}_3$  (l)<sup>19</sup> at 288 K.

unnormalised  $f(t)$  is the negative of the second derivative of  $C_m(t)$ . It is significant that for propyne, both  $f(t)$  and the corresponding experimental curve (fig. 8) show pronounced short time oscillations,<sup>10, 14</sup> a phenomenon recently observed by Gerschel<sup>15</sup> in low temperature  $\text{CHF}_3(\text{l})$ . The amplitude of these oscillations is inversely proportional to the width of the  $\alpha(\omega)$  curve in the frequency domain, and, therefore,

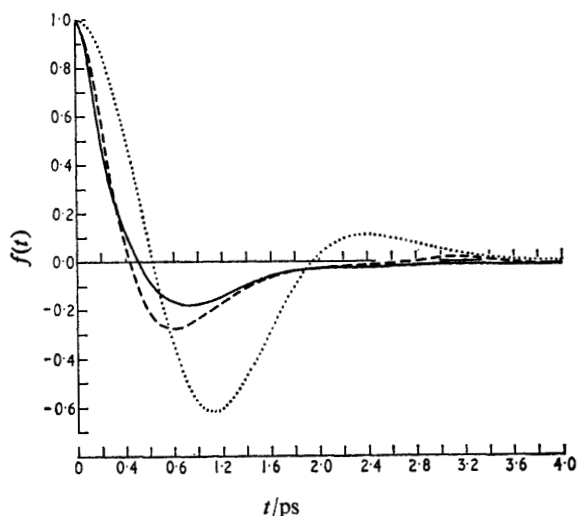


FIG. 4.— — As for fig. 2; ---  $f(t)$  from eqn (35); ..... free rotor for  $\text{CClF}_3$ <sup>19</sup> at 288 K.

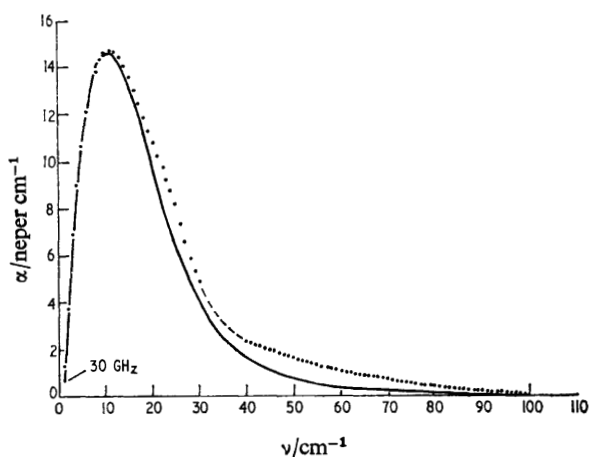


FIG. 5.—As for fig. 1 for  $\text{CBrF}_3(\text{l})$  at 295 K.

directly related to  $K_1(0)$ . This means that the oscillations in  $f(t)$  are amplified as the intermolecular mean square torque  $\langle o(v)^2 \rangle$  increases, since, for symmetric tops:<sup>16</sup>

$$K_1(0) \propto a_2 = 8 \left( \frac{kT}{I_B} \right)^2 \left( 1 + \frac{I_A}{4I_B} + \frac{\langle o(v)^2 \rangle}{k^2 T^2} \right) \quad (35)$$

where  $I_A$  and  $I_B$  correspond to the well known rotational constants  $A$  and  $B$ .

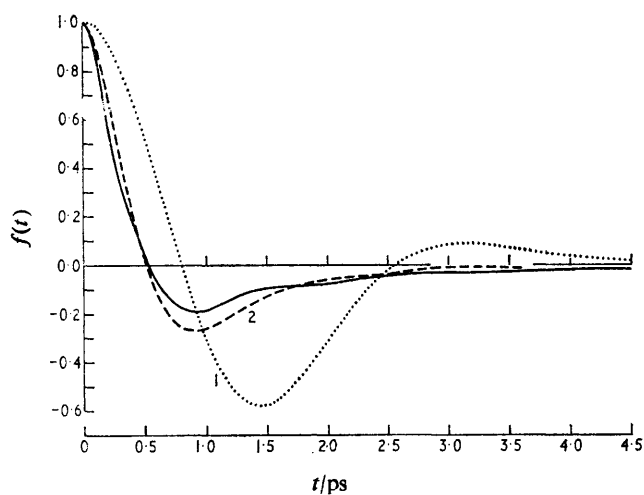


FIG. 6.— — As for fig. 2; ---  $f(t)$  from eqn (35); ..... free rotor for  $\text{CBrF}_3$  <sup>19</sup> at 295 K.

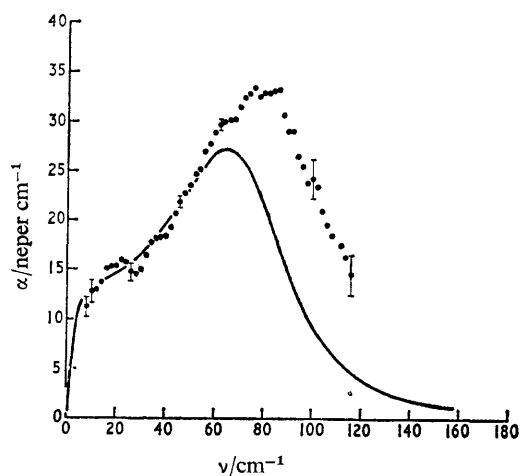


FIG. 7.—As for fig. 1 for propyne (l) <sup>12</sup> at 296 K.

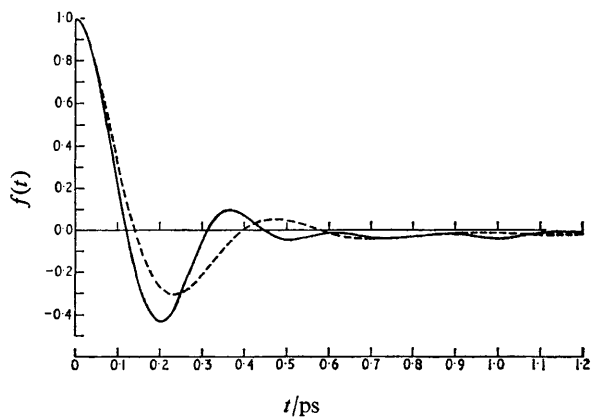


FIG. 8.— — As for fig. 2; ---  $f(t)$  from eqn (35); ..... for propyne <sup>12</sup> at 296 K.

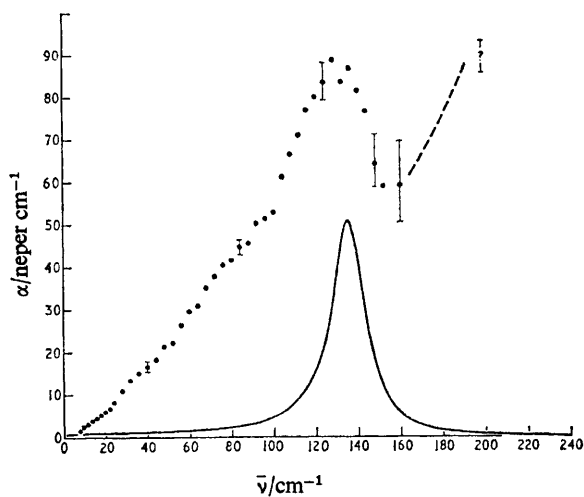


FIG. 9.—As for fig. 1 for MBBA (isotropic phase) at 340 K.

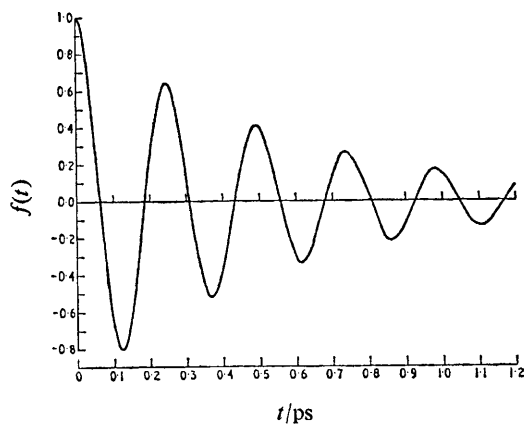


FIG. 10.— $f(t)$  for MBBA at 340 K.

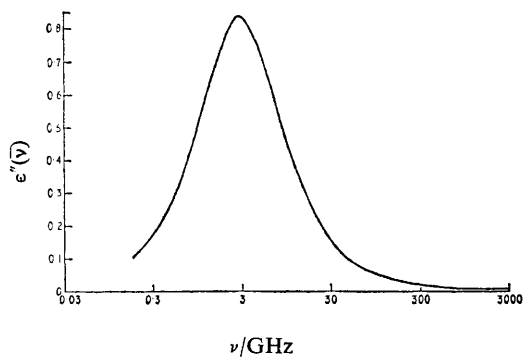


FIG. 11.—Loss curve calculated for MBBA at 340 K. Observed  $^{13}\epsilon''(\bar{\nu}) = 0.70$ , observed  $^{13}$  critical frequency = 2.6 GHz; calculated [eqn (14)] = 2.7 GHz.

In the extreme case of MBBA, the far infrared curve generated by eqn (14) from the microwave fitting is very sharp, and centred at  $130\text{ cm}^{-1}$ . The corresponding  $f(t)$  (fig. 10) oscillates violently in the 0-1.5 ps interval reflecting a very large  $\langle o(v)^2 \rangle$  and the very restricted range of torsional oscillatory frequencies available in comparison with the isotropic  $\text{CHF}_3$ . The parameters  $\gamma(\text{s}^{-1})$  and  $K_1(0)(\text{s}^{-2})$  used for the five molecules are given in the table in units of  $(2kT/gI)^{\frac{1}{2}}$  and  $(2kT/gI)$  respectively, so that  $K_0(0) = 1$  in each case.

The apparent mean square torques in MBBA : propyne :  $\text{CBrF}_3$  :  $\text{CClF}_3$  :  $\text{CHF}_3$  decrease roughly in the ratio 200 : 25 : 10 : 10 : 8. This trend is the one expected on the assumption that the greater the molecular geometrical anisotropy, the greater the mean barrier to torsional oscillation. It is perhaps surprising that eqn (20) and (21) do not describe the observed far infrared absorptions of the five molecules studied here as well as eqn (14). Both equations yield very sharp and intense functions  $\alpha(\omega)$  peaking at too low a frequency in comparison with that of the far i.r. maximum absorption. A combination of  $n$  Gaussians as an approximation to the 1st order memory function  $K_1(t)$  might lead to an equation similar to eqn (20) that would be acceptable in comparison with experimental data but this would contain  $n$  unknowns  $\gamma_n$ . On the other hand eqn (21) contains  $K_2(0)$ , which is related to the torque derivative,<sup>1, 17</sup> i.e., contains a term in  $\dot{\theta}$ , the time derivative of the angular acceleration. This leads one to think of very hard collisions, with sudden changes of angular velocity  $\dot{\theta}$  (or  $\omega$ ); interactions which on this evidence are too abrupt for the liquid state.

The final spectrum  $\alpha(\omega)$  is therefore sensitive to the level of truncation of the memory function series and to the precise form of  $K_1(t)$  if the cut-off is at first order.  $K_1(t)$  ought to be an even function of time, whereas  $K_1(0)\exp(-\gamma t)$  is not. However, taking this form for  $K_1(t)$  ensures evenness in  $C_m(t)$  up to the fourth power in time. (For comparison, truncating at zero'th order, with  $K_0(0) = \gamma$ , introduces a term in  $t$  in  $C_m(t)$ , the latter being now an exponential function.) Taking a form  $K_1(t) = K_1(0)\exp(-|\gamma t|)$  would ensure evenness, except at  $t = 0$ . Other forms of  $K_1(t)$  are discussed in appendix 2.

At low frequencies, the model gives Debye behaviour, and the microwave critical frequency increases with temperature. The parameters  $\gamma$ ,  $K_0(0)$  and  $K_1(0)$  all depend on temperature, and are related to the Debye correlation time ( $\tau_D$ ) by :

$$\tau_D^2 = \frac{[K_0(0) + K_1(0)]^2 - 2K_0(0)\gamma^2}{K_0^2(0)\gamma^2}.$$

Eqn (14) has the further property that as the microwave critical frequency increases, the far infrared peak shifts to lower frequencies in order to conserve the overall integrated intensity per molecule ( $A_1$ ). Therefore, from these considerations the equation correctly describes the observed<sup>4</sup> shift in the far i.r. peak to lower frequencies as temperature rises, and the corresponding shift in the microwave peak to higher frequencies. Furthermore, it has been observed that for a high  $\langle o(v)^2 \rangle$  the microwave and far i.r. peaks are widely separated (fig. 9, 11) whereas for a low  $\langle o(v)^2 \rangle$  (as in  $\text{CHF}_3$ ,  $\text{CClF}_3$ ,  $\text{CBrF}_3$  and perhaps propyne), the two peaks are virtually fused, since the microwave critical frequency is up to  $\sim 2\text{-}10\text{ cm}^{-1}$  in these low density, sub-critical liquids. It seems that  $\langle o(v)^2 \rangle$  decreases as the temperature increases; which means that "free volume" in the liquid (i.e., macroscopic expansion with temperature) prevails over increased barriers to torsional oscillation as the temperature rises, and molecule "disorder" increases. On the other hand,<sup>17</sup> for a harmonic well,  $\langle o(v)^2 \rangle = ckT$  where  $o(v) = c\theta$ , and for hard forces,  $\langle o(v)^2 \rangle \sim (N'/\phi)kT$  where

$N'$  is a force coefficient and  $\phi$  is a mean angle of free rotation. To resolve the issue, measurements are needed at varied  $T$  but constant density.

The effect of collision-induced absorption can be estimated as  $A_1 - A_p$ , where  $A_p$  is the Gordon sum rule estimate of the integrated intensity of all rotational type permanent dipolar movements. For  $\text{CHF}_3$ , this quantity is  $\sim 5\%$  of  $A_1$ , within the experimental uncertainty,<sup>11</sup> but for  $\text{CClF}_3$  it is larger,<sup>19</sup> and for  $\text{CBrF}_3$  is about 40 % of  $A_1$ . In propyne, it is  $\sim 30\%$  of  $A_1$ . For MBBA,  $A_p$  cannot be estimated with certainty because Gordon's estimate is for rigid rotors. Therefore, apart from frequency dependent internal field effects<sup>8</sup> (which will be small in the region of maximum absorption as  $n(\omega)$  goes through a minimum close to unity) it is justified to fit eqn (14) directly to the experimental results for  $\text{CHF}_3$  and perhaps  $\text{CClF}_3$ . In propyne, it is reasonable to fit the lower frequency far i.r. data ( $10\text{--}40\text{ cm}^{-1}$ ) directly and allow for the effect of induced absorption at the higher frequencies. In general, the method would be to fit the experimental microwave peak as exactly as possible, which would generate the far i.r. curve free of induced absorption. In MBBA, there is the added problem of a series of intramolecular modes or overtones centred at just above  $200\text{ cm}^{-1}$ , which partially obscure the librational mode at  $130\text{ cm}^{-1}$ . Future work will centre on studies of the absorption, in these regions, of selected mesophases.

## APPENDIX I

By Taylor's theorem, assuming that  $K(t)$  is continuous, single valued, with continuous derivatives up to  $K^{(N)}(t)$  in a given interval  $a < t < b$ , and that  $K^{(N+1)}(t)$  exists in  $a < t < b$ , then :

$$K(t) = \sum_{n=0}^{\infty} b_n t^n / n!$$

where  $b_n$  is real.

Using :  $pC(p) - C(0) = -K_0(p)C(p)$  and eqn (24) then :

$$\left(a_0 + \frac{a_1}{p^2} + \frac{a_2}{p^4} + \dots\right) - \frac{a_0}{p} \equiv -\left(\frac{a_0}{p} + \frac{a_1}{p^3} + \frac{a_2}{p^5} + \dots\right) \left(\frac{b_0}{p} + \frac{b_1}{p^2} + \frac{b_2}{p^3} + \dots\right).$$

Comparing coefficients of  $1/p^3, 1/p^5, \dots$  gives :

$$b_1 = b_3 = b_5 = \dots = 0.$$

$$\text{Thus } K_0(t) = \sum_{n=0}^{\infty} b_n \frac{t^{2n}}{(2n)!}$$

## APPENDIX 2

The function  $K_1(t) = K_1(0) \exp(-\gamma t)(1 + \gamma t)$  has the property  $K_1(t) \rightarrow 0$  as  $t \rightarrow \infty$ , and its Maclaurin expansion has no term in  $t$ . Thus its limited time development is more satisfactory even than the simple exponential of eqn (7). Subsequently,  $K_1(t)$  has a zero slope as  $t \rightarrow 0$ , and with :

$$K_1(p) = (p + 2\gamma)K_1(0)/(p + \gamma)^2;$$

the power spectrum is given as :

$$\alpha(\omega) \propto \frac{2\gamma^3 K_0 K_1 \omega^2}{[\omega^4 - \omega^2(\gamma^2 + K_1 + K_0) + \gamma^2 K_0]^2 + 4\omega^2 \gamma^2 [\omega^2 - (K_1 + K_0)]^2}$$

which already has a term in  $\omega^8$  in the denominator.

It is also instructive to consider  $K_1(t)$  approximated by a two parameter combination of exponentials <sup>6</sup> such as :

$$K_1(t) = \frac{K_1(0)}{(\tau_1 - \tau_2)} [\tau_1 \exp(-t/\tau_1) - \tau_2 \exp(-t/\tau_2)]$$

with  $\tau_1$  and  $\tau_2$  linked via the equations :

$$\frac{1}{\tau_1} = \frac{1}{\tau} + \left( \frac{1}{\tau^2} - \omega_0^2 \right)^{\frac{1}{2}}$$

$$\frac{1}{\tau_2} = \frac{1}{\tau} - \left( \frac{1}{\tau^2} - \omega_0^2 \right)^{\frac{1}{2}}$$

where  $\omega_0$  is the proper frequency. This has the short time expansion :

$$K_1(t) = K_1(0) \left[ 1 - \frac{t^2}{\tau_1 \tau_2} + \mathcal{O}(t^3) \right]$$

and is, therefore, better behaved as  $t \rightarrow 0$  than the simple exponential of eqn (7). The corresponding spectrum is then :

$$\alpha(\omega) = \frac{1}{D} [\omega^4 K_1 K_0 (x_1 x_2 - y_1 y_2) + \omega^2 K_1 K_0 (y_2 x_1 - y_1 x_2) x_2 y_2]$$

where :

$$D = \{ \omega^4 + \omega^2 [K_1(y_1 - x_1) - x_2 y_2 - K_0] + K_0 x_2 y_2 \}^2$$

$$+ \{ \omega^3 (x_2 + y_2) + \omega [K_1(y_1 x_2 - x_1 y_2) - K_0 (x_2 + y_2)] \}^2$$

with

$$x_1 = \frac{\tau_1}{\tau_1 - \tau_2}; \quad x_2 = \frac{1}{\tau_1}; \quad y_1 = \frac{\tau_2}{\tau_1 - \tau_2}; \quad y_2 = \frac{1}{\tau_2}.$$

This equation is dimensionally identical to eqn (14), falls off as  $\omega^{-4}$  at high frequencies, and is, therefore, expected to compare favourably with experimental data. It reduces to Debye type behaviour [ $C(t)$  a sum of exponentials] in the frequency region where  $\omega^4 \ll \omega^2$  in normalised units. A many parameter combination of exponentials would lead to a series expansion which is even in powers of time.

### APPENDIX 3

The authors are indebted to Dr. George Wyllie for the following remarks. The widespread belief that  $\alpha$  should end as  $\omega^{-2}$  is based on taking :

$$\varepsilon - 1 \sim 1/(i\omega\tau - \omega^2)$$

with  $\tau$  constant at high frequency, on the assumption that the liquid then looks like a glass with a small, possibly constant, viscosity. In the first place, this constant viscosity is no more than a plausible guess. In the second, even if it is true, it can be accounted for by putting the Fourier transform of the asymptotic  $\varepsilon$  above in the relevant memory function.

The Mori expansion affords in principle the correct assignment of successive moments of the spectrum and so of successive terms in an expansion of  $C(t)$  in powers of  $t^2$ . This description does not give a natural picture of the very long time hydrodynamic tail of the auto-correlation function of angular momentum, decaying as a fractional power of  $t$ . One expects similar behaviour in  $C(t)$ , at least for spherical

top molecules, but this should distort the spectrum only on the low frequency side of the Debye absorption.

G. J. E. thanks S.R.C. for a research studentship, and M. W. E. thanks S.R.C. for a post-doctoral fellowship. The authors are indebted to the participants of the 1975 Gregynog discussion group for many useful comments. Dr. George Wyllie and Prof. Mansel Davies are thanked for critical readings of the manuscript.

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