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SIMPLE MODEL FOR THE ORIENTATIONAL CORRELATION FUNCTIONS F DIPOLAR AND INDUCED-DIPOLAR ABSORPTIONS IN LIQUIDS

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BSTRACT

The Mori continued fraction approximation to the orientational memory unction is used to evaluate the corresponding orientational correlation unction C(t) of dipolar and induced-dipolar absorptions in liquids. In he former case the exponential part of C(t) is the Fourier transform of he relaxational Debye absorption, the short time (non-exponential) part f which is the Poley absorption characteristic of dipolar liquids in the ar infra-red. In the latter case, the corresponding C(t) is one of both olecular orientation and interaction, having a correlation time typically f much less than 1 ps. This is approximately the inverse width at half eak height of the broad induced-dipolar absorptions which characterise on-dipolar liquids in the far infra-red (1-250 cm^{-1}). This correlation unction never becomes exponential, and is damped to zero in approximately he same interval of time as its memory function - meaning that the emporary dipole absorbs only during its short lifetime. The memory unction is the correlation function of the random, fluctuating torque orces experienced by any molecule in the system, and is not a pure xponential. Therefore, this model is non-Markovian.

NTRODUCTION

The aim of this paper is to present a coherent statistical account of he rotary dynamics of dipolar and non-dipolar molecules in the liquid tate in terms of their respective orientational correlation functions

[1-4]. These are related to the broad microwave and far infra-red absorption bands of the liquid phase in the region from about 0.1 cm^{-1} (3 GHz) to 500 cm^{-1} - several decades of frequency.

In general, the above correlation functions, C(t), are related to the corresponding spectra, C(ω), by:

$$C(t) = \int_0^\infty \cos \omega t \; d\, C(\omega) \; . \tag{1}$$

This assumes that the orientational fluctuation of molecules in the liquid state is a continuous, stochastic process stationary in time, so that:

$${}'f_x \,(t_1) = {}'f_x \,(t_2) = \text{constant} \tag{2}$$

where 'f is the first order probability distribution function of a molecule fixed vector $\underline{x}$. In the case of molecules with permanent dipole moments $\underset{\sim}{\mu}$, the autocorrelation function which we use can be defined as:

$$C_1(t) = \langle \underset{\sim}{\mu}(o) . \, \underset{\sim}{\mu}(t) \rangle \; ,$$

where the brackets denote ensemble averaging over (p,q) space, and $\underset{\sim}{u}(t)$ is the unit vector along $\underset{\sim}{\mu}$ at time t. Cross-correlations [5] between different molecules are neglected. Non-dipolar molecules absorb [3,4,6] in the far infra-red and high-microwave regions because of the latent disorder in the liquid at any given instant, i.e. the fields of all other molecules in the system induce a small, temporary dipole moment on any given molecule. This can be written as:

$$\underset{\sim}{\mu}_2 \left(t, \sum_i \sum_{n=2}^{\infty} a_{i,n} \, \underset{\sim}{R}_i^{-n} \right)$$

where there are i+1 molecules present, and where the effect of the other molecules' fields is summarised in terms of point multipoles [7] $a_{i,n}$. The intermolecular vector is $\underset{\sim}{R}_i$, and the n=1 term is absent without permanent dipoles in the system. A correlation function for the system can now be defined as:

$$C_2(t) = \langle \underset{\sim}{\mu}_2(o) . \ \underset{\sim}{\mu}_2(t) \rangle + \sum_{i \neq j} \langle {}^{i}\underset{\sim}{\mu}_2(o) . \ {}^{j}\underset{\sim}{\mu}_2(t) \rangle$$

where ${}^{i}\underset{\sim}{\mu}_2$ is the vector along $\underset{\sim}{\mu}_2$ on a molecule i at time t. $C_2(t)$ is thus an orientation/interaction correlation function, dependent simultaneously at time t on the orientation of the molecule under consideration and on the orientations of all the others in the system. The correlation is between the magnitude and direction of the resultant ${}^{i}\underset{\sim}{\mu}_2$ at a time t later. Eqn (1) is a basic statistical theorem which asserts that <u>all</u> infra-red, rotational absorption bands, regardless of their molecular dynamical origin, are related to some correlation function C(t). An equation of equally general validity is:

$$C(t) = - \int_0^t K(t - \tau) \ C(\tau) \ d\tau \qquad (3)$$

where K is the response function, or memory function [8]. Eqn (3) can be regarded as a statement of Kubo's generalisation [9] of the Langevin treatment [10] of translational or rotational Brownian motion, where the motion of a massive particle is opposed by a constant "friction coefficient on the microscopic scale".

The Fourier transform of K is a frequency dependent friction coefficient, related to the random force, or torque ($\underset{\sim}{F}(t)$), exerted on a molecule by the motions of its neighbours by Kubo's second fluctuation - dissipation theorem. In the case of the reorientation of $\underset{\sim}{\mu}(t)$, for example, this can be written as:

$$\langle \underset{\sim}{\mu}(o) . \ \underset{\sim}{\mu}(o) \rangle \ K_1(t) = \langle \underset{\sim}{F}(o) . \ \underset{\sim}{F}(t) \rangle \qquad (4)$$

where $\underset{\sim}{F}$ has the units of torque.

In this work we deduce an algebraic expression for C(t) (and thus for C(ω)) using a simple approximation to the memory function K(t). The final equation contains a phenomenological correlation time γ^{-1}, and equilibrium averages $K_o(o)$ and $K_1(o)$ which have the units of S^{-2}. Estimates of these are obtained by fitting the theoretical C(ω) to the experimental data. Therefore it is possible to compute C(t) and K(t) for dipolar and non-dipolar molecules of different shapes. The advantages and limitations of this simple model are discussed below.

APPROXIMATION TO K(t)

It can be shown [11] that the mathematical set of memory functions $K_o(t)$, ..., $K_n(t)$ obey the set of coupled Volterra equations such that:

$$\frac{\partial}{\partial t} K_{n-1}(t) = -\int_o^t K_n(t-\tau) K_{n-1}(\tau) d\tau \qquad (5)$$

with n=1, ..., N. Taking Laplace transforms of eqns (3) and (5):

$$C(p) = \frac{C(o)}{p + K_o(p)} = \frac{C(o)}{p + \frac{K_o(o)}{p + K_1(p)}} = \ldots \qquad (6)$$

This is Mori's continued fraction theorem. The associated complex spectrum $C(i\omega)$ is the Fourier-Laplace transform of C(p) and can be approximated conveniently by using simple forms for $K_N(p)$. If this truncation is such that $K_o(p) = \gamma$, a constant with the units of frequency, then the expression:

$$C(t) = C(o) \exp(-\gamma t) \qquad (7)$$

is a direct consequence. This is also obtained by integrating the simple Langevin equation [10], and is equivalent to a Lorentzian in $C(i\omega)$, the classical Debye equations [12] for the dielectric loss ε'' and permittivity ε' of molecules with a permanent dipole moment.

However, C(t) (and, therefore, K(t)) are even functions of time [1,8] in the classical limit ($\hbar \to 0$), and the Maclaurin expansion of (7) has odd powers of t, with $C(-t) \neq C(t)$. Eqn (7) is particularly badly behaved at short times, i.e. a Lorentzian for $C(i\omega)$ has the consequence that $\alpha(\omega)$, the absorption coefficient per unit absorber path length, defined by $\alpha = \omega\varepsilon''/n(\omega)$, with n as the refractive index, reaches a physically unrealistic asymptote (the Debye plateau [12]) typically in the region 10-50 cm^{-1}. The observed spectra of permanent-dipolar molecules display the characteristic [5,10,12] Poley band before regaining transparency beyond 100 cm^{-1}.

more realistic choice of truncation:

$_{o}(o)\ \exp(-\gamma_{o} t)$ (8)

$$C(p) = \frac{p + \gamma_{o}}{p^{2} + p\gamma_{o} + K_{o}(o)} \qquad (9)$$

er-Laplace transform of eqn (9) yields the real part of sorption bandshape, and the imaginary parts as a dispersion. place transform yields the correlation function C(t), which en up to t^{3}, and:

(o) C(o).

have:

$$\text{Real}\left[\tilde{C}(i\omega)\right] = \frac{\gamma_{o} K_{o}(o)}{(K_{o}(o) - \omega^{2})^{2} + \omega^{2}\gamma_{o}^{2}} \qquad (10)$$

$$\left.\begin{aligned} C(t) &= \exp(-\gamma_{o} t)\left[\cos at + \frac{\gamma_{o} a}{2}\sin at\right] \\ &\text{for } K_{o}(o) > \gamma_{o}^{2}/4 \\ &= \exp(-\gamma_{o} t)\,(1 + \gamma_{o} t/2) \\ &\text{for } K_{o}(o) = \gamma_{o}^{2}/4 \\ &= \exp(-\gamma_{o} t)\left[\cosh bt + \frac{\gamma_{o} b}{2}\sinh bt\right] \\ &\text{for } K_{o}(o) < \gamma_{o}^{2}/4 \end{aligned}\right] \qquad (11)$$

$^{2} = K_{o}(o) - \gamma_{o}^{2}/4.$

he correlation function obtained by direct integration of quation of a vibrator of proper frequency ω_{o} perturbed by a process of random collisions separated by an interval τ_c:

$$\ddot{\underset{\sim}{x}} + \dot{\underset{\sim}{x}}/\tau_c + \omega_o^2 \underset{\sim}{x} = \underset{\sim}{A}(t) \qquad (12)$$

so that $\langle \underset{\sim}{x}(o) . \underset{\sim}{x}(t)\rangle / \langle \underset{\sim}{x}(o) . \underset{\sim}{x}(o)\rangle$ is given by eqn (11) with γ_o replaced by $1/\tau_c$ and $K_o(o)$ by ω_o^2. Here, $\dot{\underset{\sim}{x}}$ has the units of angular velocity, and $\underset{\sim}{A}(t)$ is the random external torque per unit mass. This is the situation where hard-core collisions between molecules take place at random times and randomise the molecular angular velocity vector in direction but not in magnitude; sometimes known as the M-diffusion model, which is thus equivalent to a single-exponential memory function. If the collisions were randomise the angular velocity in both direction and magnitude (J-diffusion), then Bliot et al. [13] have shown that the equivalent memory function is:

$$K_o(t) = K_{FR}(t) \exp(-\gamma_J |t|)$$

where $K_{FR}(t)$ corresponds to a Gaussian distribution of freely rotating molecules. $K_o(o)$ is thus a mean square angular velocity of a Gaussian ensemble of molecules.

As would be expected from a model involving instantaneous re-orientations of angular velocity, the correlation function is still badly behaved at short times, and the spectral intensity distribution at high frequencies is such [14] that transparency is regained much too slowly. The intermolecular mean square torque[1], $\langle O(V)^2\rangle$, becomes instantaneously infinite in elastic collisions, whereas Gordon [15] has shown that for linear, dipolar molecules, a finite torque term exists in the following expansion for C(t) in the classical limit:

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

$$= 1 - \frac{2kT}{I}\frac{t^2}{2!} + \left[8\left(\frac{kT}{I}\right)^2 + \frac{\langle O(V)^2\rangle}{I^2}\right]\frac{t^4}{4!} - \dots \qquad (13)$$

From eqns (2) and (13) it follows that K is also an even function of time:

$$K_j(t) = \sum_{n=0}^{\infty} {}^{j}k_n \frac{t^{2n}}{(2n)!} \qquad (14)$$

so that: $${}^{o}k_N = - a_{N+1} - \sum_{n=1}^{N} {}^{o}k_{N-n}\, a_n \qquad (15)$$

and thus: $$\left.\begin{aligned} {}^{o}k_o &= K_o(o) = - a_1 = 2kT/I \\ {}^{1}k_o &= K_1(o) = a_1 - \frac{a_2}{a_1} \\ &= K_o(o) + \frac{<O(V)^2>}{2kTI} \end{aligned}\right] \qquad (16)$$

Thus, for any permanent dipolar absorption, a truncation of the series of eqns (6) which precludes the equilibrium average $K_1(o)$ cannot adequately account for the changes in $<O(V)^2>$at short times. A simple way of involving $K_1(o)$ in a model is to truncate [16] with:

$$K_1(t) = K_1(o) \exp(-\gamma_1|t|) \qquad (17)$$

so that:

$$C(i\omega) = \frac{K_1(o) - \omega^2 - i\omega\gamma_1}{i\omega^3 - \omega^2\gamma_1 - i\omega\,(K_1(o) + K_o(o)) + \gamma_1\, K_o(o)}$$

is the complex spectral function. The optical absorption coefficient is then given 5 by:

$$\alpha(\omega) = \frac{(\epsilon_o - \epsilon_\infty)\Lambda}{n(\omega)\ c} \text{Real} \left[C(i\omega)\right] \omega^2 \qquad (18)$$

with

$$\text{Real}\left[C(i\omega)\right] = \frac{K_o(o)\ K_1(o)\,\gamma_1}{\gamma_1^{\,2}\ (K_o(o) - \omega^2)^2 + \omega^2\ (\omega^2 - (K_o(o) + K_1(o)))^2}$$

i.e. $\alpha(\omega)$ is now asymptotic as ω^{-4} at high frequencies, Λ is a correction [17] for the internal field. In the far infra-red, it is almost band-shape independent [5], and can be roughly approximated by the Polo/Wilson factor of $\Lambda = 9n_D^{2}/(n_D^{2} + 2)^{2}$, where n_D is the D line refractive index. $(\varepsilon_o - \varepsilon_\infty)$ is the total dispersion equivalent, through the Kramers-Krönig relations to the total absorption, and $n(\omega)$ is the frequency dependent refractive index.

The correlation function equivalent to eqn (18) ($C_m(t)$) is extracted by inverse Laplace transformation, using the Heaviside expansion theorem, giving:

$$C_m(t) = \left(\frac{\cos\beta t}{1+\Gamma} + \frac{1}{\beta}\left(\frac{\alpha_1 + \Gamma\alpha_2}{1+\Gamma}\right)\sin\beta t\right)\exp(-\alpha_1 t) + \frac{\Gamma}{1+\Gamma}\exp(-\alpha_2 t) \qquad (19)$$

where $$\Gamma = \frac{2\alpha_1(2\beta^2 - \alpha_1^2)}{\alpha_2(3\alpha_1^2 - \beta^2 - \alpha_2^2)},$$ with

$$\alpha_2 = -S_1 - S_2 + \gamma/3; \quad \alpha_1 = \frac{1}{2}(S_1 + S_2) + \frac{\gamma}{3};$$

$$\beta = \frac{\sqrt{3}}{2}(S_1 - S_2).$$

The parameters S_1 and S_2 are defined by:

$$S_1 = \left[-\frac{B}{2} + \left(\frac{A^3}{27} + \frac{B^2}{4}\right)^{\frac{1}{2}}\right]^{\frac{1}{3}}$$

$$S_2 = \left[-\frac{B}{2} - \left(\frac{A^3}{27} + \frac{B^2}{4}\right)^{\frac{1}{2}}\right]^{\frac{1}{3}}$$

with $A = K_o(o) + K_1(o) - \gamma_1^{2}/3$;

$$B = \frac{\gamma_1}{3}\left(\frac{2\gamma_1^{2}}{9} + 2K_o(o) - K_1(o)\right).$$

e correlation time, τ'_m, defined by:

$$\tau'_m = \int_o^\infty C_m(t)\,dt$$

s evaluated easily from eqn. (19) as:

$$\tau'_m = \frac{1}{1+\Gamma}\left(\frac{2\alpha_1+\Gamma\alpha_2}{\alpha_1^2+\beta^2}+\frac{\Gamma}{\alpha_2}\right) \qquad (20)$$

he memory function of $C_m(t)$, linked to it by:

$$K_m(p) = p + C_m^{-1}(p),$$

an now be evaluated as:

$$K_m(t) = K_o(o)\,f(t) \qquad (21)$$

here f(t) is given by the RHS of eqn (11) with γ_o replaced by γ_1, and
$_o$(o) by K_1(o). Therefore, the overall memory function $K_m(t)$ is the same
n form as the correlation function deduced from the M-diffusion model of
ntermolecular dynamics. By Doob's theorem [8,9], and the second fluctu-
tion-dissipation theorem, the random torque $\underset{\sim}{F}(t)$ on a given molecule is
ot Markovian, since the memory function $K_m(t)$ is not exponential, and so
future conditional probability distribution will be affected by the
istory of the molecular motions.

It is interesting to speculate that the truncation of eqn (17) may
e physically equivalent to a randomisation of the direction of the
olecular angular acceleration vector upon interaction, since the
implest truncation K(p) = γ, or K(t) = γf(t), corresponds to the Debye
odel, which neglects all dynamical coherence, including inertia, i.e.
randomisation of orientation upon interaction, the correlation function
aving a term in t. The M-diffusion truncation corresponds to random-
sation of the direction of the angular velocity vector, the torque F
eing Markovian, and the correlation function having no term in t but
ne in t^3, this being an "inertia-corrected" Debye model. Since
$_m$(t) of eqn (21) is M-diffuse in character, the time-derivative of the

external torque $\underset{\sim}{F}(t)$ of which $K_m(t)$ is the correlation function, is randomised in direction by events separated by the time γ_1^{-1}, in a way analagous to that where the derivative of position (the angular velocity) is randomised in direction by events separated by the critical time of the M-diffusion model.

At low frequencies, eqn (18) reduces to:

$$\alpha(\omega) \rightarrow \frac{A\omega^2 K_o(o) K_1(o)\gamma_1}{\gamma_1^2 K_o^2(o) + (K_o^2(o) + K_1^2(o) + 2K_o(o)(K_1(o) - \gamma_1'^2))\omega^2} \qquad (22)$$

with $A = \Lambda(\varepsilon_o - \varepsilon_\infty)/n(\omega)c$,

the form of the classical Debye curve of permanent dipolar absorption. In this case, the classical Debye relaxation time is given by:

$$\tau_D^2 = \frac{(K_o(o) + K_1(o))^2 - 2K_o(o)\gamma_1'^2}{\gamma_1^2 K_o^2(o)}$$

In the case of induced dipolar absorption in non-dipolar liquids (or gases), both $K_o(o)$ and $K_1(o)$ are dependent on the intermolecular potential energy and thus on its derivative with respect to angular orientation - the torque (see appendix). Both $K_o(o)$ and $K_1(o)$ could be evaluated analytically for the case of bimolecular collisions in gases [6], but no satisfactory account has been developed of the detailed (non-statistical) mechanism of induced dipolar absorption in liquids. In this paper we evaluate $C_m(t)$ for non-dipolar liquids by fitting eqn (18) to the experimental far infra-red/microwave absorption bands, thus finding values for $K_o(o)$, $K_1(o)$ and γ which can be used in eqns (19) and (21) for the analytically related correlation and memory functions. A typical example of this fit (which is always very satisfactory) is given in fig (1), the theoretical and experimental curves being very often indistinguishable. Thus, for non-dipolar liquids, $C_m(t)$ and $K_m(t)$ can be regarded virtually as the experimental curves. This is the first attempt at evaluating orientation/interaction correlation functions of this type for collision-induced absorption, since the "obvious" method of direct Fourier transformation is difficult to carry out in practice, very accurate data being needed down to <0.1 cm^{-1}.

The same curve fitting method can be used for permanent dipolar rptions, but here only $K_1(o)$ and γ are empirical; $K_o(o)$ is a single cule property given for linear and symmetric top molecules by I_B.

TATIONS OF THE MODEL

An obvious limitation is that $K_1(t)$ is ideally expanded in even rs of time. This is not so for $K_1(t)$ of eqn (17), the reason that spectrum (eqn (18)) is a very good approximation to the experimental hat $C_m(t)$ is even up to t^4, and is thus reasonably well-behaved at t times, and pseudo-exponential at long times. The memory function) has a term in t^3, and is thus even up to t^2 only. Furthermore, the nd derivative $\ddot{K}_m(o)$ is not defined uniquely, differentiating $K_m(t)$ e leads to the following contradiction.

the case $K_1(o) > \gamma_1^2/4$, we have:

$$(1) \quad \ddot{K}_m(o) = -K_o(o)\,K_1(o) \qquad (23)$$

or $K_1(o) < \gamma_1^2/4$. However, for the case $K_1(o) = \gamma_1^2/4$, we have:

$$(2) \quad \ddot{K}_m(o) = -\gamma_1^2\,K_o(o)/4 \qquad (24)$$

hat, if a contradiction is to be avoided,

$$(1) \quad \ddot{K}_m(o) \neq (2) \quad \ddot{K}_m(o)$$

ver, for dipolar absorption in a linear molecule, it follows from (13) that:

$$K_m(t) = \frac{2kT}{I} - \left[4\left(\frac{kT}{I}\right)^2 + \frac{<O(V)^2>}{I^2}\right]\frac{t^2}{2!} + \ldots \qquad (25)$$

$\ddot{K}_m(o)$ is theoretically unique. The problem disappears only when $)^2> = 0$, i.e. for no interaction - a Gaussian system of individual rs. The correlation function for dipolar molecules for this system nown [5] to be very well approximated by the hypergeometric function ummer. The agreement of our model with $<O(V)^2> = 0$ is poor, except

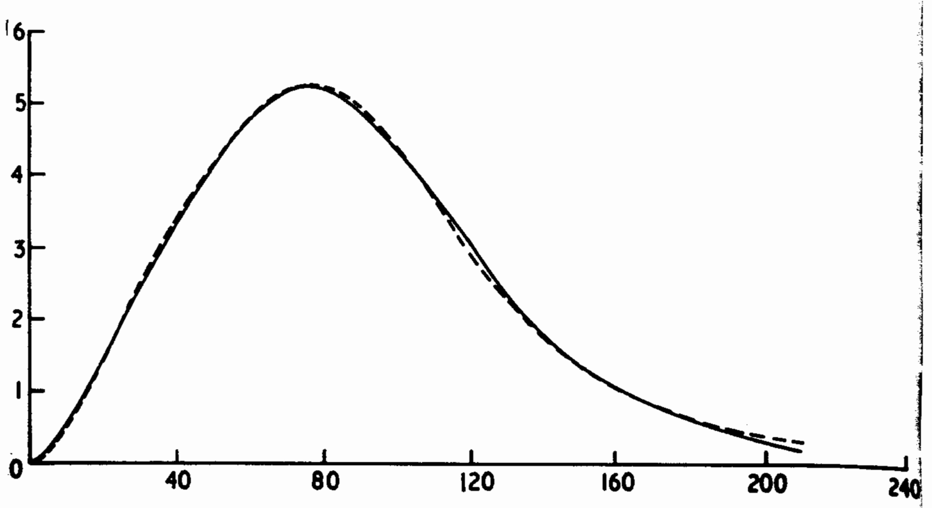


Fig. 1. —— Experimental 3,4 absorption of liquid benzene at 298K in the far infra-red (uncertainty of ± 2%).
- - - Eqn (18) with the parameters tabulated in the text.
Ordinate: α/neper cm^{-1}; abscissa: $\bar{\nu}/cm^{-1}$.

Table 1. Parameters used in calculating C(t) and K(t)

Liquid	Temp /K	$K_0(o)$ /(2kT/I)	$K_1(o)$ /(2kT/I)	γ $/(2kT/I)^{\frac{1}{2}}$	τ_m /ps	10^{40} I /g cm^2	Ref
CHF_3	298	1·0	8·0	4·0	$0{\cdot}5_3$	81·1	(6),
CB_rF_3	296	1·0	10·5	5·0	$1{\cdot}0_3$	400	(6),
CH_3 C ≡ CH	296	1·0	25·0	4·0	$2{\cdot}2_3$	98·2	(20),
MBBA	340	0·68	200·0	2·0	54·6	470	(14),
$(CH_3)_3$ CCl(r)	238	1·0	103·5	13·8	$4{\cdot}7_0$	269	(14)
$(CH_3)_2$ $CClNO_2$	293	1·0	115·6	12·2	$5{\cdot}8_9$	494	(14)
N_2	76·4	5·9	37·8	10·4	0·08	12·23	(19),
CH_4	98	16·8	75·7	14·5	0·04	5·34	(19),
CH_4(r)	77	14·7	47·9	10·6	0·07	5·34	(19),
CO_2	273	8·6	51·9	11·5	$0{\cdot}1_1$	71·2	(19),
$(CN)_2$	301	14·9	66·5	10·9	$0{\cdot}1_8$	155·1	(19),
cyclohexane	296	28·4	194·2	21·1	$0{\cdot}1_1$	178·0	(19)
trans decalin	296	70·7	335·3	22·7	$0{\cdot}2_7$	1020·0	"
benzene	296	20·8	100·6	12·8	$0{\cdot}1_9$	148·0	"
polifluorobenzene	296	45·2	247·0	20·7	$0{\cdot}2_2$	652·2	"
CS_2	315	29·9	212·0	27·0	$0{\cdot}1_3$	258·6	(19)
CS_2	296	26·2	170·2	20·3	$0{\cdot}1_6$	258·6	"
CS_2	232	21·9	114·3	12·0	$0{\cdot}2_1$	258·6	"
CS_2	293 (11·6 kbar)	79·9	247·6	32·7	$0{\cdot}0_4$	258·6	(19),
CCl_4	296	10·9	80·6	14·2	$0{\cdot}1_9$	247	(19)
CCl_4	313	10·2	65·1	12·2	$0{\cdot}2_1$	247	"
CCl_4	328	9·1	51·2	10·1	$0{\cdot}2_5$	247	"

at very short times. The reason is that $C_{\underset{\sim}{m}}(t)$ contains too many odd powers of time and is thus damped out too slowly, the disagreement becoming more and more pronounced as t increases. A possible remedy is to truncate the series of eqns (6) at higher and higher order, but this merely introduces an unacceptable number of empirical equilibrium averages $K_2(o)$, ..., $K_N(o)$. This failure to reproduce the free rotor behaviour is perhaps the major drawback of the present function $C_{\underset{\sim}{m}}(t)$. However, it must be stated that the classical Debye model fails both in this respect and also, at the other extreme, in neglecting dynamical coherence.

Finally, Wyllie has pointed out [18] that the Mori expansion affords in principle the correct assignment of successive moments of the spectrum $C(i\omega)$, and so of successive terms in the expansion of $C(t)$ in powers of t^2. However, this description does not give a natural picture of the very long time hydrodynamic tail of the autocorrelation function of angular momentum, decaying as a fractional power [10] of time (i.e. $t^{-3/2}$). Similar behaviour is expected in $C_{\underset{\sim}{m}}(t)$, at least for spherical tops (e.g. F_3CCD_3 or CCl_4), but this would distort the spectrum only on the <u>low</u> frequency side of the Debye absorption.

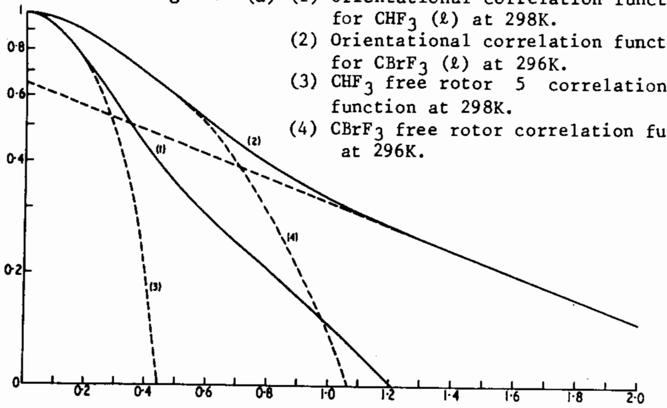
RESULTS AND DISCUSSION

Eqn (18) has been fitted by a least mean squares procedure to the experimental [6,12,14,19] absorption bands of the molecules listed in table 1; also given are the values of $K_o(o)$, $K_1(o)$ and γ needed for best fit. Using these values, correlation and memory functions have been evaluated with eqns (19) and (21) (figs (2)-(5)) and correlation times from eqn (20), these being the areas under each correlation function.

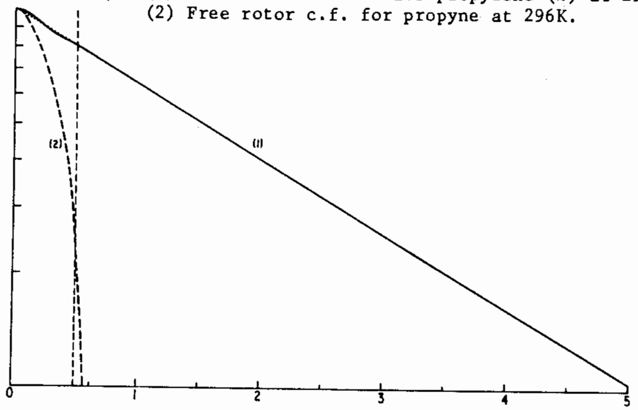
DIPOLAR MOLECULES

In evaluating correlation functions by this method, dipolar molecules have been selected which reflect an increasing molecular geometrical anisotropy and macroscopic density in the liquid state. These factors can be discussed in relation to the changing nature of the

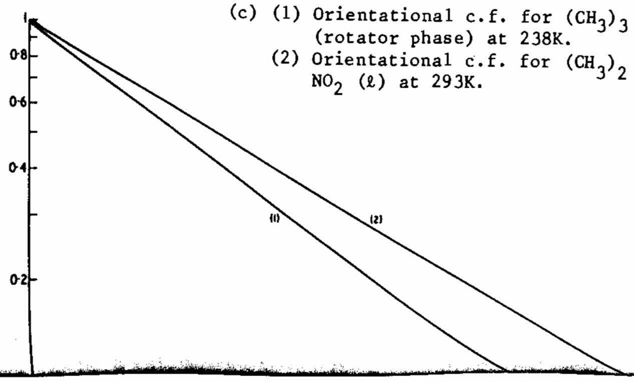
Fig. 2.



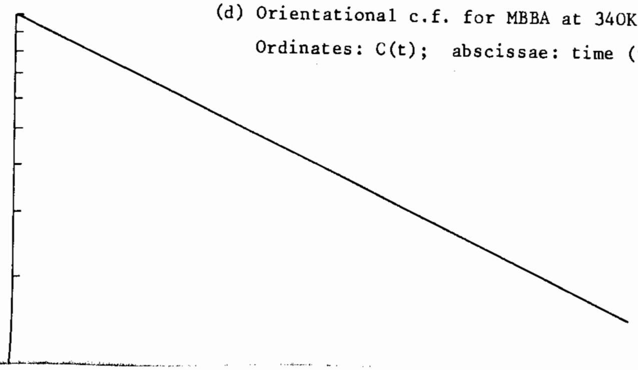
(a) (1) Orientational correlation function for CHF_3 (ℓ) at 298K.
(2) Orientational correlation function for $CBrF_3$ (ℓ) at 296K.
(3) CHF_3 free rotor 5 correlation function at 298K.
(4) $CBrF_3$ free rotor correlation function at 296K.



(b) (1) Orientational c.f. for propylene (ℓ) at 296K.
(2) Free rotor c.f. for propyne at 296K.



(c) (1) Orientational c.f. for $(CH_3)_3$ CCl (rotator phase) at 238K.
(2) Orientational c.f. for $(CH_3)_2$ CCl NO_2 (ℓ) at 293K.



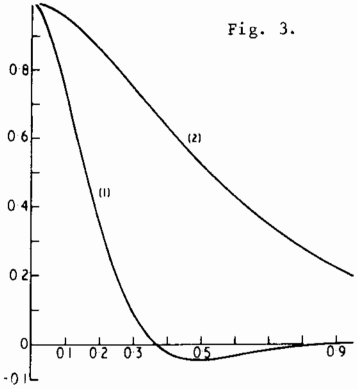
(d) Orientational c.f. for MBBA at 340K.

Ordinates: C(t); abscissae: time (t)/ps.

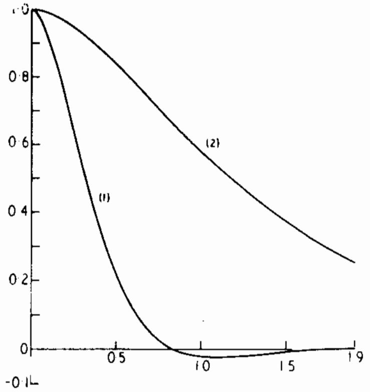
molecular rotatory dynamics by reference to the correlation functions of Figs 2(a) to 2(d). $C_{\underline{m}}(t)$ for the low density liquids [6] CHF_3 and $CBrF_3$ (fig 2(a)) become exponential only after a significant period of time during which fairly free rotation through large angles is possible. The corresponding free rotor functions are shown for comparison, and it is clear that the CHF_3 molecule rotates for an average of about 0.2 ps before correlation is retained by collision; and $CBrF_3$ behaves likewise for about 0.5 ps. The correlation times are very short (table 1), the overall picture being one of perturbed large angle rotation rather than rotational diffusion. In contrast, $C_{\underline{m}}(t)$ for the pseudo spherical molecules [14] $(CH_3)_2 CClNO_2$ (dense liquid), and $(CH_3)_3 CCl$ (rotator phase) (fig. 2(c)) are exponential for all but an initial fraction of the time scale over which the absorption process occurs, a fraction which corresponds to the far infra-red [14] portion of the overall absorption.

The $C_{\underline{m}}(t)$ for propyne (ℓ) [20] (fig. 2(b)) at 296K oscillates before becoming exponential after 0.5 ps, indicating that the mechanism of absorption on this interval is whole molecule torsion or libration in potential energy wells formed by neighbours. Free rotation is possible only for about 0.03 ps, a small fraction of the total correlation time of 2.23 ps. The longest lived process (with $\tau'_{\underline{m}} = 55$ ps) is the rotational diffusion of the stick-like molecule [14,24] [illegible]methoxy benzylidene p n butyl aniline (MBBA) in its isotropic phase at 340K, a few degrees above the nematic phase of this molecule. The correlation function is exponential (fig 2(d)) and corresponds to the Debye-type absorption observed [22] in the 10^6 Hz frequency region. In contrast, the normalised memory function for this molecule (fig 3(f)) displays pronounced oscillations in the region 0-2 ps, caused by the unusually high value of $K_1(o)$ (and thus of $<O(V)^2>$) needed for the least mean squares fit [23] to the overall low frequency/far infra-red absorption process which stretches over many decades of frequency. These oscillations are related to the fact that MBBA has a nematic phase where the molecules are constrained [24] to librate only about their long axes, although rotational diffusion can occur about all three molecular axes x, y, z.

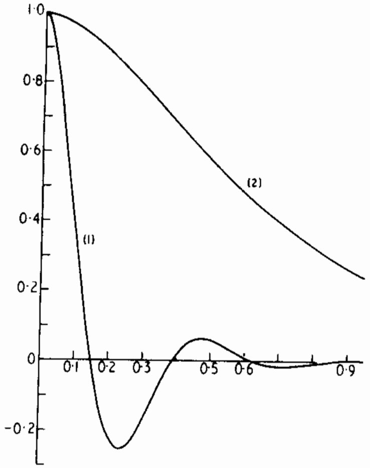
Fig. 3.



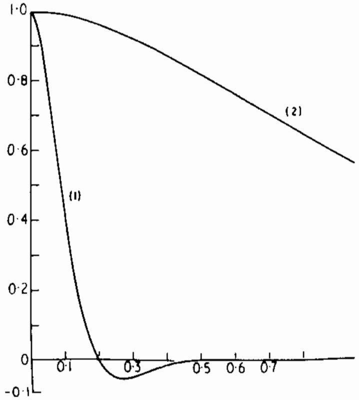
(a) (1) Orientational memory function for CHF_3 (ℓ) at 298K.
(2) Memory function for $\langle O(V)^2\rangle = 0$.

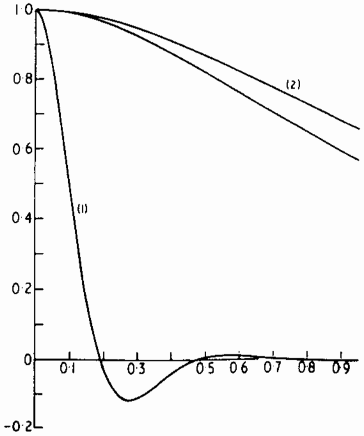


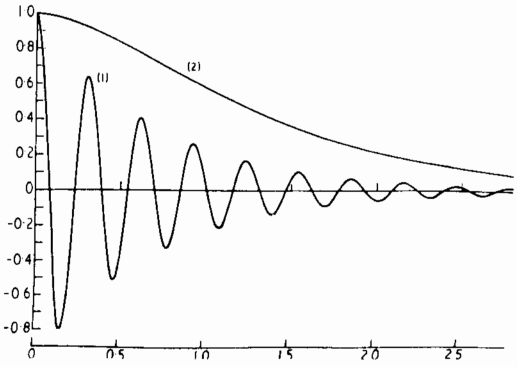
(b) (1) Orientational memory function for $CBrF_3$ (ℓ) at 296K.
(2) Memory function for $\langle O(V)^2\rangle = 0$.

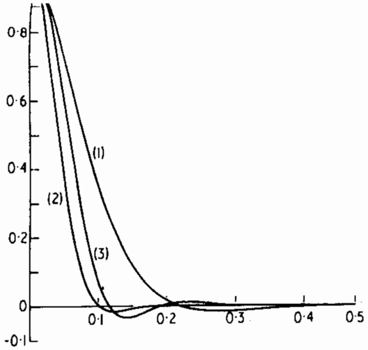


(c) (1) Orientational memory function for $CH_3C{\equiv}CH$ (ℓ) at 296K.
(2) Memory function for $\langle O(V)^2\rangle = 0$.

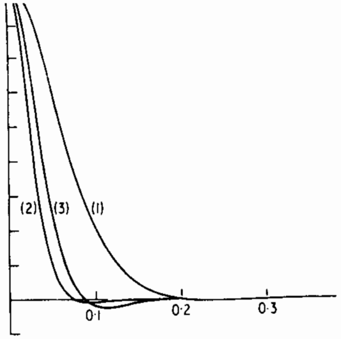




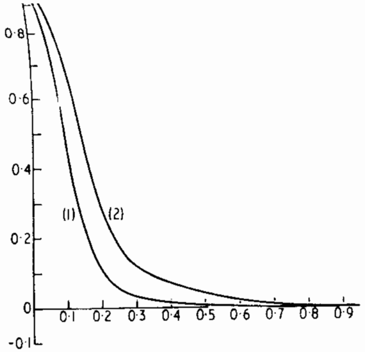




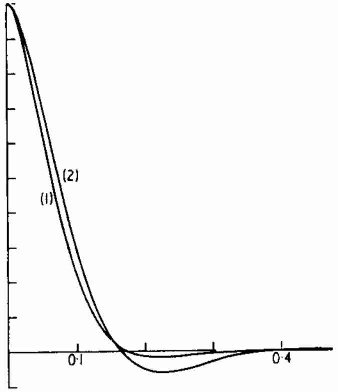
(a) (1) Interaction/orientation c.f. for N_2 (ℓ) at 76.4K.
(2) Interaction/orientation c.f. for CH_4 (ℓ) at 98K.
(3) Interaction/orientation c.f. for CH_4 (r) at 77K.



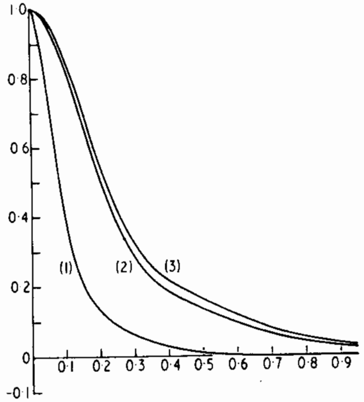
(b) (1) Interaction/orientation m.f. of N_2 (ℓ) at 76.4K.
(2) Interaction/orientation m.f. for CH_4 (ℓ) at 98K.
(3) Interaction/orientation m.f. for CH_4 (r) at 77K.



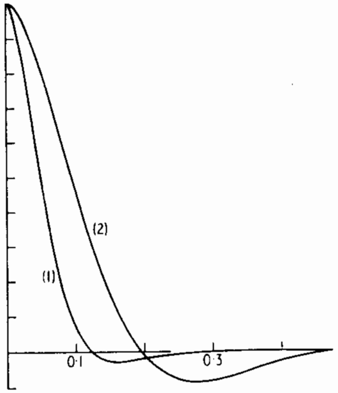
(c) (1) Interaction/orientation c.f. for CO_2 (ℓ) at 273K.
(2) Interaction/orientation c.f. for $(CN)_2$ (ℓ) at 301K.



(d) (1) Interaction/orientation m.f. for CO_2 (ℓ) at 273K.
(2) Interaction/orientation m.f. for $(CN)_2$ (ℓ) at 301K.



(e) (1) Interaction/orientation c.f. for cyclohexane at 296K.
(2) Interaction/orientation c.f. for trans decaline at 296K.
(3) Interaction/orientation c.f. for dioxane at 296K.

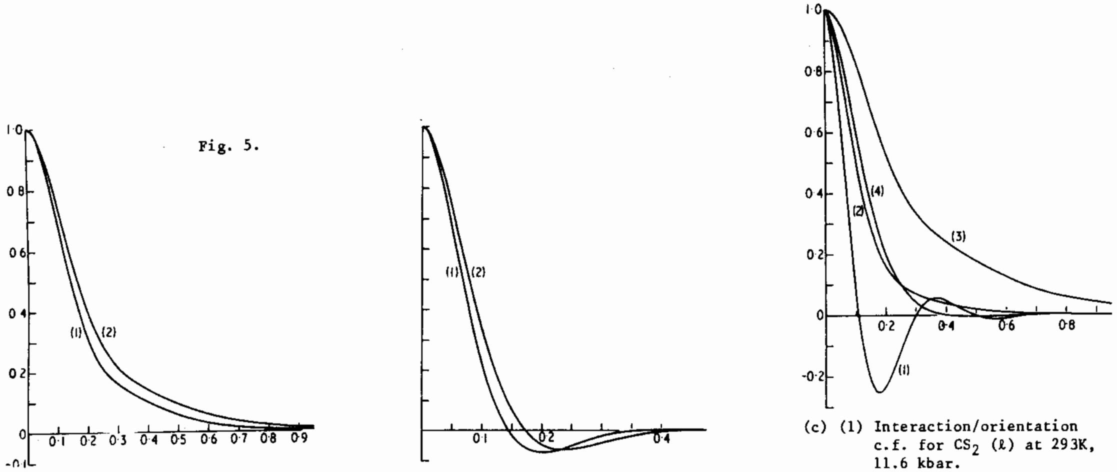


(f) (1) Interaction/orientation m.f. for cyclohexane at 296K.
(2) Interaction/orientation m.f. for trans decalin at 296K.

Ordinates: (a), (c), (e) : C(t); (b), (d), (f) : K(t).

Abscissae : time (t)/ps.

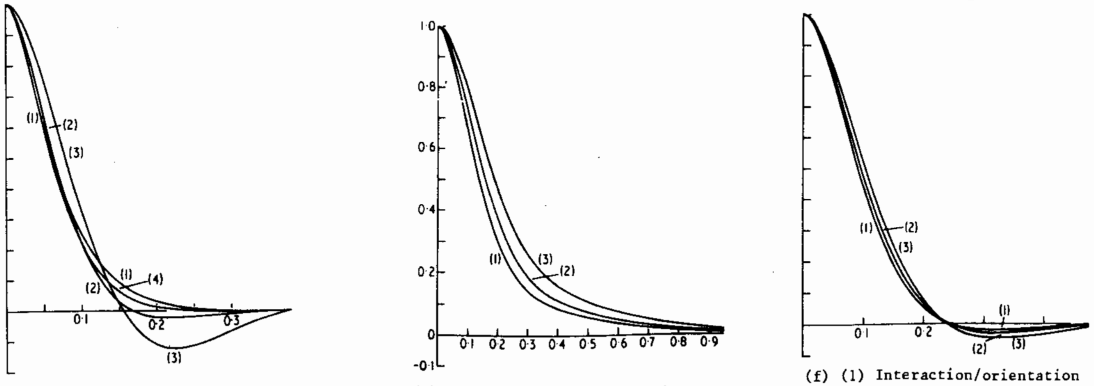
Fig. 5.



(a) (1) Interaction/orientation c.f. for benzene at 296K.
(2) Interaction/orientation c.f. for p difluobenzene at 296K.

(b) (1) Interaction/orientation m.f. for benzene at 296K.
(2) Interaction/orientation m.f. for p difluorobenzene at 296K.

(c) (1) Interaction/orientation c.f. for CS_2 (ℓ) at 293K, 11.6 kbar.
(2) Interaction/orientation c.f. for CS_2 (ℓ) at 296K.
(3) Interaction/orientation c.f. for CS_2 (ℓ) at 232K.
(4) Interaction/orientation c.f. for CS_2 (ℓ) at 315K.



(d) (1) Interaction/orientation m.f. for CS_2 (ℓ) at 293K,11.6 kbar
(2) Interaction/orientation m.f. for CS_2 (ℓ) at 296K.
(3) Interaction/orientation m.f. for CS_2 (ℓ) at 232K.

(e) (1) Interaction/orientation c.f. for CCl_4 at 296K.
(2) Interaction/orientation c.f. for CCl_4 at 313K.
(3) Interaction/orientation c.f. for CCl_4 at 328K.

(f) (1) Interaction/orientation m.f. for CCl_4 at 296K.
(2) Interaction/orientation m.f. for CCl_4 at 313K.
(3) Interaction/orientation m.f. for CCl_4 at 328K.

Normalised memory functions for the other dipolar molecules are displayed in figs 3(a) to 3(e), together with the curves for $<O(V)^2> = 0$. As discussed above, this is not a good representation of the free rotor curve, since $K_{\underset{\sim}{m}}(t)$ is even up to t^2 only. However, approximate as these functions are, they are sensitive to the nature of the intermolecular mean square torque - i.e. for MBBA the molecules are packed in a way that is similar to crystalline packing, and dynamical memory is retained as torsional oscillation in a fairly well defined potential energy well takes place. The external torque correlation function $K_{\underset{\sim}{m}}(t)$ being very different from the Markov exponential. Memory is lost in the curve for $<O(V)^2> = 0$ only because of the statistical spread of molecular rotational velocities. Some much less pronounced oscillations occur in the propyne memory function (fig 3(c)), and are damped out in about 1.0 ps; while for the more spherical type molecules (fig 3(a) and 3(b)) where the density of the liquid is low [6], memory is lost more quickly, oscillations being damped out completely. The memory curves for $(CH_3)_2\ CClNO_2$ (ℓ) and $(CH_3)_3\ CCl$ (rotator phase) might contain some intermediate features of highly, but not completely, damped oscillation.

NON-DIPOLAR LIQUIDS

In this case the correlation function $C_{\underset{\sim}{m}}(t)$ is simultaneously one of orientation and interaction, and never becomes exponential (figs 4 and 5). The time scale of the absorption is much shorter than that for the overall dynamical process in dipolar molecules (table 1); the correlation time being typically a fraction of a ps, comparable with the inverse width at half peak height of a typical [3,4,12] induced-absorption band in the liquid phase. Memory functions are damped out to zero in approximately the same time range as the correlation functions - unlike the case of dipolar absorption. This is linked with the fact that induced-dipolar absorption occurs only during the lifetime of the interaction giving rise to it, and thereafter all correlation and memory is lost.

An unexpectedly long-lived memory function may indicate a "sticky collision" process or formation of a long-lived complex. From data [19] on liquid CS_2 at various temperatures and pressures there are indications (fig 5(d)) that the memory function becomes longer lived and more pronouncedly oscillatory as thermal energy (kT) decreases and collisions become less "violent" as a consequence. In contrast, the application of 11.6 kbar of pressure [25] at 293K produces a highly oscillatory correlation function (fig 5(c)) and a short lived, highly damped memory function (fig 5(d)), implying that the dipole is induced by short interactions in a reasonably ordered, lattice-like environment. The interactions seem to be shorter lived than those in the CS_2 (ℓ) at 232K, since the latter memory function is less damped and longer lived, and by implication the molecular dynamics in the solid CS_2 produced at 293 by about 12 kbar of external pressure will be different from the solid obtained by freezing the liquid at 1 bar.

In contrast, the memory function becomes slightly longer lived and less damped as temperature rises in liquid CCl_4 from 296K to 328K (fig 5(f)), and the torque dependent parameters $K_o(o)$ and $K_1(o)$ fall. The opposite dependence of $<O(V)^2>$ upon temperature is predicted by both harmonic well dynamics, where $<O(V)^2> \propto kT \propto \theta$, the angular displacement, and in hard-core collisions, where $<O(V)^2> \propto \frac{N'}{\phi}$ kT, with N' a force coefficient and ϕ a mean angle of free rotation. Consequently, the increase in free colume, allowing the CCl_4 molecules to undergo extended periods of rotation, uninterrupted by torque interaction, must be overcoming the purely thermal effect where $<O(V)^2>$ increases with T. It is relevant to note that the nuclear magnetic resonance spin-rotation relaxation time [26] T_1 of liquids is observed to decrease as temperature is raised, following an Arrhenius law. T_1 is inversely proportional to τ_J, the angular momentum correlation time, which thus increases with temperature. τ_J is a measure of the mean time during which a molecule seems to retain its angular momentum, and in spherical top molecules [26-28] in the liquid state it is known that spin-rotation interaction is the dominant relaxational mechanism, τ_J becoming long even at temperatures well below the critical point, thus implying a considerable degree of rotatory freedom.

The correlation functions for the lighter molecules such as N_2 and CH_4 go negative, which means that in these cases, also, the orientational freedom is great. These functions for the more anisotropic molecules seldom become negative, although the memory functions tend to have a pronounced negative lobe for highly anisotropic cases such as transdecalin (fig 4(f)) and $(CN)_2$ (ℓ) (fig 4(d)).

APPENDIX

In the special case 2,6 of bimolecular quadrupole-induced absorption in linear molecules, C(t) is given by:

$$C(t) = A \int_0^\infty f(\bar{\upsilon}) \int_0^\infty 4\pi R^{-6} \exp\left(-U(R)/kT\right) dR \cos\left(2\pi\bar{\upsilon}ct\right) d\bar{\upsilon}$$

$$\text{where } f(\bar{\upsilon}) = \left(\frac{\bar{\upsilon}}{2B} - \frac{2B}{\bar{\upsilon}}\right) \exp\left(-\frac{hcB}{4kT}\left(\frac{\bar{\upsilon}}{2B} - 3\right)\left(\frac{\bar{\upsilon}}{2B} - 1\right)\right)$$

with A a constant, B the rotational constant (cm^{-1}), R the intermolecular distance, and U(R) the intermolecular potential energy, radially averaged in the above expression, which is valid strictly only for a central (non-angular dependent) U(R).
Now, if we define:

$$C(t) = \sum_{n=0}^{\infty} (-1)^n m_{2n} \frac{t^{2n}}{(2n)!}$$

$$= \langle \underset{\sim}{U}(o) . \underset{\sim}{U}(t) \rangle ,$$

we have, by stationarity properties in time:

$$m_{2n} = \left\langle \left[\frac{d^n \underset{\sim}{U}}{dt^n} \right]^2 \right\rangle$$

$$\propto \int_0^\infty \frac{\alpha(\omega)}{\omega} \omega^{2n-1} d\omega$$

Thus $m_2 = K_o(o)$

$$\propto \int_0^\infty \alpha(\omega)\, d\omega$$

$$= A \int_0^\infty f(\bar{\upsilon}) \int_0^\infty 4\pi R^{-6} \exp\,(-U(R)/kT)\; dR\, d\bar{\upsilon}$$

i.e. $K_o(o)$ is dependent on the space average of U(R), and thus on the mean of its derivative with respect to angular displacement, the torque.

In the liquid, the bimolecular approximation to the many-body interactions characteristic of this phase is a poor one [6] but in general, C(t) and thus $K_o(o)$ is interaction dependent by definition for induced dipolar absorption.

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