

RECENT DEVELOPMENTS IN THE STATISTICAL TREATMENT OF MOLECULAR  
RELAXATION IN THE CONDENSED PHASE.

MYRON WYN EVANS\*

Wolfson College, Oxford, (Gt. Britain)

\* Visiting Fellow at U.C.W., Aberystwyth, Chemistry Department

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ABSTRACT

The report deals with a representative fraction of the theoretical and experimental work of approximately the last decade on molecular relaxation (taken to mean dissipation of the energy of a small external field by molecular fluctuations in a fluid) in the following areas of study.

- (i) Dielectric complex susceptibility in the range of frequencies up to  $10^{13}$  Hz (i.e. into the far infra-red) related to the motion of a unit vector  $\underline{u}$  in the dipolar axis, or the temporary induced dipole in the case of far infra-red absorptions in liquids and gases of non-dipolar molecules.
- (ii) Spin-rotation and spin-spin relaxation times of nuclear magnetic resonance, related to the molecular angular velocity  $\underline{J}$  and  $\underline{u}$  respectively.
- (iii) Depolarised Rayleigh bands of scattered light, related to the second harmonic orientational correlation function of  $\underline{u}$  (permanent or induced).

The fundamental fluctuation-dissipation theorem (and its derivation from the classical Liouville equation of a canonical ensemble) is described fully. The important equation linking the complex susceptibility to the dipole orientational correlation function follows from this treatment. Recent advances in dealing with the "dynamic internal field" are then reviewed in relation to the absorption/dispersion of permanent dipoles in the liquid phase.

The properties of the correlation function  $\langle \underline{u}(0) \cdot \underline{u}(t) \rangle$  as first delineated by Gordon about 10 years ago, are described. This leads on to a major theme of the review - the model representations of the correlation functions related to phenomena (i), (ii) and (iii) above. The limitations

of the Langevin equation are revealed and the recent work of Kubo, Mori, Gordon, Brot, Wyllie and others in extending the simple representation to take account of, among other factors, a finite external torque correlation time is discussed in detail. The use of this theory to give a unified molecular dynamical view of the microwave/far infra-red absorptions of dipolar and non-dipolar molecules is then described, followed by a brief survey of the history of far infra-red observations in fluids, confined significantly to the last decade.

The rotational correlation function  $C_R(t) = 1/2 \langle 3[\underline{u}(0) \cdot \underline{u}(t)]^2 - 1 \rangle$  is observed as the Fourier transform of depolarised Rayleigh bands, the work in this field having benefited recently from the development of the unified description of molecular dynamics in fluids, which embodies and typifies the correlation function formalism. The work of approximately the last ten years in this area is reviewed in relation to similar advances made in the far infra-red/microwave region, and possible applications of the extended Langevin equation of Kubo and Mori are discussed.

Nuclear magnetic resonance spin-rotation relaxation gives an insight into the angular velocity in relation to  $\langle \underline{J}(0) \cdot \underline{J}(t) \rangle$ , and spin-spin relaxation times to  $C_R(t)$ . The vast recent literature of NMR relaxation studies is sampled with the intent of showing how these relaxation times yield important information on the anisotropy of molecular rotation, e.g. that about the long axis of a lath-like molecule can be many times faster than about the perpendicular axis. These representative results are presented in comparison with those of (i) and (ii) and also compared with computer simulations of the molecular angular velocity. Finally translational motions are considered in relation to generalised Langevin theory. An appendix explains the statistical terms used such as correlation, Markov's hypothesis, the central-limit theorem etc.

## INTRODUCTION

Dynamic properties of molecules in gases and solids have been studied since the turn of the century, and, a very few years after that, the first attempts were made at understanding their behaviour in liquids. These early attempts, though elegant in concept and mathematical technique, were often based on some phenomenological, or macroscopic ideas (such as the coefficient of friction) on the microscopic scale. The factors sought were then calculated by returning to the macroscopic level.

Over the last score or more years, some concepts and vocabulary have been borrowed from the field of mathematical statistics and new modes of approach to the different aspects of transport phenomena and spectroscopic properties of fluid matter have been developed. These techniques of equilibrium and non-equilibrium statistical mechanics form a mould within which is cast a general formalism connecting various macroscopic observables to the space-and-time microscopic behaviour of the molecules of the fluid.

Basic among these concepts are the binomial distribution, the variate (or random variable), the stochastic process, correlation, the autocorrelation function, the spectral function, and Markov's hypothesis, which are defined in Appendix 1. Some theorems involving these features are outlined in Appendix 2.

Some examples of observable macroscopic phenomena and their molecular relatives are as follows.

- (1) Dielectric complex susceptibility in the frequency range  $10^{-4}$  -  $10^{13}$  Hz, related to the motion of a unit vector  $\underline{u}$  in the direction of the resultant dipole moment.
- (2) Bandshapes of near infra-red and Raman absorptions related to a unit vector along the molecular transition dipole.
- (3) Depolarised Rayleigh bands of scattered light, related to  $\underline{u}$ .
- (4) Spin-rotation, relaxation times of nuclear magnetic resonance, related to the molecular angular velocity  $\underline{J}$ .
- (5) Bandshape of nuclear magnetic resonance absorptions related to  $M_x$ , the x-component of the magnetization.
- (6) Bandshape of polarised and depolarised Brillouin scattering, related to the trace of the molecular polarisability tensor and the xy'th element respectively.
- (7) Neutron scattering, related to  $\underline{r}_i$ , the position of the i'th nucleus in a fluid.
- (8) Isotope mass diffusion, related to the linear velocity  $\underline{v}$  of the molecules centre-of-mass.
- (9) Mössbauer bandshape, related to  $\underline{r}_i$ , the position of the i'th nucleus in a fluid.
- (10) Complex dynamic shear compliance, a mechanical analogue to the electric responses involved in (1).
- (11) Those macroscopic dynamic variables (such as viscosity) dependent upon the microscopic parameters of Lennard-Jones (or other) intermolecular potentials vital for computer experiments on molecular dynamics.

This report deals mainly with a small, representative, fraction of theoretical and experimental work in the fields (1), (3) and (4) in the last decade or so. It begins with a derivation of the fundamental fluctuation-dissipation theorem in classical mechanics.

#### THE FLUCTUATION-DISSIPATION THEOREM

The nature of molecular dynamics in the liquid phase can be represented in terms of a degree of statistical ordering [1] in the mean positions of the molecules, which in turn may be attributed to a mean local structure. This ordering has a statistical character, both in space, about centres separated by distances of molecular dimensions, and in time over intervals dictated by molecular velocities and molecular separations. The existence of steric constraints imposed by the geometry of the molecules explains the collective character of the translational and rotational movements, as distinct from the individual character of those in the dilute gaseous state. At the same time, the fluctuations in the local structure allow occasional movements of large amplitude (translations of the order of a molecular diameter, rotations of a radian or so) to occur under favourable circumstances.

In an isolated system, the existence of any fluctuation in a particular macroscopic property of the system implies that there are other degrees of freedom available to that system which can interact with the degree(s) of freedom which determine the magnitude of the property. In the case of the kinetic energy ( $T$ ), any fluctuations must be caused by transfer of energy to or from the other degrees of freedom available (e.g. rotation or vibration). There is thus a relationship between the "frictionless" spontaneous fluctuations of a property and the "friction" characterising energy dissipation from the appropriate degrees of freedom. This provides the connection between irreversible processes where energy dissipation from a particular degree of freedom occurs, and the statistical fluctuations in the equilibrium state, provided that the non-equilibrium state is only slightly displaced from the original. This argument is expressed in the fluctuation-dissipation theorem of irreversible statistical mechanics [1-11].

The configuration of a dynamical system at each time  $t$  may be represented by coordinates  $q$ . No matter how the  $q$  values are chosen, the kinetic energy of an inertial system always turns out to be a quadratic function of the velocities  $\dot{q}$ :

$$T = \frac{1}{2} \sum_{rs} a_{rs} \dot{q}_r \dot{q}_s$$

where the  $a$  values may be functions of the  $q$  values. A function of the coordinates ( $q$ ) and momenta ( $p$ ) of the particles in such a system that remains constant throughout the motion of a system is the total energy  $E$ , the sum of the kinetic and potential energies. (The latter is defined such that when a dynamical system of particles behaves such that it has a total mechanical energy which is constant in time, then the external force on the system can be represented in terms of the gradient of the scalar potential function  $V$ , which depends on time explicitly, but is not a function of the velocities ( $\dot{q}$ ) of the particles in the system). When  $E$  is expressed in terms of the coordinates ( $q$ ) and momenta ( $p$ ) it is called the hamiltonian function  $H$ . The fluctuation-dissipation theorem is applicable only in the domain of linear response, i.e. if the energetic effect of the perturbation applied to the system is small compared with its equilibrium hamiltonian.

If the system has  $r$  degrees of freedom,  $r$  can be chosen so that it is independent of the  $q$  values ( $q_1, \dots, q_r$ ) which will completely specify the configuration, and similarly  $r$  independent momenta ( $p_1, \dots, p_r$ ) can also be chosen by:  $p_r = \partial T / \partial \dot{q}_r$ , where  $T$  is the total kinetic energy, as above. Newton's equations of motion can now be expressed in terms of Hamilton's canonical equations as:

$$\dot{q}_r = \frac{\partial H}{\partial p_r}; \quad \dot{p}_r = -\frac{\partial H}{\partial q_r} \quad (1)$$

Since  $H$  is independent of time:

$$\frac{dH}{dt} = \frac{\partial H}{\partial q} \frac{dq}{dt} + \frac{\partial H}{\partial p} \frac{dp}{dt} = 0 \quad (2)$$

One can now develop a technique of simultaneously transforming from the conjugate pairs ( $p, q$ ) to other new pairs ( $P, Q$ ) by a transformation that keeps the canonical eqns (1) invariant in form. Such a process is called a canonical transformation. A whole class of invariants such as the hamiltonian can be expressed most conveniently in terms of Poisson brackets, which for two arbitrary functions  $u$  and  $v$  of the  $p$  and  $q$  values are defined as follows:

$$[u, v] = \sum_{r=1}^n [ (\partial u / \partial p_r) (\partial v / \partial q_r) - (\partial u / \partial q_r) (\partial v / \partial p_r) ]$$

and have the following properties:

- (i)  $[u, K] = 0$ , where  $K$  is a constant;
- (ii)  $[u, v+w] = [u, v] + [u, w]$ ;
- (iii)  $[u+v, w] = [u, w] + [v, w]$ ;
- (iv)  $[uv, w] = u[v, w] + v[u, w]$ ;
- (v)  $[u, v] = -[v, u]$ .

The dynamical equations set up in terms of Poisson brackets are invariant under canonical transform. Thus eqn.(1) becomes:

$$\dot{q}_r = [H, q_r] ; \quad \dot{p}_r = [H, p_r] .$$

The behaviour of a function such as  $C$ , which depends on time  $t$  by the intermediary of the coordinates  $q_r$  and  $p_r$  (e.g. the Euler angles defining the orientation of molecules) can be written as:

$$\frac{dC}{dt} = \sum_r \left( \dot{q}_r \frac{\partial C}{\partial q_r} + \dot{p}_r \frac{\partial C}{\partial p_r} \right) .$$

Using eqn.(1):

$$\frac{dC}{dt} = \sum_r \left( \frac{\partial H}{\partial p_r} \frac{\partial C}{\partial q_r} - \frac{\partial H}{\partial q_r} \frac{\partial C}{\partial p_r} \right) = [H, C], \quad (3)$$

which is the Liouville equation of motion [1,2,4]:

$$\frac{dC}{dt} = LC . \quad (4)$$

The mean observed value of  $C$  is given by [1-4, 7-10]:

$$\langle C(t) \rangle = \int_{\Gamma} C(p, q) {}^1f_c(p, q, t) dpdq , \quad (5)$$

where  ${}^1f_c$  is the first-order space distribution function of the random variable  $C$ . For an isolated system  $d{}^1f_c/dt = 0$  by Liouville's theorem, and therefore:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_r \left[ \dot{q}_r \frac{\partial f}{\partial q_r} + \dot{p}_r \frac{\partial f}{\partial p_r} \right] = 0 ,$$

$$\text{i.e.} \quad \frac{\partial f}{\partial t} = - \sum_r \left[ \dot{q}_r \frac{\partial f}{\partial q_r} + \dot{p}_r \frac{\partial f}{\partial p_r} \right] = -L f . \quad (6)$$

Suppose that an external perturbing force  $F(t)$  results in a change  $H'$  in the Hamiltonian of the system at equilibrium ( $H_0$ ). The new Hamiltonian is given by:

$$H = H_0 + H' . \quad (7)$$

If  $A(p_r, q_r)$  is the property of the system responsible for this increase in the Hamiltonian, then:

$$H' = -A(p_r, q_r)F(t),$$

since  $H'$  is the internal reaction to the external time-dependent perturbation  $F(t)$  (action and reaction being equal and opposite).

For example, the force  $F$  may be an electric field, and  $A$  then will have the units of the electric dipole [11]. It is assumed that the system can be observed by a study of a property  $B$  (related to  $A$ ). The new distribution function is defined by:

$$f = f_0 + f'(t); \quad (9)$$

Denoting, respectively,  $L_0$  and  $L'$  the operators associated via eqns. (3) and (4) with  $H_0$  and  $H'$ , and using eqn.(6),

$$\begin{aligned} L(f_0 + f'(t)) &= [H, f_0 + f'(t)] \\ &= [H, f_0] + [H, f'(t)], \end{aligned}$$

so that

$$\begin{aligned} \frac{\partial f_0}{\partial t} + \frac{\partial f'}{\partial t} &= -L_0(f_0 + f') - L'(f_0 + f') \\ &= -L_0 f_0 - L_0 f' - L' f_0 - L' f' \end{aligned}$$

Now, since  $\frac{\partial f_0}{\partial t} + L f_0 = 0$ , then:

$$\frac{\partial f'}{\partial t} = -L_0 f' - L' f_0 - L' f' \quad (10)$$

If the perturbation is weak, the last term is negligible, since it is the product of the increment of an operator with the increment of a function<sup>[10]</sup>. Also, starting from eqn.(8) then:

$$\begin{aligned} L' &= \sum_r \left[ \frac{\partial H'}{\partial p_r} \frac{\partial}{\partial q_r} - \frac{\partial H'}{\partial q_r} \frac{\partial}{\partial p_r} \right] \\ &= -F(t) D, \end{aligned} \quad (11)$$

$$\text{where } D = \sum_r \left[ \frac{\partial A}{\partial p_r} \frac{\partial}{\partial q_r} - \frac{\partial A}{\partial q_r} \frac{\partial}{\partial p_r} \right].$$

Equation (10) thus becomes:

$$\frac{\partial f'}{\partial t} = -L_0 f' + F(t) D f_0. \quad (12)$$

This can be formally integrated [1-4, 10] to give:

$$f'(t) = \int_{-\infty}^t \exp(-(t-t') L_0) F(t') D f_0 dt' \quad (13)$$

if  $L'(-\infty) = 0$  (i.e.  $F$  zero at  $t = -\infty$ ). Taking the mean value of  $B$  as defined by eqn.(5), and using eqn.(13), then:

$$\begin{aligned} \langle B(t) \rangle &= - \int_{\Gamma} B(p, q) F(p, q, t) dp dq \\ &= B_{eq} + \int_{-\infty}^t F(t') dt' \int_{\Gamma} B(t') e^{-(t-t') L_0} D f_0(t') dp dq \end{aligned}$$

which can be written as:

$$\langle B(t) \rangle = B_{eq} + \int_{-\infty}^t F(t') \psi_{BA}(t, t') dt' . \quad (14)$$

The Liouville equation (4) has no quantity depending explicitly on time, and can be formally integrated as:

$$C(t) = \exp \left[ (t - t') L_0 \right] C(t') , \quad (15)$$

so that:

$$C(2t' - t) = e^{(t' - t) L_0} C(t') ,$$

by stationarity. Applying this equation with

$$\begin{aligned} \psi_{BA}(t, t') &= \int_{\Gamma} B(t') Df_0(2t' - t) dpdq \\ &= \int_{\Gamma} B(t - t') Df_0(0) dpdq . \end{aligned} \quad (16)$$

The second equality results from the stationary character in time of  $Df_0$ , which is taken at equilibrium, and of  $B$ , which depends only on coordinates and momenta.  $\psi_{BA}$  depends only on the change  $\delta t = t - t'$ . Equation (16) shows that  $\psi_{BA}$  is the response of  $B$  to a unit impulse of  $F$  and is therefore called the response function<sup>[1]</sup>, or the after-effect function.

To calculate  $Df_0$ , the type of set to which the system belongs must be chosen. For the canonical set:

$$f_0 \propto \exp(-H_0/kT)$$

one has

$$Df_0 = \sum_r \left[ \frac{\partial A}{\partial p_r} \frac{\partial f_0}{\partial H_0} \frac{\partial H_0}{\partial q_r} - \frac{\partial A}{\partial q_r} \frac{\partial f_0}{\partial H_0} \frac{\partial H_0}{\partial p_r} \right] \quad (17)$$

and using eqn. (3):

$$Df_0 = \frac{f_0 \dot{A}}{kT} .$$

Rewriting eqn.(16) using angular brackets<sup>[1-10, 12]</sup> to denote means over  $p, q$  and  $t$ :

$$\begin{aligned} \psi_{BA}(t) &= \frac{1}{kT} \langle \dot{A}(0) B(t) \rangle = \frac{1}{kT} \langle A(0) \dot{B}(t) \rangle \\ &= -\frac{1}{kT} \frac{d}{dt} \langle A(0) B(t) \rangle . \end{aligned} \quad (18)$$

Therefore

$$\langle B(t) \rangle = B_{eq} - \frac{1}{kT} \int_{-\infty}^t F(t') \dot{\phi}(t - t') dt' , \quad (19)$$

where by definition

$$\phi_{BA}(t) = \langle A(0) B(t) \rangle .$$



is a correlation function of A at  $t = 0$  with B at  $t = t$ . Thus eqn. (19) allows the calculation of the forced response of the system from the correlation function of the spontaneous fluctuations at equilibrium of the magnitudes A and B.

Very often, and without loss of generality<sup>[4]</sup> in the domain of linear response  $F(t)$  is represented by a single sinusoidal component, so that:

$$F(t) = F_0 \text{ Real } [\exp(i\omega t)] = \text{Real } [p(t)] ,$$

$$B(t) = \text{Real } [B \exp(i\omega t)] .$$

Using eqn. (14) with  $B_{eq} = 0$ , as is frequently assumed, then:

$$\begin{aligned} \langle B(t) \rangle &= F_0 \text{ Real } \int_{-\infty}^t \exp(i\omega t') \psi_{BA}(t-t') dt' \\ &= F_0 \text{ Real } [\exp(+i\omega t) \int_0^{\infty} \exp(-i\omega t_0) \psi_{BA}(t_0) dt_0] . \end{aligned} \quad (20)$$

If one now defines generalised complex susceptibility<sup>[1]</sup>

$\chi_{BA}^*$  by:

$$B(t) = F_0 \text{ Real } [\exp(i\omega t) \chi_{BA}^*(\omega)] ,$$

$$B(0) = F_0 \chi_{BA}^*(\omega) ,$$

then from equation (20):

$$\begin{aligned} \chi_{BA}^*(\omega) &= \chi'_{BA}(\omega) - i\chi''_{BA}(\omega) \\ &= \int_0^{\infty} \exp(-i\omega t) \psi_{BA}(t) dt ; \end{aligned} \quad (21)$$

so that:

$$\chi_{BA}^*(\omega) = -\frac{1}{kT} \int_0^{\infty} e^{-i\omega t} \frac{d}{dt} (\phi_{BA}(t)) dt ,$$

$$\text{or } \chi_{BA}^*(\omega) = \frac{\phi_{BA}(0)}{kT} - \frac{i\omega}{kT} \int_0^{\infty} \phi_{BA}(t) \exp(-i\omega t) dt . \quad (22)$$

#### ABSORPTION DISPERSION DUE TO PERMANENT DIPOLES

The fluctuation-dissipation theorem given in its general form in eqn.(22) can be applied to this case where the "external force" applied is a periodic electric field<sup>[6-10, 13]</sup>, the response of the system being the electric polarisation which it develops under the influence of this field<sup>[11]</sup>. The observable quantity is this latter parameter, the polarisation, which is the moment per unit volume. The behaviour

of this moment in phase with the field corresponds to the dispersion element, and its behaviour in quadrature produces the absorption. One has:

$$E_0 e^{i\omega t} = \left( \frac{\epsilon^*(\omega) + 2}{3} \right) E_e e^{i\omega t} \quad (23)$$

where  $\epsilon^*(\omega)$ ,  $E_0 e^{i\omega t}$  and  $E_e e^{i\omega t}$  are respectively the complex dielectric constant, the external applied field, and the electric field which figures in the Maxwell equations in the system<sup>[14]</sup>. This is related to the dielectric constant and to the polarisation  $\langle \underline{M}_Z \rangle / V$ , where  $\langle \underline{M}_Z \rangle$  is the moment in the direction of the field due to the field  $E_0 e^{i\omega t}$  and  $V$  the volume of the system. The susceptibility is now defined<sup>[13, 14, 15]</sup>:

$$\chi^*(\omega) = \frac{\epsilon^*(\omega) - 1}{4\pi} = \frac{\langle \underline{M}_Z(t) \rangle}{VE_e e^{i\omega t}} \quad (24)$$

Using eqn.(21) one has:

$$\chi_e(\omega) = \frac{\langle \underline{M}_Z(t) \rangle}{E_0 e^{i\omega t}} = \int_0^\infty e^{-i\omega t} \psi_Z(t) dt$$

where  $\psi_Z(t) = -\frac{1}{kT} \langle \underline{M}_Z(0) \cdot \dot{\underline{M}}_Z(t) \rangle$

The correlation function  $\langle \underline{M}_Z(0) \cdot \underline{M}_Z(t) \rangle$  is that of spontaneous fluctuations, and because of the mean isotropy in liquids, it becomes:

$$\frac{1}{3} \langle \underline{M}(0) \cdot \underline{M}(t) \rangle$$

Using eqns.(22) - (24), then

$$\frac{\epsilon^*(\omega) - 1}{\epsilon^*(\omega) + 2} = -\frac{4\pi}{9kTV} \int_0^\infty \exp(-i\omega t) \dot{\phi}(t) dt$$

where  $\phi(t) = \langle \underline{M}(0) \cdot \underline{M}(t) \rangle$ .

#### GAS PHASE

Equation (25) is of general validity, whatever the origin of the dipole moment of the system (atomic polarisation, ionic, orientational, etc.), but it cannot always be easily applied because it refers to the fluctuating moment of a macroscopic sphere in vacuo<sup>[8, 14, 15]</sup>. For a fluid of dipolar molecules whose spontaneous fluctuations are unrelated<sup>[3, 12]</sup> (so that  $\phi(t)$  can be written as the correlation function for monomolecular orientation); and where the molecules are only slightly polarisable (so that  $\epsilon^*(\omega)$  differs only slightly from unity), the deformation polarisation being negligible, one has:

$$\langle \underline{M}(0) \cdot \underline{M}(t) \rangle = \sum_{ij} \langle \underline{\mu}_i(0) \cdot \underline{\mu}_j(t) \rangle$$

with  $\langle \underline{\mu}_i(0) \cdot \underline{\mu}_j(t) \rangle = 0$  for  $j \neq i$ .

Thus 
$$\begin{aligned} \phi(t) &= N \langle \underline{\mu}_i(0) \cdot \underline{\mu}_i(t) \rangle \\ &= N\mu^2 F_V(t) \end{aligned}$$

where  $F_V(t) = \langle \underline{u}(0) \cdot \underline{u}(t) \rangle$ , where  $\underline{u}$  is a unit vector along the permanent dipole moment. Thus

$$4\pi\chi'(\omega) = \epsilon'(\omega) - 1 = \frac{4\pi N\mu^2}{3kTV} \left[ 1 - \omega \int_0^\infty F_V(t) \sin \omega t dt \right] \quad (26)$$

$$\omega^{-1} c\alpha(\omega) = \epsilon''(\omega) = \frac{4\pi N\mu^2 \omega}{3kTV} \int_0^\infty F_V(t) \cos \omega t dt \quad (27)$$

with  $\frac{4\pi\mu^2}{3kTV} = \epsilon_0 - 1 = 4\pi\chi_0$ ,

where  $\epsilon_0$  is the dielectric constant (electric permittivity) at zero frequency, and  $\chi_0$  the corresponding susceptibility. Equations (26) and (27) apply when the fluid is relatively dilute, but sufficiently dense to produce a continuous spectrum to broaden and overlap the rotational quantum transitions<sup>[12]</sup> since classical mechanics has been used throughout. The quantised version of eqn.(27) is given by Gordon<sup>[3,12]</sup> as:

$$\frac{c\alpha(\omega)}{\omega} = \epsilon''(\omega) = \frac{4\pi^2 N}{3\hbar V} (1 - e^{-\hbar\omega/kT}) \mu^2 \tilde{F}_V(\omega);$$

$\tilde{F}_V(\omega)$  being the Fourier transform of  $\langle \underline{\mu}_{op}(0) \cdot \underline{\mu}_{op}(t) \rangle$  the non-symmetrical quantum correlation function.

#### DIPOLAR MOLECULES IN THE PURE LIQUID PHASE

Each molecular dipole polarises its neighbours which in turn react upon it<sup>[14,15]</sup>. The corresponding static problem has been treated by Onsager<sup>[8,14,15]</sup>, assuming that there are no forces at short distances to correlate with the orientation of the molecules. (A parameter  $g$  was later introduced by Kirkwood<sup>[14]</sup>, and then by Frohlich to represent such correlations).

The equivalent dynamic formalism has been recently reviewed by Brot<sup>[8]</sup>, here it is exemplified with a relation derived by Cole<sup>[3]</sup> which is linear in  $\epsilon(\omega)$  :

$$\frac{\epsilon(\omega) - n^2}{\epsilon_0 - n^2} = \left[ 1 + \frac{3\epsilon_0}{2\epsilon_0 + n^2} \left( \int_0^\infty e^{i\omega t} [-\dot{F}_V(t)] dt \right)^{-1} \right]^{-1}, \quad (28)$$

where

$$\epsilon_0 - n^2 = \frac{4N}{V} \left( \frac{3\epsilon_0}{2\epsilon_0 + n^2} \right) \left( \frac{n^2 + 2}{3} \right)^2 \frac{\mu^2}{3kT}, \quad (29)$$

$n$  being the refractive index at, say,  $150 \text{ cm}^{-1}$ . If  $\epsilon_0 \neq 1$ , eqns. (28) and (29) reduce to their precursors. One can therefore say that eqn. (28) contains a correction for the internal field, i.e. it takes account of inter-correlation terms due to dipolar forces. In eqn. (28) inter-correlations of the orientation of molecules due to forces at short distances are not accounted for. From the static point of view, Kirkwood's parameter  $g$  is the answer; the analogous dynamic treatment has been pursued by Brot<sup>[8]</sup> who treated the problem of the internal field in a group of inter-correlated molecules constrained in a cavity just large enough for the correlations to be negligible outside. Using the Lorentz field<sup>[14,15]</sup>, he obtains:

$$F_V(t) = \frac{27kT}{4\pi^3 N \mu^2} \int_0^\infty \frac{\alpha(\bar{\nu}) n(\bar{\nu}) \cos(2\pi\bar{\nu}ct) d\bar{\nu}}{\bar{\nu}^2 ([\epsilon'(\bar{\nu}) + 2]^2 + \epsilon''(\bar{\nu})^2)};$$

and with the Onsager field:

$$F_V(t) = \frac{27kT}{4\pi^3 N \mu^2} \frac{(2\epsilon_0 + \epsilon_\infty)^2}{(\epsilon_\infty + 2)^2} \int_0^\infty \frac{\alpha(\bar{\nu}) n(\bar{\nu}) \cos(2\pi\bar{\nu}ct) d\bar{\nu}}{\bar{\nu}^2 [(\epsilon'(\bar{\nu}) + 2\epsilon_0)^2 + \epsilon''(\bar{\nu})^2]};$$

where  $\omega = 2\pi\bar{\nu}c$ , and  $\alpha$  is the absorption coefficient. Above  $10 \text{ cm}^{-1}$ , i.e. in the far infra-red<sup>[14,16]</sup>,  $\epsilon'(\bar{\nu}) \doteq \epsilon_\infty$ , and  $\epsilon''(\bar{\nu})$  is small (although  $\alpha(\bar{\nu})$  is large). Using these approximations, both these eqns. reduce to:

$$F_V(t) = \frac{3kT}{4\pi^3 N \mu^2} \left[ \frac{9n}{(n^2 + 2)^2} \right] \int_0^\infty \frac{\alpha(\bar{\nu})}{\bar{\nu}^2} \cos(2\pi\bar{\nu}ct) d\bar{\nu};$$

where the square brackets enclose the often-used<sup>[16]</sup> Polo-Wilson non-dispersive correction.

#### PROPERTIES OF THE CORRELATION FUNCTION $F_V(t)$

Using eqns. (22) and (27), it is seen that  $F_V(t)$  is a real, even function of time, so that it can be expanded as follows<sup>[3,4]</sup>:

$$\langle \underline{u}(0) \cdot \underline{u}(t) \rangle = \langle \underline{u}^2(0) \rangle - \frac{t^2}{2!} \langle \underline{\dot{u}}^2(0) \rangle + \frac{t^4}{4!} \langle \underline{\ddot{u}}^2(0) \rangle - \dots$$

with  $\langle \underline{u}^2(0) \rangle = 1$  by definition. For a linear molecule

$$-\ddot{F}_V(0) = \langle \underline{\dot{u}}^2(0) \rangle = 2kT/I,$$

where  $I$  is the moment of inertia, since for rotational kinetic energy,  $(1/2)I\omega^2$  becomes on average  $kT$ . The mean square acceleration  $\langle \underline{\ddot{u}}^2(0) \rangle$

is the sum of a radial part (centripetal acceleration owing to the fact that the vector  $\underline{y}$  is of a fixed length), independent of interactions and having the value of  $8k^2T^2/I^2$ ; and a tangential part  $\langle O(V)^2 \rangle / I^2$  produced by the mean square torque  $\langle O(V)^2 \rangle$  that the environment produces on the molecule.

Grouping together these results, one has, for a linear molecule

$$F_V(t) = 1 - \frac{kTt^2}{I} + \left[ \frac{k^2T^2}{3I^2} + \frac{\langle O(V)^2 \rangle}{24I^2} \right] t^4 - \dots$$

Gordon<sup>[17]</sup> has calculated the first two odd moments, which are of a quantum origin, as well as some quantum contributions to the even moments. The second moment above can be used to provide a "sum rule" for pure dipolar absorption. In the classical limit, ( $\hbar \rightarrow 0$ ):

$$\ddot{F}_V(t) = \frac{3kTVnc}{4\pi^2N\mu^2} \int_{-\infty}^{\infty} \exp(i\omega t) \alpha(\omega) d\omega,$$

so, at  $t = 0$ ,

$$\ddot{F}_V(0) = \frac{2kT}{I} = \frac{3kTVnc}{4\pi^2N\mu^2} \cdot 2 \int_0^{\infty} \alpha(\omega) d\omega,$$

from which, for the integrated absorption intensity per molecule for all rotational type (microwave and far infra-red) absorptions, one has:

$$\int_0^{\infty} \frac{V}{N} \alpha(\omega) d\omega = \frac{4\pi^2\mu^2}{3Inc} \quad (30)$$

which is Gordon's sum rule in the absence of an internal field correction [8].

#### MODELS FOR THE CORRELATION FUNCTION-ROTATIONAL BROWNIAN MOTION

The equation proposed by Langevin<sup>[18,11,7]</sup> to account for translational Brownian motion can be extended to describe the rotational counterpart. Thus, in the fixed frame<sup>[9]</sup>

$$\frac{d\tilde{J}}{dt} + \tilde{\zeta}_R \cdot \tilde{J} = \tilde{\Gamma}(t) \quad (3)$$

where  $\tilde{J}$  is the kinetic moment of the particle,  $\tilde{\zeta}_R$  is the rotational "friction" tensor and  $\tilde{\Gamma}(t)$  is a random torque having the following properties<sup>[1]</sup>:

- (i)  $\tilde{\Gamma}(t)$  is stationary and Gaussian;
- (ii) It has an infinitely short correlation time<sup>[4]</sup>, so that  $\langle \tilde{\Gamma}(0) \cdot \tilde{\Gamma}(t) \rangle = 2D_J \delta(t)$ , where  $\delta(t)$  is the delta-function in time;
- (iii) No correlation exists between the kinetic moment of the particle

and the random couple, so that:

$$\langle \underline{J}(0) \cdot \underline{\Gamma}(t) \rangle = 0.$$

It is often advantageous to write the Langevin equation in a molecular frame of coordinates such as that along the principal axes of inertia:

$$\bar{I} \frac{d\omega}{dt} + \omega \times (\bar{I} \cdot \omega) + \zeta_R \cdot (\bar{I} \cdot \omega) = \underline{\Gamma}(t)$$

This is a non-linear differential equation which can be simplified if it is assumed that the angular velocity of the particle is sufficiently small that the non-linear term be negligible. Therefrom:

$$\frac{d\omega}{dt} + \bar{\beta}\omega = \underline{\Gamma}^*(t) \quad (32)$$

where  $\underline{\Gamma}^*(t)$  has the properties of angular acceleration, or torque per unit I. The autocorrelation which this equation yields, upon integration<sup>[7]</sup> is:

$$\langle \overline{\omega(0)\omega(t)} \rangle = \exp(-\bar{\beta}|t|) \langle \overline{\omega(0)\omega(0)} \rangle \quad (33)$$

from which a complex spectral density:

$$|\bar{\beta} + i\omega|^2 \bar{S}_{\omega}(\omega) = 2\bar{D}_{\omega}^* \quad (33a)$$

can be calculated by Fourier inversion,  $D_{\omega}^*$  being defined as in condition (ii) above.

Doob's theorem<sup>[4]</sup> states that a random, stationary, Gaussian process is Markovian<sup>[19]</sup> if, and only if, its autocorrelation function is exponential. Thus the above velocity  $\omega(t)$  is rigorously Markovian, Gaussian, and stationary in time, given the restrictions upon  $\underline{\Gamma}^*(t)$ . If a second order conditional distribution function of  $\omega$  is defined such that

$$\lim_{t \rightarrow \infty} {}^2f_{\omega}^{\text{cond}} = {}^1f_{\omega}(\omega) \quad (\text{cf. eqn. (5)})$$

then  ${}^2f_{\omega}^{\text{cond}}$  satisfies the general Fokker-Planck equation<sup>[1,9,20-22]</sup> established<sup>[23]</sup> for all Markovian processes, uni- or multi-dimensional. In the case of a uni-dimensional, Markovian process of free rotation disturbed by collisions:

$$\frac{\partial}{\partial t} [{}^2f_{\omega}^{\text{cond}}] = -\frac{\partial}{\partial \omega} [A(\omega) {}^2f_{\omega}^{\text{cond}}] + \frac{1}{2} \frac{\partial^2}{\partial \omega^2} [B(\omega) {}^2f_{\omega}^{\text{cond}}] .$$

The transition moments  $A(\omega)$  and  $B(\omega)$  of first and second order respectively, can be easily deduced from the Langevin equation as:

$$A(\omega) = \lim_{\Delta t \rightarrow 0} \frac{\langle \Delta \omega \rangle}{\Delta t} = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left[ -\beta \omega \Delta t + \lim_{t \rightarrow \infty} \frac{1}{t} \int_t^{t+\Delta t} \Gamma^*(t') dt' \right]$$

$$= -\beta \omega,$$

$$B(\omega) = \lim_{\Delta t \rightarrow 0} \frac{\langle \Delta^2 \omega \rangle}{\Delta t} = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left[ \beta^2 \omega^2 \Delta t^2 + \lim_{t \rightarrow \infty} \frac{1}{t^2} \iint_t^{t+\Delta t} \Gamma^*(t') \Gamma^*(t'') dt' dt'' \right]$$

$$= 2D_{\omega}^* .$$

The classical diffusion equation is then deduced as:

$$\frac{\partial}{\partial t} ({}^2f_{\omega} \text{cond}) = \frac{\partial}{\partial \omega} [\beta \omega + D_{\omega}^* \frac{\partial}{\partial \omega}] ({}^2f_{\omega} \text{cond}) .$$

The only solution which yields a  $\delta(\omega - \omega_0)$  as  $t \rightarrow 0$  is:

$${}^2f_{\omega} \text{cond} = \frac{1}{2\pi q^2} \exp(-(\omega - p)^2 / 2q^2)$$

with  $p = \omega_0 \exp(-\beta|t|)$  and

$$q = \frac{D_{\omega}^*}{\beta} (1 - \exp(-2\beta|t|)) .$$

The non-zero, stationary solution is:

$$\lim_{t \rightarrow \infty} {}^2f_{\omega} \text{cond} = \frac{\beta}{2\pi D_{\omega}^*} \exp\left[-\frac{\beta \omega^2}{2D_{\omega}^*}\right] = {}^1f_{\omega}(\omega) .$$

The identification of  ${}^1f_{\omega}$  with the Maxwell-Boltzmann distribution is a fundamental hypothesis leading to:

$$D_{\omega}^* = \frac{kT}{I} \beta$$

where  $D_{\omega}^*$  is the diffusion coefficient in velocity space. Berne<sup>[4]</sup> has shown that this identification is equivalent to:

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

It is possible to deduce the following relations, starting from the expression for  ${}^1f_{\omega}$

$$\langle \omega(t) \rangle = \langle \omega \rangle = 0 ,$$

$$\langle \omega(0) \omega(0) \rangle = \langle \omega^2 \rangle = \sigma_{\omega}^2 = kT/I ,$$

the latter being well-known from kinetic theory.

#### MEMORY FUNCTIONS [24,25]

To solve the simple Langevin equation, some classical hypotheses concerning  $\Gamma^*(t)$  have been used above which can, unfortunately, lead to physically unacceptable results. The theory of random functions<sup>[20-22]</sup> shows that a necessary and sufficient condition for a stationary process

$\omega(t)$  to be well-behaved is that the second derivative of its auto-correlation function be defined at  $t = 0$ . If  $\bar{C}_\omega(t) = \exp(-\beta|t|)\bar{C}_\omega(0)$ , it is clear that the quantity  $|\bar{C}_\omega(t)|_{t=0}$  is not defined, and that the random process  $\omega(t)$  is not differentiable.

This means that a random process  $\Gamma^*(t)$ , of infinitely small correlation time, has no physical reality. In general [24,4], it is required that:

- (i)  $\Gamma^*(t)$  be not Gaussian;
- (ii)  $\Gamma^*(t)$  have a finite correlation time;
- (iii) the friction tensor be not independent of time,  $t$ .

A more general form of Langevin's equation has been proposed by Kubo [1,24] and others [25,2,4]:

$$\frac{d}{dt} \omega(t) + \int_0^t \bar{K}_\omega(t-\tau') \omega(\tau') d\tau' = \Gamma^*(t), \quad (34)$$

where  $\bar{K}_\omega(t)$  is a time-dependent friction tensor. It can be verified that the following hypotheses are implied:

$$\begin{aligned} \langle \Gamma^*(t) \rangle &= 0, \\ \langle \overline{\omega(0)\Gamma^*(t)} \rangle &= \bar{0}. \end{aligned}$$

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

$$\begin{aligned} \frac{d}{dt} \langle \overline{\omega(0)\omega(t)} \rangle &= - \int_0^t \bar{K}_\omega(t-\tau') \langle \overline{\omega(0)\omega(\tau')} \rangle d\tau' \\ &\quad + \langle \overline{\omega(0)\Gamma^*(t)} \rangle, \end{aligned} \quad (35)$$

with  $\langle \overline{\omega(0)\Gamma^*(t)} \rangle = \bar{0}$ .

This equation has been called a "memory equation" with  $\bar{K}_\omega(t)$  as a "memory" tensor [9]. It can be solved via a Laplace transformation [26]:

$$[p + \bar{K}_\omega(p)] \bar{S}_\omega(p) = \langle \overline{\omega(0)\omega(0)} \rangle$$

where  $\bar{K}_\omega(p)$  and  $\bar{S}_\omega(p)$  are the Laplace transforms of  $\bar{K}_\omega(t) = \langle \overline{\omega(0)\omega(t)} \rangle$  and of  $\bar{K}_\omega(t)$ . It is possible to deduce the following property of the memory tensor:

$$\langle \overline{\omega(0)\omega(0)} \rangle \bar{K}_\omega(t) = \langle \overline{\Gamma^*(0)\Gamma^*(t)} \rangle \quad (36)$$

which is the Kubo [1,24] second fluctuation-dissipation theorem [4].

However, the "equilibrium" properties of the system remain unchanged. For a unidimensional process of free rotation disturbed by collision, the Maxwell-Boltzmann equilibrium distribution is regained:

$${}^1 f_\omega = \frac{I}{2\pi kT} \exp\left(-\frac{I\omega^2}{2kT}\right)$$

with, as above,  $\langle \omega \rangle = 0$ ,



$$\langle \omega(0)\omega(0) \rangle \quad \sigma_{\omega}^2 = kT/I.$$

Thus the second fluctuation-dissipation theorem can be written as

$$K_{\omega}(t) = \frac{I}{kT} \langle \Gamma^*(0)\Gamma^*(t) \rangle = \frac{1}{IkT} \langle \Gamma(0)\Gamma(t) \rangle.$$

If the autocorrelation function of the random torque  $\Gamma^*(t)$  is a Dirac delta-function, then so is  $K_{\omega}(t)$ , and classical Langevin theory results:

$$D_{\omega}^* = \int_0^{\infty} \langle \Gamma^*(0)\Gamma^*(t) \rangle dt = D_J/I^2 = \frac{1}{I^2} \int_0^{\infty} \langle \Gamma(0)\Gamma(t) \rangle dt$$

$$\beta_{\omega} = \int_0^{\infty} \frac{I}{kT} \langle \Gamma^*(0)\Gamma^*(t) \rangle dt = \frac{I}{kT} D_{\omega}^*.$$

#### APPLICATION TO MICROWAVE AND FAR INFRA-RED ROTATIONAL ABSORPTIONS

In general, as has been shown previously, rotational type<sup>[8,16]</sup> far infra-red and microwave bands of dipolar molecules have their associated time autocorrelation functions defined<sup>[12]</sup>, in the absence of cross-correlations, by:

$$C_m(t) = \langle \underline{u}(0) \cdot \underline{u}(t) \rangle = \int_0^{\infty} \exp(i\omega t) \frac{3\hbar c}{4\pi^2} \frac{\sigma(\omega) d\omega}{\omega (-\exp(-\hbar\omega/kT))}, \quad (37)$$

where  $\underline{u}$  is the dipole unit vector, and  $\sigma(\omega)$  is the absorption cross section.

Using  $C_m(t)$  in eqn.(34) gives

$$\dot{C}_m(t) = - \int_0^t K_o(t-\tau') C_m(\tau') d\tau',$$

with  $K_o(t-\tau')$  as the associated response function whose Fourier transform would be the frequency-dependent friction coefficient<sup>[7]</sup>.

It can be shown<sup>[25]</sup> that the set of memory functions  $K_o(t), \dots, K_n(t)$  obey the set of coupled Volterra equations such that:

$$\frac{\partial}{\partial t} K_{n-1}(t) = - \int_0^t K_n(t-\tau') K_{n-1}(\tau') d\tau', \quad (38)$$

with  $n=1, \dots, N$ . Taking Laplace transforms:

$$\tilde{C}_m(p) = \frac{\tilde{C}_m(0)}{p + \tilde{K}_o(p)} = \frac{\tilde{C}_m(0)}{p + \frac{\tilde{K}_o(0)}{p + \tilde{K}_1(p)}} = \dots \quad (39)$$

This is Mori's continued fraction theorem<sup>[4,25]</sup>. The associated spectrum of frequencies,  $\tilde{C}_m(i\omega)$ , which is the Fourier-Laplace transform of  $\tilde{C}_m(p)$ , can

now be obtained by truncating the series of eqns.(39) using a convenient form for  $\tilde{K}_N(p)$ .

If this truncation is such that  $\tilde{K}_0(p) = \gamma$ , a constant, then:

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

which is the simple, classical, Langevin behaviour of eqn.(33). Cole<sup>[13]</sup> has given a careful exposition of how the Debye equations for  $\epsilon''$  and  $\epsilon'$  result from this exponential dipolar correlation function. It has been shown above that this  $C_m(t)$  is badly behaved at  $t=0$ , thus by implication, the Debye relations are unacceptable<sup>[8,16]</sup> at higher frequencies (above ca.  $2 \text{ cm}^{-1}$  into the far infra-red). The spectral function defined by eqn.(33a) leads to an asymptotic constant absorption in terms of the absorption coefficient  $\alpha(\bar{\nu})$  from about  $10 \text{ cm}^{-1}$  onwards (often called<sup>[14]</sup> the Debye plateau). The experimental behaviour of  $\alpha(\bar{\nu})$  is such as to exceed this plateau in every dipolar liquid thus far observed. This excess is known as the Poley<sup>[27]</sup> absorption, first clearly foreseen in 1955.

As an illustration of the physical significance of the series of eqns.(38) or (39), and in order to show how the above behaviour of  $\alpha(\bar{\nu})$  can be simulated theoretically, it is instructive to consider the truncation:

$$K_0(t) = K_0(0) \exp(-\gamma_0 t), \quad (40)$$

so that:

$$\tilde{K}_0(p) = \tilde{K}_0(0) / (p + \gamma_0),$$

$$\text{and} \quad \tilde{C}_m(p) = \frac{p + \gamma_0}{p^2 + p\gamma_0 + K_0(0)} \quad (41)$$

From eqn.(41) one can proceed in two ways. Firstly, the Fourier-Laplace transform yields the real part of  $C_m(i\omega)$  as an absorption bandshape, and the imaginary part as proportional to a spectral dispersion. Secondly, the Laplace inverse transform yields an expression for  $C_m(t)$ . Therefore one has:

$$\text{Real} [\tilde{C}_m(i\omega)] = \frac{\gamma_0 K_0(0)}{K_0(0) - \omega^2 + \omega^2 \gamma_0^2} \quad (42)$$

$$C_m(t) = \exp(-\gamma_0 t) \cos \left[ \left( K_0(0) - \frac{\gamma_0^2}{4} \right)^{\frac{1}{2}} t \right] + \frac{\gamma_0}{2} \left[ K_0(0) - \frac{\gamma_0^2}{4} \right]^{-\frac{1}{2}} \sin \left[ \left( K_0(0) - \frac{\gamma_0^2}{4} \right)^{\frac{1}{2}} t \right]$$

for  $K_0(0) > \gamma_0^2/4$  ;

$$= \exp(-\gamma_0 t) (1 + \gamma_0 t/2) \text{ for } K_0(0) = \gamma_0^2/4 ;$$

$$= \exp(-\gamma_0 t) \cosh \left[ \left( \frac{\gamma_0^2}{4} - K_0(0) \right)^{\frac{1}{2}} t \right]$$

$$+ \frac{\gamma_0}{2} \left[ \frac{\gamma_0^2}{4} - K_0(0) \right]^{-\frac{1}{2}} \sinh \left[ \left( \frac{\gamma_0^2}{4} - K_0(0) \right)^{\frac{1}{2}} t \right]$$

for  $K_0(0) < \gamma_0^2/4$  .

The short-time expansion of  $C_m(t)$  has no term in  $t$  but one in  $t^3$ , so this form is an improvement over the pure exponential, since  $C_m(t)$  should be an equilibrium, even function.

A physical meaning of eqns. (40 - 43) becomes clear if it is noticed that the  $C_m(t)$  of eqn. (43) is that corresponding to the rotational Langevin equation of a vibrator of proper frequency  $\omega_0$  perturbed by a process of random collisions [7,8] separated by an interval  $\tau_c$ :

$$\ddot{\underline{x}} + \dot{\underline{x}}/\tau_c + \omega_0^2 \underline{x} = \underline{A}(t) \quad (44)$$

so that  $\langle \underline{x}(0) \cdot \underline{x}(t) \rangle / \langle \underline{x}(0) \cdot \underline{x}(0) \rangle$  is given by eqn. (43) with  $\gamma_0$  replaced by  $1/\tau_c$  and  $K_0(0)$  by  $\omega_0^2$ . Here  $\dot{\underline{x}}$  has the units of angular velocity, and  $\underline{A}(t)$  is a stochastic torque per unit mass. The situation is identical with that where hard-core collisions between molecules are envisaged to take place at random times (28 - 30). These collisions randomise the direction of the molecular angular velocity vector, so that the macroscopic value is the root mean square  $\omega_0$ . This is usually known as the M-diffusion model of Gordon [28], which is therefore equivalent to a single-exponential memory function.

Bliot et al [31] have shown that if the collisions were to randomise the angular velocity in both direction and magnitude (J-diffusion), then

$$K_0(t) = K_{FR}(t) \exp(-\gamma_J |t|)$$

would be the equivalent memory function representation where  $K_{FR}(t)$  would be that corresponding to a Gaussian distribution of freely rotating molecules. This gives a clue as to the meaning of  $K_0(0)$  in eqn. (40), i.e. a mean square angular velocity of a Gaussian ensemble of molecules.

As analytical equation for  $C_m(t)$  of the M-diffusion limit was evaluated by Brot [29], who extended the application to the autocorrelation function of a vibrator in a multi-well potential formed by neighbouring molecules [8]. Libration, or torsional oscillation, of a permanent dipole within a potential well is assumed to be perturbed by 'weak' thermal collisions of a given mean frequency, while 'strong' collisions (of frequency weighted by a Boltzmann distribution) induce relaxational jumps from one well to another [30]. The theoretical absorption curves have been compared with far infra-red and microwave results in the plastic crystalline (rotator) and dense liquid phases of a wide range of molecules of different shapes by Larkin et al [32]. The behaviour of the corresponding  $C_m(t)$  has been investigated by Evans [33] for ca. thirty molecules (Figs 1 - 7)

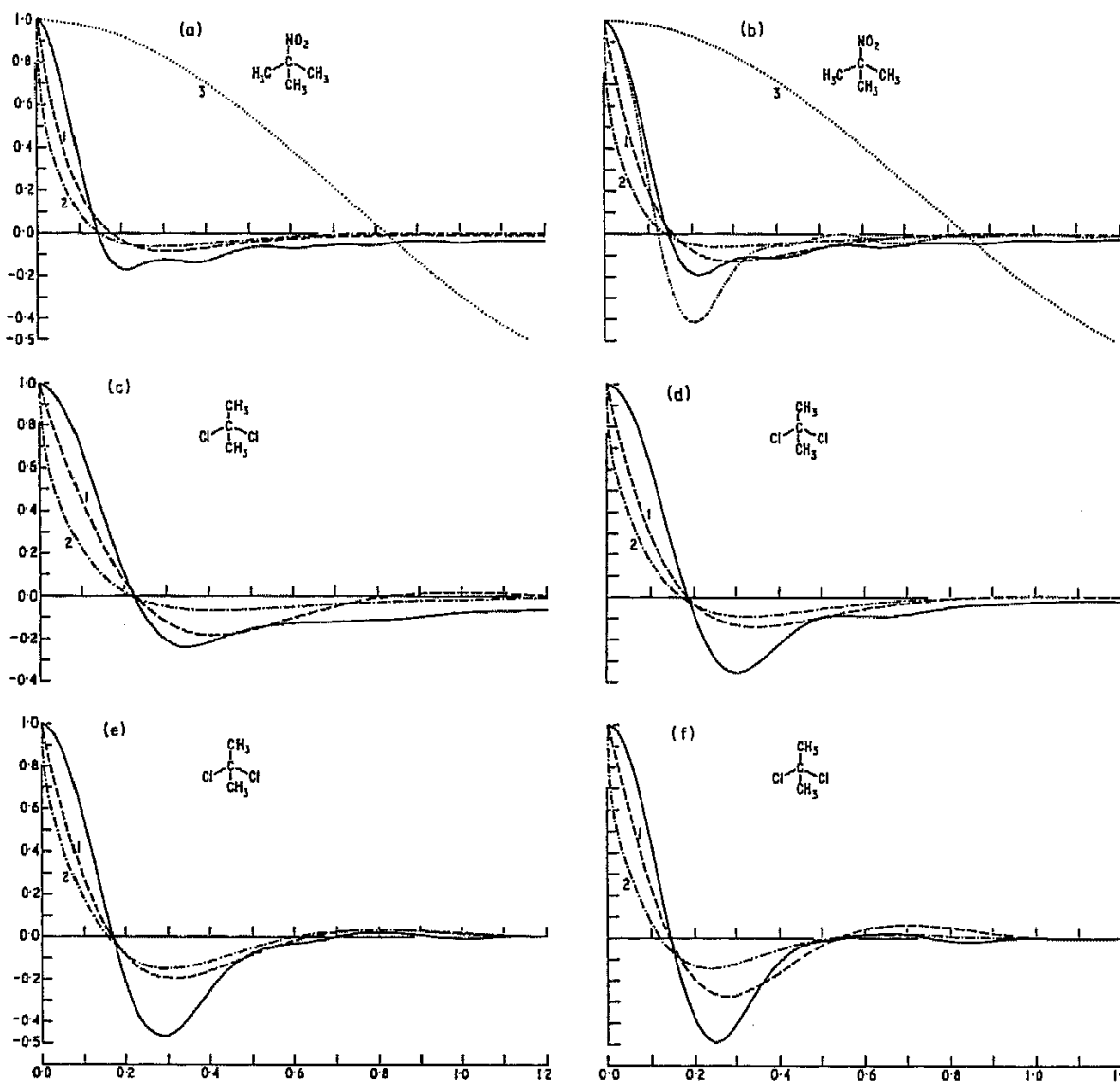


Fig. 1. (—) Experimental [32,33]  $C(t) = -\ddot{C}_m(t)$  (eqn. (37)). (---) (1) Brot-Larkin model [32,33,8]; (2) The itinerant oscillator model [7,33]; (3) Free rotation ( $\langle \omega^2 \rangle = 0$ ). (a) 2-methyl-2-nitropropane (rotator phase I) at 294 K; (b) 2-methyl-2-nitropropane (rotator phase I) at 273 K and 219 K; (c) 2,2-dichloropropane (liquid) at 295 K; (d) 2,2-dichloropropane (liquid) at 241 K; (e) 2,2-dichloropropane (rotator phase) at 235 K; (f) 2,2-dichloropropane (rotator phase) at 192 K. Abscissa time ( $t$ ) (ps), ordinate ( $C(t)$ ). Reproduced by permission from ref.33.

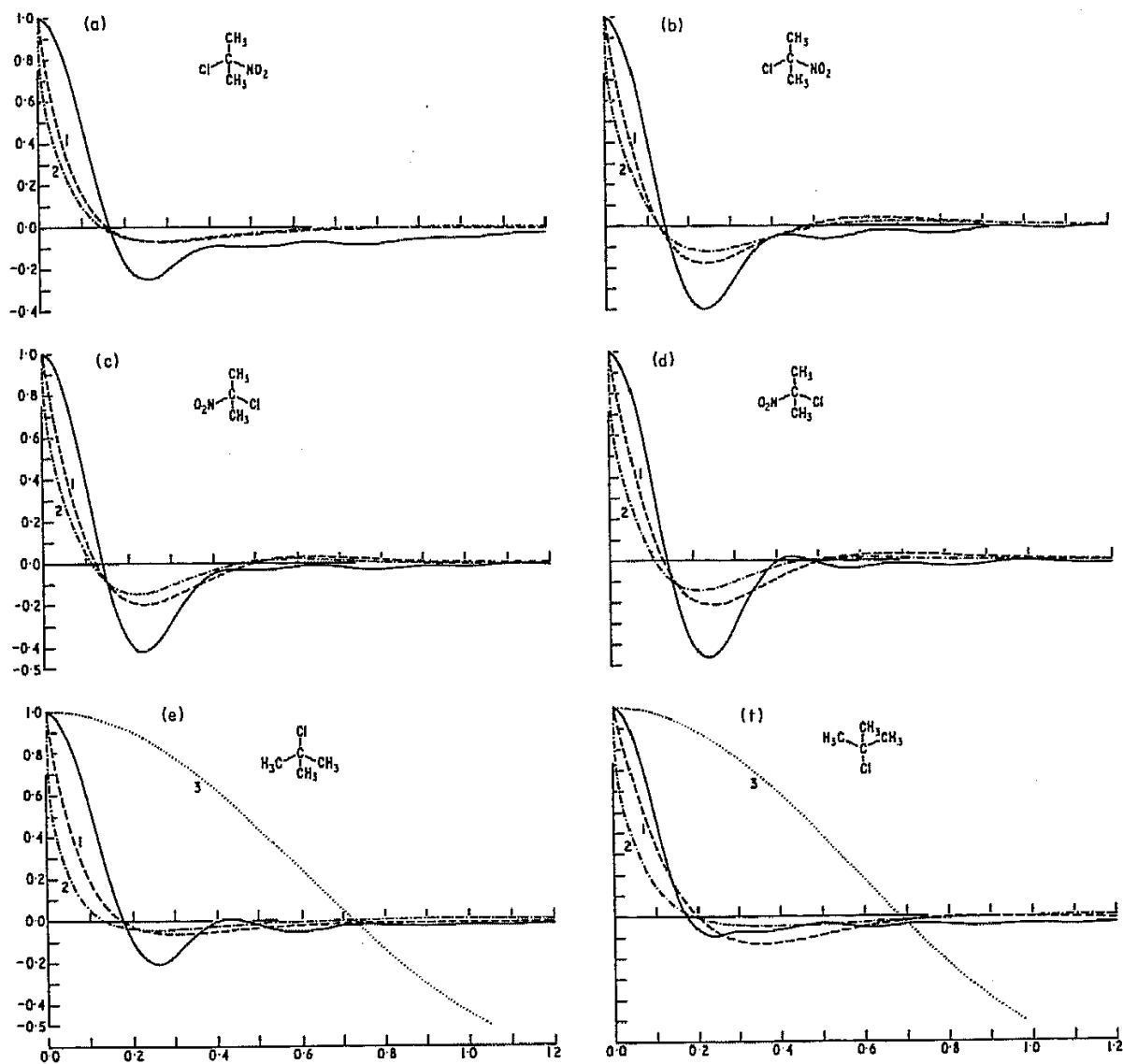


Fig. 2. As for Fig.1. (a) 2-chloro-2-nitropropane (liquid) at 293 K ; (b) 2-chloro-2-nitropropane (liquid) at 253 K; (c) 2-chloro-2-nitropropane (rotator) at 233 K; (d) 2-chloro-2-nitropropane (rotator) at 209 K; (e) t-butyl chloride (rotator) at 238 K (see also Fig.7); (f) t-butyl chloride (liquid) at 274 K. Abscissa and ordinate as for Fig.1.

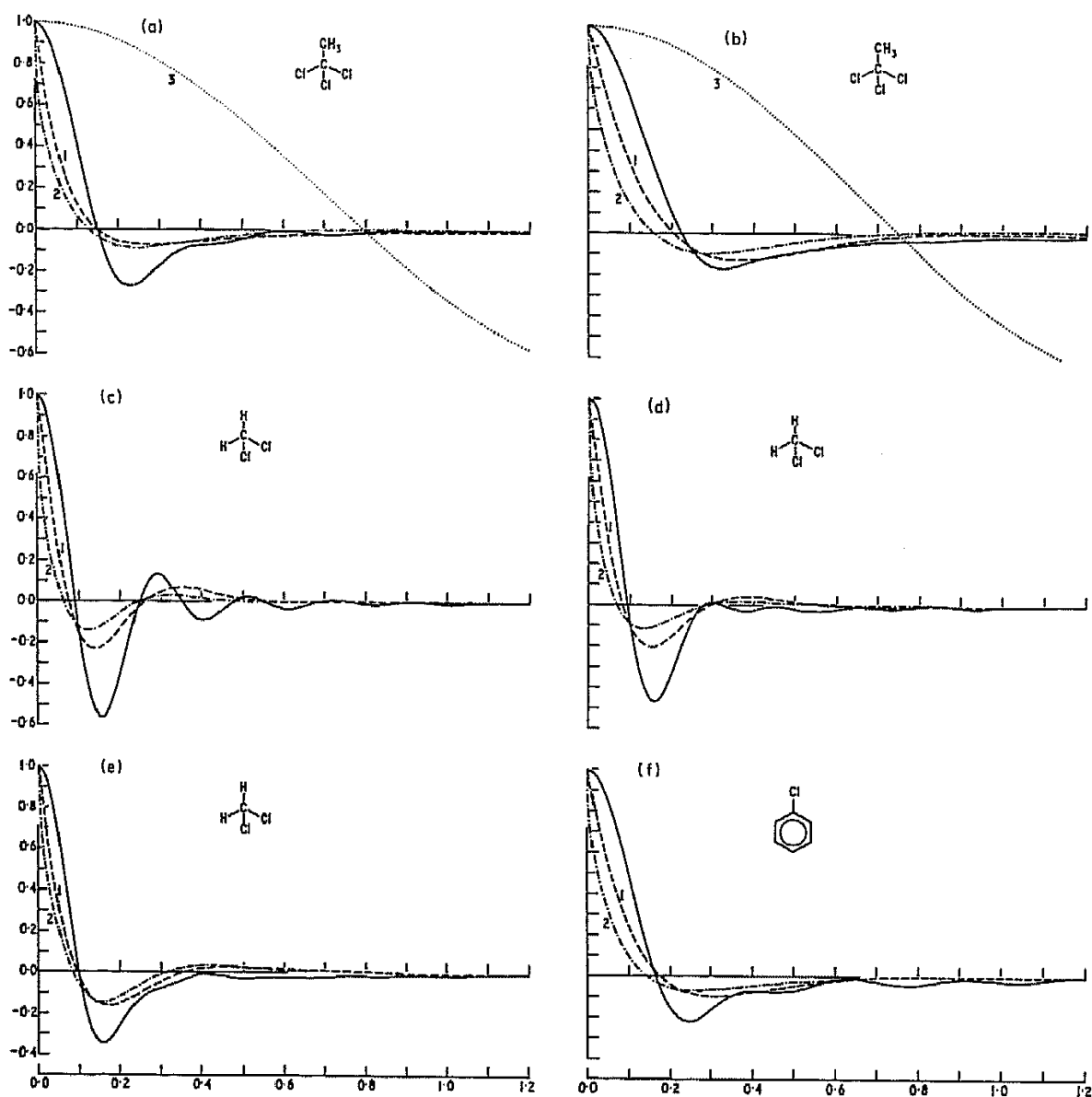


Fig. 3. As for Fig.1. (a) 1,1,1-trichloroethane (rotator) at 233 K; (b) 1,1,1-trichloroethane (liquid) at 293 K; (c) dichloromethane at 188 K (liquid); (d) dichloromethane at 249 K (liquid); (e) dichloromethane at 298 K (liquid); (f) chlorobenzene (liquid) at 293 K. Abscissa and ordinate as for Fig.1.

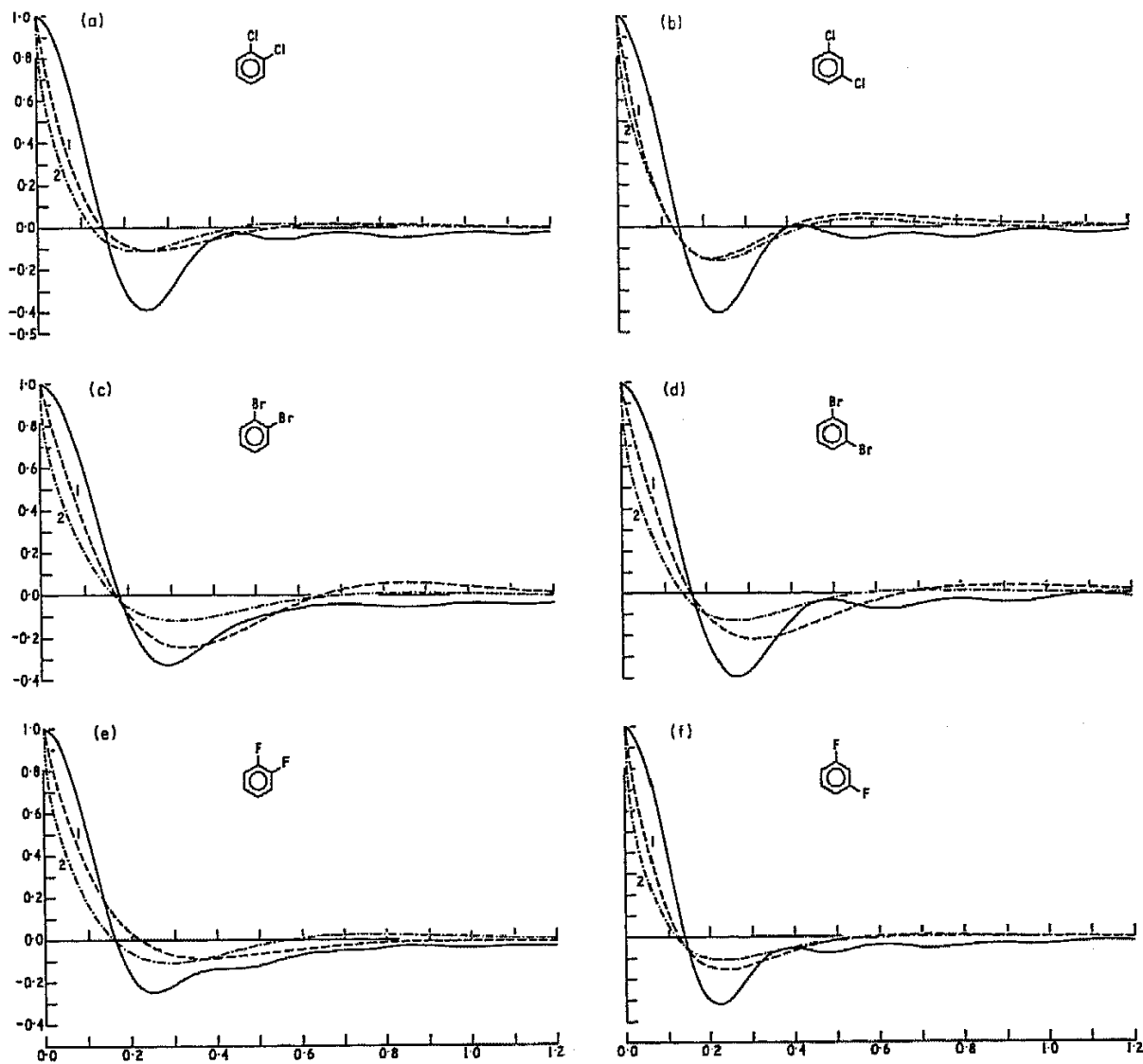


Fig. 4. As for Fig.1. (a) o-dichlorobenzene (liquid) at 293 K; (b) m-dichlorobenzene (liquid) at 293 K; (c) o-dibromobenzene (liquid) at 293 K; (d) m-dibromobenzene (liquid) at 293 K; (e) o-difluorobenzene (liquid) at 293 K; (f) m-difluorobenzene (liquid) at 293 K. Abscissa and ordinate as for Fig.1.

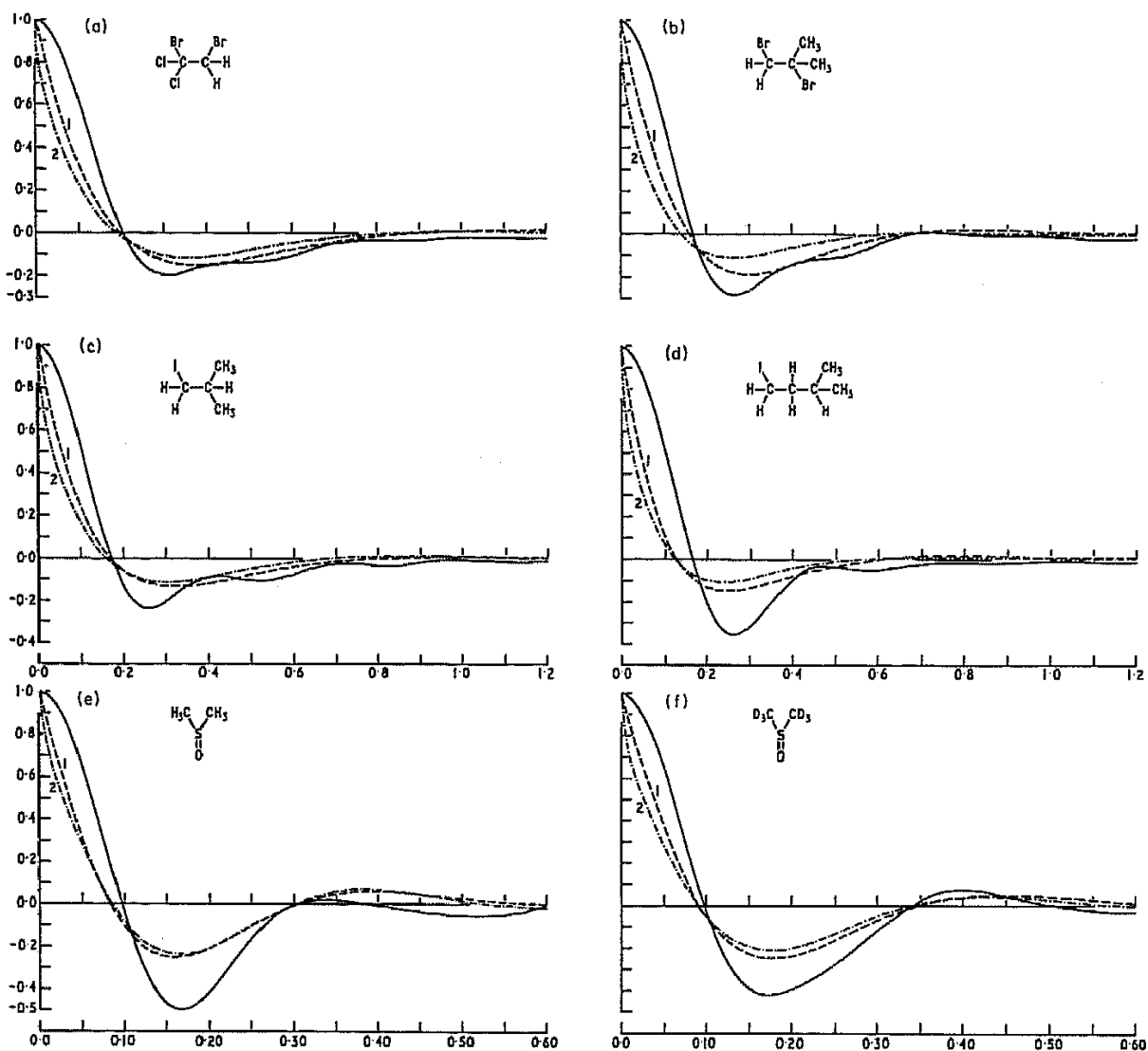


Fig. 5. As for Fig.1. (a) 1,2-dibromo-1,1-dichloroethane ( $\ell$ ) at 295 K; (b) 1,2-dibromo-2-methylpropane ( $\ell$ ) at 295 K; (c) 1-iodo-2-methylpropane ( $\ell$ ) at 295 K; (d) 1-iodo-3-methylbutane ( $\ell$ ) at 295 K; (e)  $[^1\text{H}_6]$  dimethyl sulphoxide ( $\ell$ ) at 293 K; (f)  $[^2\text{D}_6]$  dimethyl sulphoxide ( $\ell$ ) at 293 K. Abscissa and ordinate as for Fig.1.



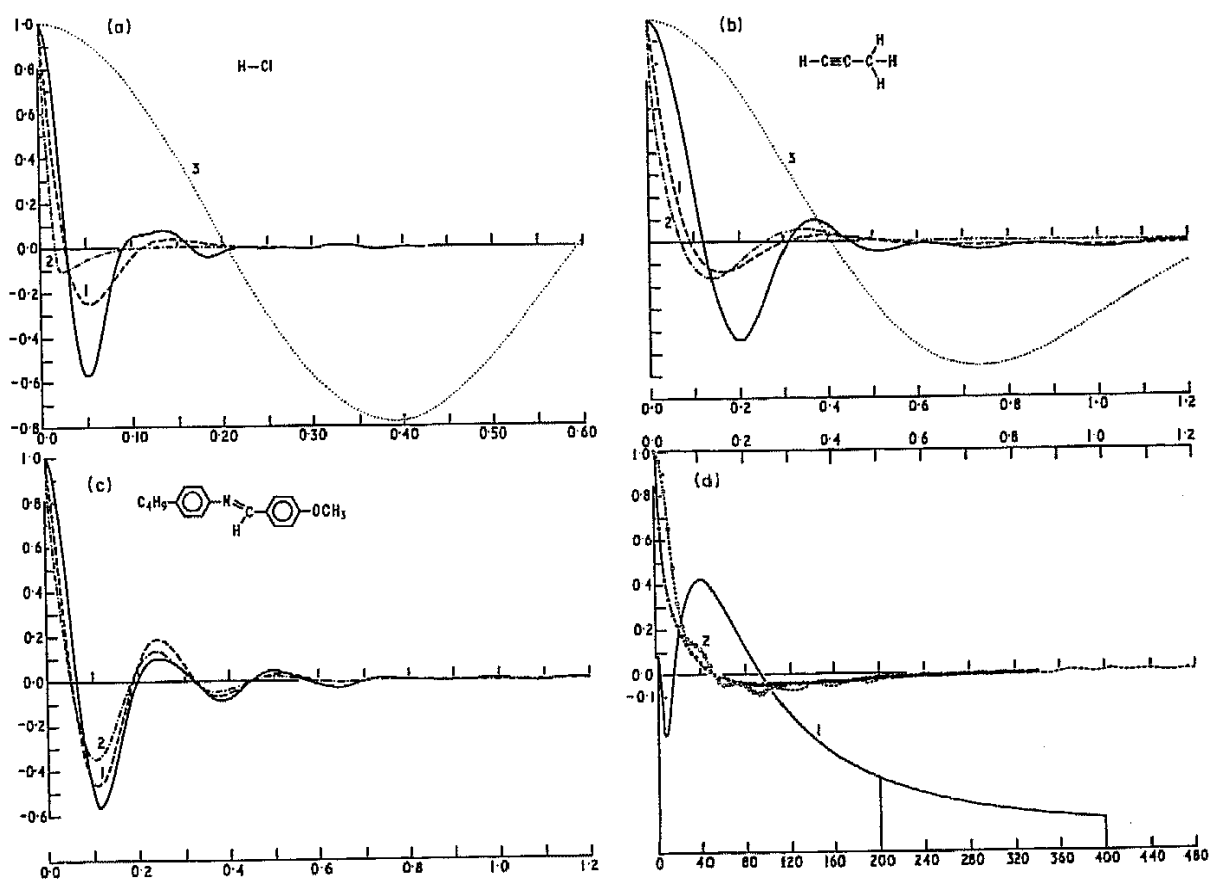


Fig. 6. (a) - (c) as for Fig.1. (a) HCl (rotator phase) at 100 K; (b) Propyne (liquid) at 293 K; (c) p-methoxybenzylidene-p-N-butylaniline (nematic phase) at 296 K; (d) Curve 1 - Frequency domain curve of  $\alpha(\bar{\nu})$  predicted by the itinerant oscillator model [7,32,33] at 238 K for the rotator phase of t-butyl chloride. Integration of this curve up to  $400 \text{ cm}^{-1}$ , only produces the spurious oscillations of curve 2, which is the correlation function. It is necessary (because of the asymptotic  $\omega^{-2}$  behaviour at high frequencies) to integrate up to  $3000 \text{ cm}^{-1}$  before these disappear. Abscissae upper-time (t)(ps); lower -  $\bar{\nu} (\text{cm}^{-1})$ . Ordinate  $f(t)$  or  $\alpha(\bar{\nu})$ . For Fig.6(a) - (c), the ordinate and abscissae are those of Fig.1.

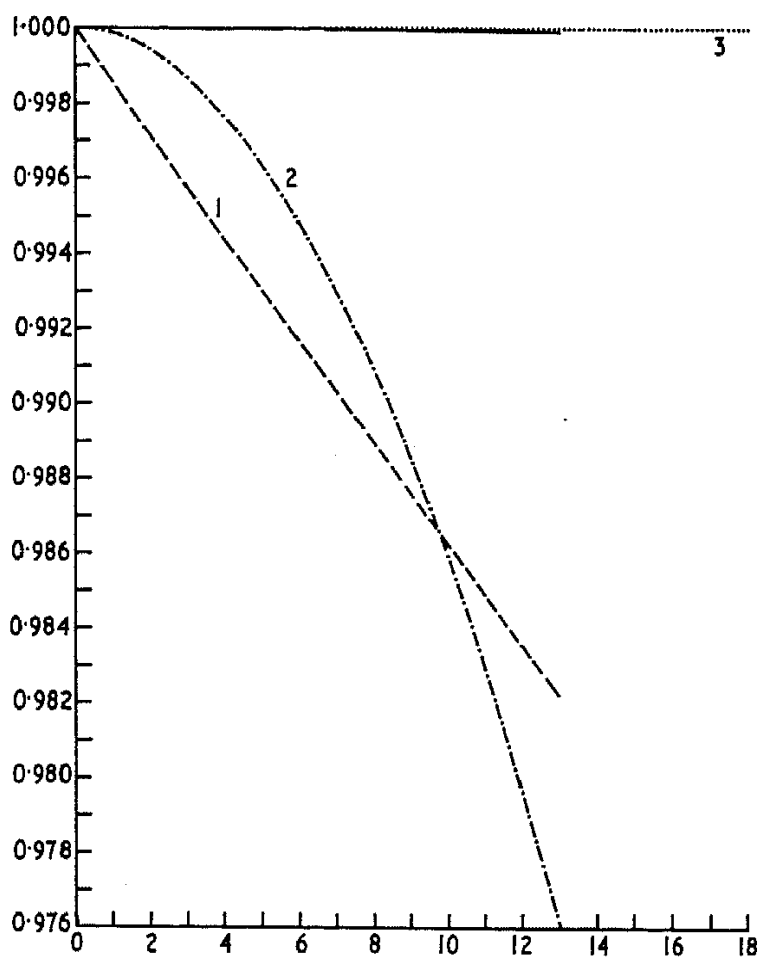


Fig. 7. Short-time behaviour of the Brot-Larkin [32,33] and the itinerant oscillator [7,32,33] models for *t*-butyl chloride (rotator phase) at 238 K. (—) as for Fig.1; (----) as for Fig.1. Abscissa  $10^4 t$ (ps); ordinate  $t$ . Figs. 1-7 are reproduced by permission of the Chemical Society from *J. Chem. Faraday II*, 71 (1975) 2051.

As would be expected from a model involving instantaneous reorientations of angular velocity, the correlation function is badly behaved at short times<sup>[33]</sup>, and the spectral intensity distribution at high frequencies is such that transparency is regained too slowly<sup>[32]</sup> (the  $\omega^{-2}$  asymptotic behaviour of  $\alpha(\omega)$  in eqn.(42),  $\alpha(\omega)$  being proportional to  $\omega^2 \times \text{Real} [C_m(i\omega)]$ ). The intermolecular mean square torque,  $\langle O(V)^2 \rangle$  becomes instantaneously infinite in all such models of elastic, instantaneous, molecular collisions, whereas a finite torque term  $\langle O(V)^2 \rangle$  exists in the  $a_2$  term of the classical, even-time expansion of  $C_m(t)$ :

$$C_m(t) = \sum_{n=0}^{\infty} a_n \frac{t^{2n}}{(2n)!}, \quad (45)$$

as was demonstrated above in the particular case using  $F_V(t)$ . In eqn.(45)  $a_0$  is unity, and successive  $a_n$  are alternatively negative and positive<sup>[4]</sup>. From eqns.(39) and (40):

$$K_j(t) = \sum_{n=0}^{\infty} j_{kn} \frac{t^{2n}}{(2n)!}, \quad (46)$$

so that:

$${}^0k_n = -a_{N+1} - \sum_{n=1}^N {}^0k_{N-n} a_n$$

and:

$${}^0k_0 = K_0(0) = -a_1, \quad (47a)$$

$${}^1k_0 = K_1(0) = a_1 - \frac{a_2}{a_1} \quad (47b)$$

$${}^2k_0 = K_2(0) = (a_2^2 - a_1 a_3) / ((a_2 - a_1^2) a_1), \quad (47c)$$

so that for any permanent dipolar absorption, a truncation of the series of eqns.(39) which precludes the term  $K_1(0)$  cannot take account of the finite mean square torque  $\langle O(V)^2 \rangle$ .

Quentrec and Bezot<sup>[34]</sup> have recently involved both  $K_0(0)$  and  $K(0)$  in an evaluation of  $C_m(i)$  with the truncation at first order:

$$K_1(t) = K_1(0) \exp(-\gamma_1 |t|),$$

so that

$$C_m(i\omega) = \frac{K_1(0) - \omega^2 - i\omega\gamma_1}{i\omega^3 - \omega^2\gamma_1^2 - i\omega(K_1(0) + K_0(0)) + \gamma_1 K_0(0)}$$

is extracted by Fourier-Laplace transformation. The optical absorption coefficient is then given by<sup>[8]</sup>:

$$\alpha(\omega) = \frac{A\omega^2 K_0(0) K_1(0) \gamma_1}{\gamma_1^2 (K_0(0) - \omega^2)^2 + \omega^2 \{\omega^2 - (K_0(0) + K_1(0))\}^2}, \quad (48)$$

the correlation function being now of the form:

$$C_m(t) = (\Gamma_0 \cos \beta t + \Gamma_1 \sin \beta t) \exp(-\alpha_1 t) + \Gamma_2 \exp(-\alpha_2 t)$$

where  $\Gamma_0$ ,  $\Gamma_1$ ,  $\Gamma_2$ ,  $\alpha_1$ ,  $\alpha_2$ , and  $\beta$  are functions of  $K_0(0)$ ,  $K_1(0)$  and  $\gamma$  such that  $C(t)$  is even up to  $t^4$  in its Maclaurin expansion. The proportionality constant  $A$  is given by  $A(\epsilon_0 - \epsilon_\infty)/n(\omega)c$ , where  $n(\omega)$  is the refractive index. The problem of the internal field correction ( $\Lambda$ ) has been discussed by many authors in the past<sup>[35]</sup>, but a recent study<sup>[36]</sup> leads to the conclusion that such an involved correction might be often overestimated in importance. Certainly<sup>[37]</sup>, at far infra-red frequencies it is of a Polo-Wilson kind and therefore almost independent of bandshape. Thus  $\Lambda = 9n/(n^2 + 2)^2$  is a fair approximation, where  $n$  is the refractive index at the high frequency limit of the relaxation (ca.  $200 \text{ cm}^{-1}$ ).

The overall response function (eqn.(35)) corresponding to the truncation of Quentrec and Bezot is given by:

$$K_m(t) = K(0)f(t) \quad (49)$$

where  $f(t)$  is defined by the right-hand side of eqn.(43) with  $K_0(0)$  replaced by  $K_1(0)$ , and  $\gamma_0$  by  $\gamma_1$ . Therefore  $K_m(t)$  of eqn.(49) is even up to  $t^2$ , and thus the corresponding  $C_m(t)$  is even in time up to  $t^4$ . To extract the physical meaning of this truncation, it is useful to note that  $K_m(t)$  is exactly the same in form as the  $C_m(t)$  of the M-diffusion model (eqn.(43)). Using Kubo's second fluctuation-dissipation theorem (eqn.(36)) it is seen that the time-autocorrelation of the random force associated with  $K_m(t)$  is M-diffuse in character. This implies that the derivative of this force is randomised in direction by events separated by a correlation time  $\gamma_1^{-1}$ , in a way exactly analagous to that where the derivative of position (the angular velocity) is randomised in direction by events separated by the critical time  $\tau_c$  of the M-diffusion model. The force correlation function corresponding to  $K_m(t)$  is no longer exponential, so the statistical behaviour of the force is no longer Markovian<sup>[19]</sup>, i.e. the conditional probability distribution<sup>[21]</sup> of such a force at any future instant may be dependent on past events.

Equation (48) reduces to the Debye-type<sup>[8,11,14,15]</sup>;

$$\alpha(\omega) \rightarrow \frac{A\omega^2 K_0(0)K_1(0)\gamma_1}{\gamma_1^2 K_0^2(0) + (K_0^2(0) + K_1^2(0) + 2K_0(0)K_1(0) - \gamma_1^2)\omega^2}$$

so that the familiar Debye-type absorption curve (plotted<sup>[16]</sup> in terms of  $\epsilon''(\omega) = \alpha(\omega)/n(\omega)\omega$ ) is regained at microwave<sup>[14]</sup> frequencies.

Wyllie<sup>[38]</sup> has pointed out that the Mori expansion affords in principle the correct assignment of successive moments of the spectrum  $C_m(i\omega)$ , and so of successive terms in the expansion of  $C_m(t)$  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 of time (i.e.  $t^{-3/2}$ ). Similar behaviour is expected in  $C_m(t)$ , at least for spherical tops (e.g.  $F_3CCD_3$ ), but this would distort the spectrum only on the low frequency side of the Debye absorption. For linear and symmetric top molecules with a permanent dipole [6,7,12,28]:

$$K_0(o) = -a_1 = 2kT/I_B$$

and for linear dipolar molecules [12]:

$$a_2 = \left[ \frac{1}{3} \left( \frac{kT}{I} \right)^2 + \frac{\langle O(V)^2 \rangle}{24I^2} \right] 4!$$

as was shown above. Here  $I_B$  is the component of the moment of inertia about an axis perpendicular to that of the permanent dipole, so that, in principle,  $\langle O(V)^2 \rangle$  and  $\gamma_1$  are the two phenomenological equivalent variables in eqn. (48). The latter is related [38] to the Debye relaxation time  $\tau_D$  by:

$$\tau_D^2 = \frac{(K_0(o) + K_1(o))^2 - 2K_0(o) \gamma_1}{\gamma_1^2 K_0^2(o)}$$

Quentrec and Bezot [34] found that  $\alpha(\omega)$  of eqn. (48) is sensitive to small change in  $K_1(o)$  and  $\gamma_1$ . They found good agreement between theory and experimental results in the whole of the microwave and far infra-red range of frequencies (up to 4 decades) for liquid-furan at 219 K and 272 K, and for liquid chloroform at 213 K and 293 K. By the second fluctuation-dissipation theorem [24,4] :

$$K_1(t) = \frac{1}{\langle F^2(o) \rangle} \langle F_1(o)F_1(t) \rangle$$

where  $F_1(t)$  is Markovian. If  $F_1(t)$  were not so, then eqn (48) would be invalidated. A possible example of a non-Markovian  $F_1(t)$  would be that associated with a vortex phenomenon of linear momentum [39] existing in the neighbourhood of a given molecule.

Evans and Evans [38] have used eqn. (48) to fit the far infra-red and microwave absorption of the liquids  $CHF_3$ ,  $CClF_3$ ,  $CB_rF_3$ ,  $CH_3C \equiv CH$ , and the nematogenic molecule N-(p-methoxybenzylidene)-p'-n-butyl-aniline (MBBA), a series chosen to cover the extremes of geometrical isotropy and anisotropy.  $K_1(o)$  and  $\gamma_1$  were estimated from the experimental data using Newton-Gauss minimisation. The mean square torque  $\langle O(V)^2 \rangle$  increases with molecular anisotropy until very sharp far infra-red librational bands appear at  $\geq 100 \text{ cm}^{-1}$ . Work is currently in progress exploring the limitations of eqn. (48) by

comparing the predicted  $\alpha(\omega)$  with the observed absorptions [32] in plastic crystalline phases of spherical molecules, and in the mesophases of lath-like molecules such as MBBA.

Some progress has been made by van Kampen [40] in treating thermal fluctuations in non-linear systems with the Chapman-Kolmogorov equation for the probability distribution function of a Markovian fluctuating quantity  $q$ . This approach may be fruitful if eqn (34) can be generalised to give a non linear response theory of motions in condensed phases.

#### FAR INFRA-RED ABSORPTION IN NON-DIPOLAR LIQUIDS

Early evidence of an absorption at high microwave frequencies in highly purified non-dipolar liquids was presented by Whiffen [41]. The absorption intensity in these liquids is an order of magnitude lower than the corresponding absorption [14,16] in dipolar liquids, and the bands are even broader. Despite early suggestions by these and other authors [16], the maxima do not correspond to any known fundamental or difference modes.

The first indication that the absorptions are of a rotational rather than a purely translational origin came from the results of Savoie and Fournier [44] who obtained the far infra-red spectra of  $\text{CH}_4$  and  $\text{CD}_4$  as the liquid and solid (rotator I) down to 12 K. The liquid exhibits a broad maximum at ca.  $200 \text{ cm}^{-1}$  for  $\text{CH}_4$  and ca.  $150 \text{ cm}^{-1}$  for  $\text{CD}_4$ , which the authors interpreted as being an indication of  $I^{1/2}$  (rotational) rather than  $M^{1/2}$  (translational) dependence. Peterman et al. [45] studied the far infra-red absorptions of benzene,  $\text{CCl}_4$  and  $\text{CS}_2$  as a function of temperature, and found that as this increased, the peak shifted to higher frequencies and became broader. Pardoe [46] obtained similar results for  $\text{CS}_2$  and cyclopentane. Davies et al. [47] made the first attempt at an interpretation of these bands in terms of the torsional oscillation of a molecule within the cage formed by its neighbours. They carried out refractive-index measurements on non-dipolar liquids, and discovered that these indices had shallow minima in the far infra-red region.

In two recent papers, Davies et al. [48] have obtained the far infra-red spectra of a number of non-dipolar liquids, and have carried out dilution studies on trans 1,2-dichloroethylene, p-difluorobenzenes, and benzene in solution with cyclohexane, carbon tetrachloride, and carbon disulphide. The characteristic integrated absorption intensity of non-

dipolar liquids in the far infra-red was evaluated in terms of an "effective" quadrupole moment of the molecules involved. The absorptions of the non-dipolar mixtures were subsequently analysed in terms of a "collisional" process, whereupon a number of mixtures [49] showed distinct evidence of a new "complex" or "sticky" collision interaction.

Evidence of a substantial intermolecular mean square torque which hinders the molecular rotational type motions in liquid  $\text{CO}_2$  was put forward by Birnbaum and co-workers [50]. The absorption of the liquid at 273 K has an integrated intensity an order of magnitude less than that in the gas phase, where rotational type  $J \rightarrow J + 2$  collisionally-broadened, overlapping lines predominate. Significant intermolecular forces shift the peak by ca.  $25 \text{ cm}^{-1}$  to higher frequencies in the liquid. The authors argue that the large quadrupole moment of  $\text{CO}_2$ , which has a dominant effect on the gas phase absorption, is apparently much reduced in value in the liquid. This is the result of the "local order" and the symmetry arising, e.g. in three-body collisions, the net (effective) induced dipole being smaller. Collision-induced absorption would disappear if each molecule occupied a site of inversion symmetry. Such behaviour was verified by Evans [51] in the more strongly quadrupolar cyanogen ( $\text{N} \equiv \text{C} - \text{C} \equiv \text{N}$ ). No feature specific to the critical point was implied in these gas-liquid systems which was also the conclusion of Gershel et al [37] and Darmon et al. [52], who have made careful analogous studies on the dipolar molecules  $\text{OCS}$ , chloroform, chlorobenzene, and fluorobenzene for the whole range of the liquid-state along the orthobaric curve and into the co-existing dense gas. In the lower density phases (including the liquid a few tens of degrees below the critical point) the rotational motion was evaluated as a collision-perturbed free rotation. In the dense (cold) liquids, the rotational motion at short times is better described as damped librational (torsional oscillatory).

Thus the evidence is in favour of a torsional and rotational diffusion type of motion as the principal source of the far infra-red absorptions in these non-dipolar liquids, closely analogous to that in their dipolar liquids, closely analogous to that in their dipolar counterparts, so that the modified Langevin equation can be used to predict the spectral function  $C(i\omega)$ . However, there is the important difference that  $K_0(0)$  and  $K_1(0)$  of eqn. (48) cannot yet be easily related to simple molecular constants such as the multipole moments [53] of the electrostatic field or to components of the moment of inertia [17]. Assuming that the cross-correl-

ation functions associated with these bands can be expanded in powers of time for the simplest case of bimolecular interaction [54], then expressions for  $a_1$  and  $a_0$ , analagous to those of Gordon [17] for dipolar linear molecules and Desplanques [55] for symmetric top molecules will link the non-dipolar  $K_0(\omega)$  and  $K_1(\omega)$  to the intermolecular mean square torque. In the absence of a resultant, induced dipole moment due to interaction between molecules (e.g. the dilute gaseous phase), there would be no absorption in the far infra-red at all, and therefore neither  $K_0(\omega)$  nor  $K_1(\omega)$  can be a single molecule property.

The  $(\epsilon_0 - \epsilon_\infty)$  factor of eqn. (48) is given for non-dipolar species by the Kramers-Kronig relation [14,15]  $n(\omega)$  being effectively constant. Using  $K_0(\omega)$ ,  $K_1(\omega)$  and  $\gamma_1$  as variables, eqn (48) has been fitted by Davies and Evans[56] to a range of far infra-red bands of non-dipolar molecules, from that of liquid-nitrogen at 76.4 K to trans-decalin at 296 K. The results are illustrated in Figs. 8 - 10, the fit in every case being satisfactory. Therefore, it seems as if the analytical dependence of  $\alpha$  upon  $\omega$  in non-dipolar liquids can be provided by eqn.(48) but the physical significance of  $K_0(\omega)$  and  $K_1(\omega)$  will have to be explored further by an investigation of the terms in the expansion of the time cross-correlation function associated with such bands. A substantial amount of further insight is needed before the magnitude of  $(\epsilon_0 - \epsilon_\infty)$  can be predicted with any certainty. This quantity has been usefully expressed in the past as an induced molecular [16] "effective dipole moment", or to an "effective molecular quadrupole moment" or higher multipole[48], given some simplifying assumption about the molecular dynamical and electrostatic origin of the absorption.



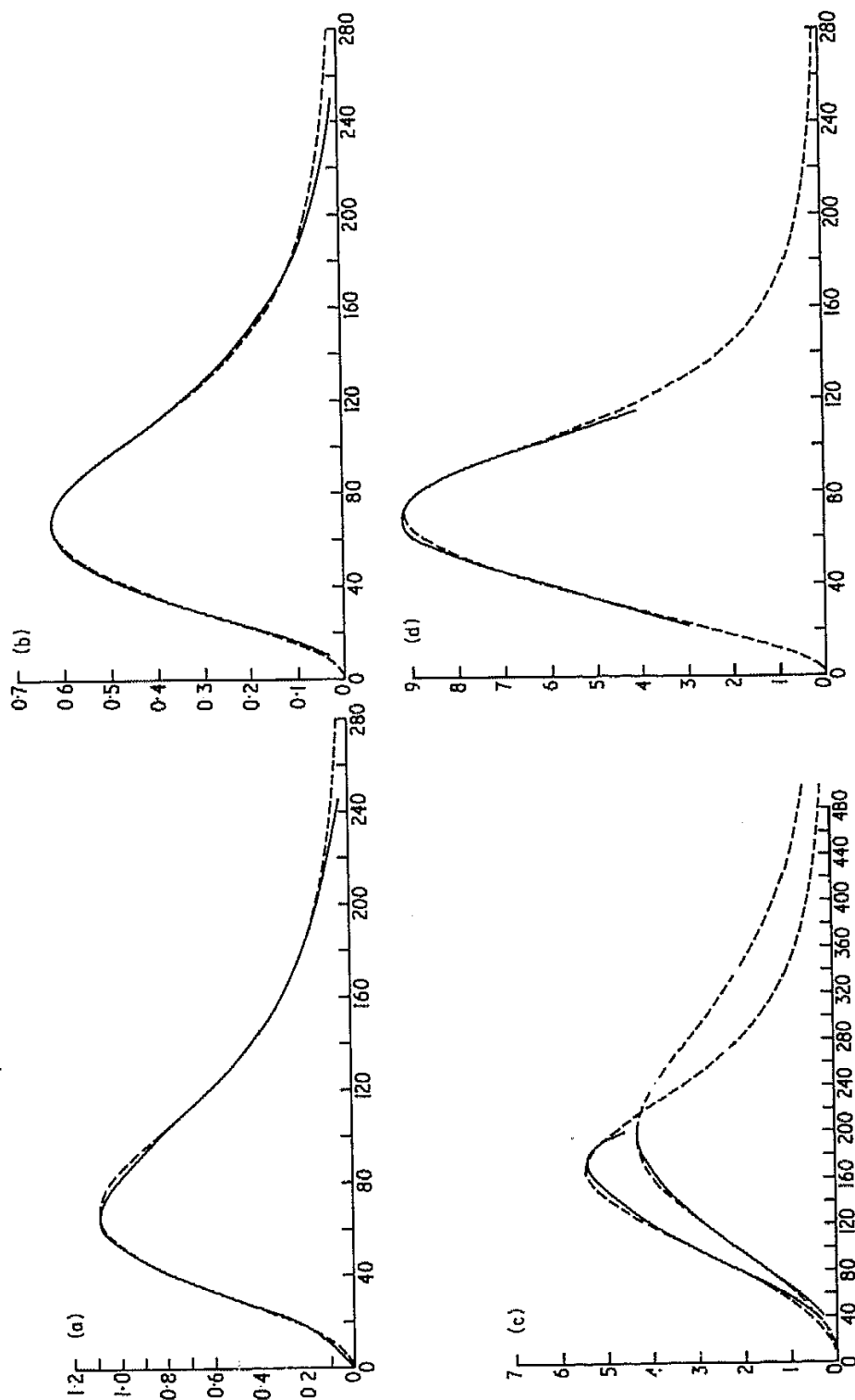


Fig. 8. (—) Experimental absorption in the far infra-red; (---) Eqn. 48. (a) Liquid-nitrogen [126] at 76.4 K; (b) Liquid carbon dioxide [50] at 273 K; (c) Methane [44], rotator phase at 77 K (curve (a) ) and liquid at 98 K (curve (b) ); (d) Liquid cyanogen [5] at 301 K. Ordinates:  $\alpha(\nu)$  (neper  $\text{cm}^{-1}$ ); abscissae:  $\nu$  ( $\text{cm}^{-1}$ ). Reproduced by permission from ref. 56.

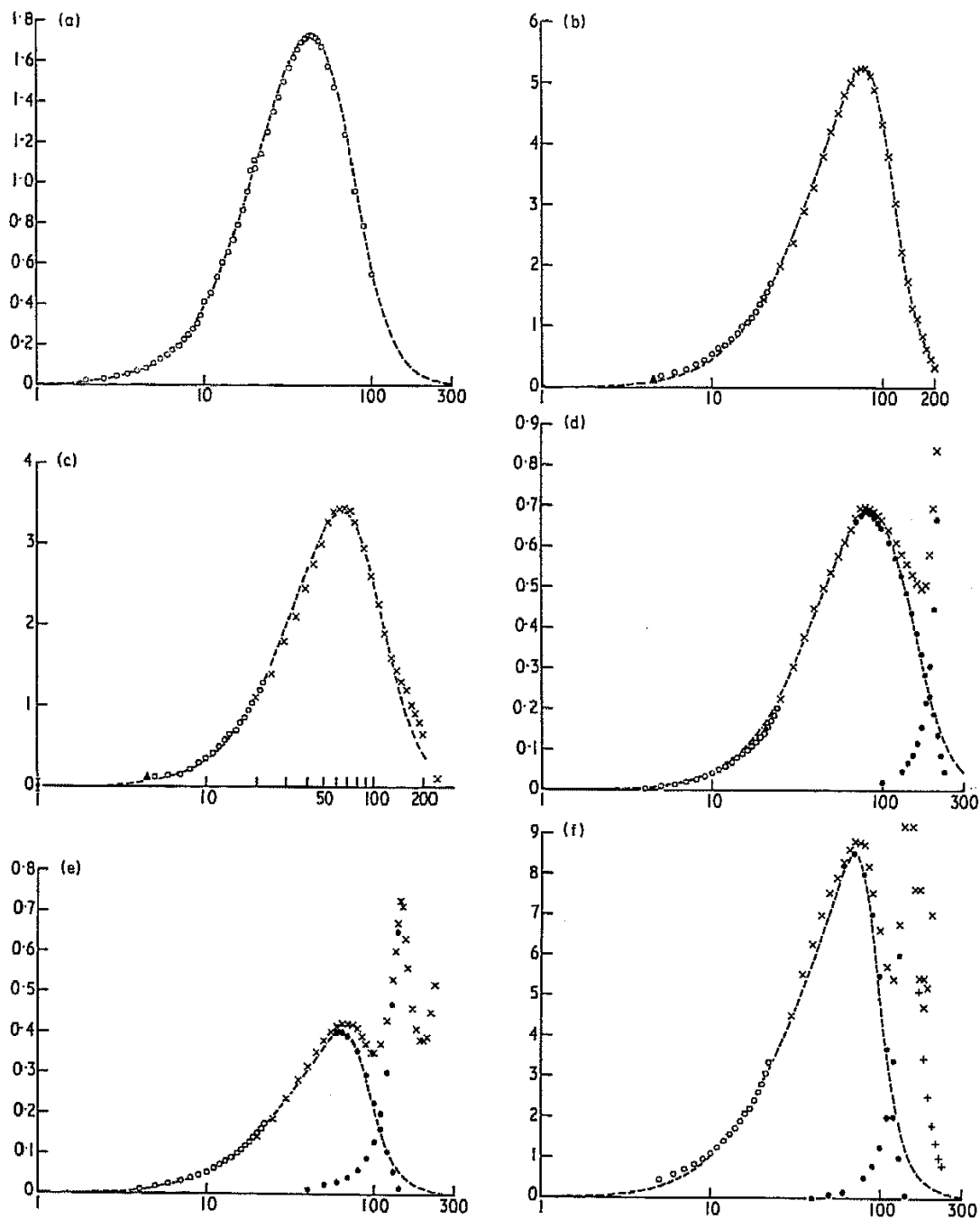


Fig. 9. Experimental absorptions [56] in the high microwave and far infrared at 296 K for non-dipolar liquids. Absorptions deduced as estimations for component (overlapping) absorptions. (-----) Eqn. 48. (a) Carbon tetrachloride; (b) benzene; (c) carbon disulphide; (d) cyclohexane; (e) trans-decalin; (f) 1,4-dioxane. Ordinates and abscissae as for Fig.8.

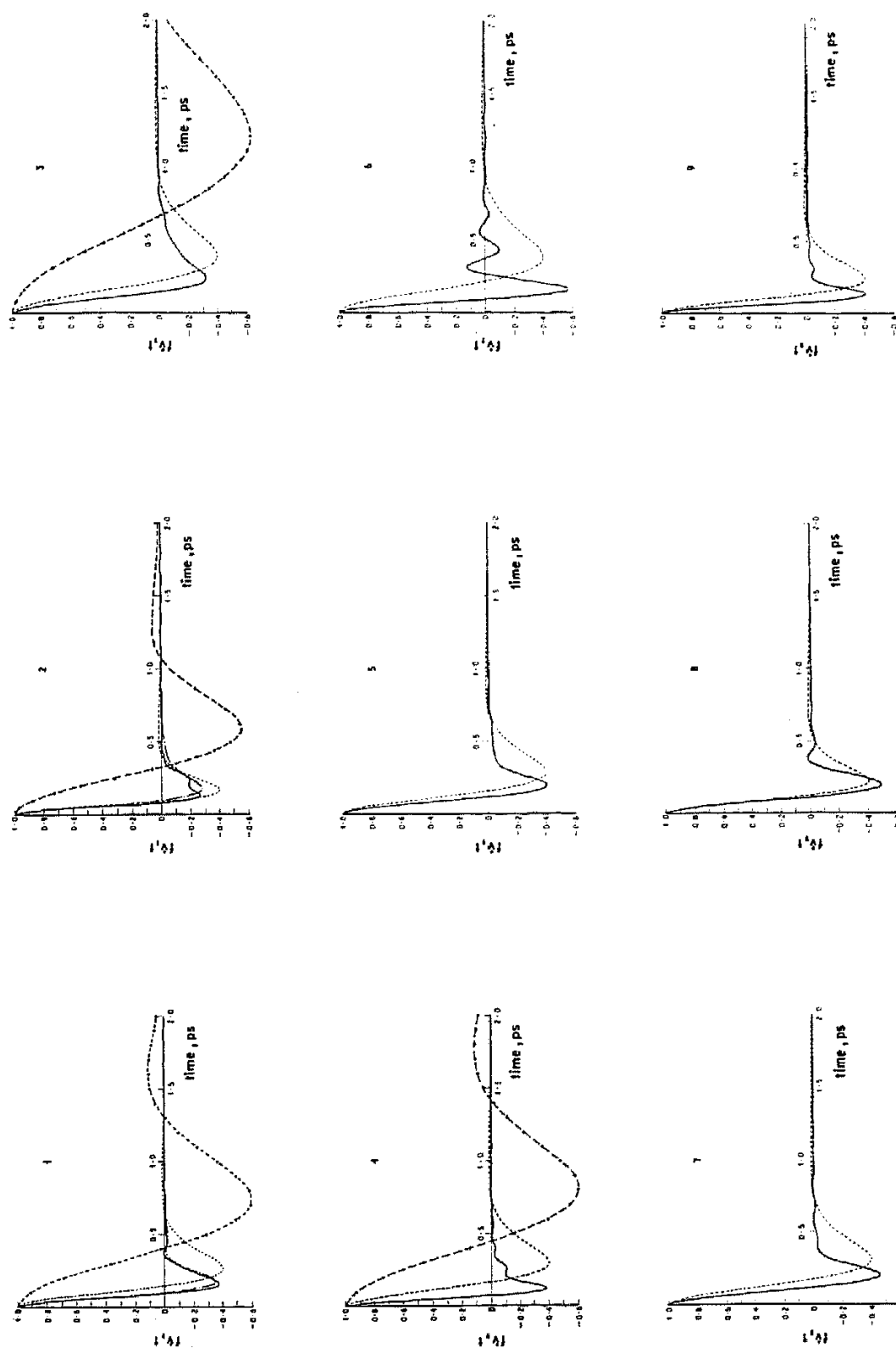


Fig. 10. (—) Experimental function [56]  $C(t) = -\dot{C}_m(t)$  for non-dipolar absorptions of liquids at 296 K. (---) Litovitz model [68,56] (eqn. (64) Fourier transformed). (---) Model of multipole induced absorption in a bimolecular collision [54]. (1) benzene; (2)  $CS_2$ ; (3)  $CCl_4$ ; (4) cyclohexane; (5) p-difluorobenzene; (6) bicyclohexyl; (7) trans-decalin; (8) 1,4-dioxane; (9) trans-1,2-dichloroethylene. Ordinates: (t); abscissae: time (t) (ps).

## ROTATIONAL CORRELATION FUNCTIONS FROM DEPOLARISED RAYLEIGH SCATTERING OF LIGHT

In the last decade or so, the use of lasers has made possible the accurate quantitative study of the detailed structure of the spectrum of light scattered by molecules. Considerable attention was paid in most measurements [56 - 60] to the so-called "Rayleigh wings", i.e. the depolarised light scattered owing to anisotropy fluctuations in the liquids [61 - 65]. In molecules such as benzene, these wings are composed of a relatively narrow diffuse line superimposed on a much broader background. High resolution, high power measurement [61], have disclosed some additional features - notably a very narrow central doublet. Stegemann and Stoicheff [61], having analysed the shape of the spectrum, have been able to say that in its general contours and its dependence on the scattering angle and polarisations, the diffuse line with the central doublet fits the theory of Rytov [66] which phenomenologically associates the diffuse line with scattering by transverse shear waves.

However, Ben Reuven and Gershon [63] point to two features of this spectrum which can be interpreted differently. First, the absolute integrated intensities (which can be obtained by comparison with intensities of the polarised Rayleigh and Brillouin spectrum) are very close to those predicted from theoretical expressions [3] obtained for the reorientations of single (uncorrelated) molecules. Second, the inverse half-width of the diffuse line (the relaxation time) fits reasonably well in magnitude, temperature dependence and activation energy into a broader scheme [1-10] in which other phenomena such as the above dielectric susceptibility theory, and nuclear spin-rotation relaxation (below) are well described by reorientational relaxation of single molecules (with, at most, near neighbour correlations).

Thus these authors conclude that what is seen in the diffuse line is a result of the reorientation of single molecules in the liquid. This seems to be in contradiction with the phenomenological interpretation above [66,67] which is in terms of collective (shear wave) modes. There still remains the possibility, however, that the background (together with the doublet) should be associated with shear waves. The presence of the doublet is revealed only for certain liquids [61], and it is not possible to link its

existence or absence to a definite property such as viscosity. Moreover, its variation with temperature does not correspond to shear wave theory, and remains unexplained by it [63].

The present review stresses the microscopic [1-10,12] or correlation function treatment of depolarised Rayleigh scattering, which is fruitful in comparison with a similar treatment of dielectric relaxation and far infra-red absorption in both dipolar and non-dipolar molecules. First, some of the main points of the microscopic theory [59,63] will be reviewed. If incoming light is incident upon a sample in the x-direction, and polarised in the z direction, and the scattered light polarised in the x direction is observed along the y axis, then one is observing the radiation spectrum  $I_{\text{VH}}(\omega)$  from a dipole induced along the x axis by an electric field along the z axis. Such a dipole is proportional to the xz element of the electric polarisability of the scattering volume. For systems with scalar polarisabilities, this element is zero (e.g.  $\text{CCl}_4$ ).

Gordon [3,12] demonstrated in 1965 that this depolarised component of a "pure rotational Raman" bandshape is the Fourier transform of the average motion of the polarisability tensor of a molecule, and thus of the correlation function:

$$C_R(t) = \text{Tr} \langle \beta_1(0) \beta_1(t) \rangle + \sum_{i \neq 1} (\text{Tr} \langle \beta_1(0) \beta_i(t) \rangle),$$

where  $\beta_i$  is the tensor of electric polarisability anisotropies for the i'th molecule, and the trace ( $T_R$ ) is over the x, y, z-components of  $\beta$ . In the specific case of self-correlation in a linear molecule,  $C_R(t)$  is given by:

$$\begin{aligned} C_R(t) &= \frac{1}{2} \langle 3[\underline{u}(0) \cdot \underline{u}(t)]^2 - 1 \rangle \\ &= 1 - \frac{3kT}{I} t^2 + \left[ 4 \left( \frac{kT}{I} \right)^2 + \frac{1}{8I^2} \langle 0(V)^2 \rangle \right] t^4 - \dots, \end{aligned} \quad (50)$$

where  $\underline{u}$  is a unit vector along the molecular axis,  $I$  is the moment of inertia, and  $\langle 0(V)^2 \rangle$  the mean square torque. The depolarised light scattering from liquids with molecules having an anisotropic polarisability is mainly due to local fluctuations in the orientation of these from the random isotropic average. If it is assumed that the movement of neighbouring molecules is uncorrelated, i.e.

$$\sum_{i \neq 1} (T_R \langle \beta_1(0) \beta_i(t) \rangle) = 0,$$

then the depolarised scattered spectral intensity as a function of  $\omega$ , the angular frequency shift of the scattered light from the central line, is given by:

$$I_{\text{VH}}^*(\omega) \propto (\alpha_{11} - \alpha_{\perp})^2 \int_{-\infty}^{\infty} \exp(-i\omega t) C_{\text{R}}(t) dt \quad (51)$$

for a linear or symmetric top molecule. This can be compared directly with the quantum equation<sup>[12,17]</sup> for the spectral intensity distribution of the rotational microwave and far infra-red band:

$$A^*(\omega) \propto \frac{\alpha(\omega)}{\omega(1 - \exp(-\hbar\omega/kT))} \propto \mu^2 \int_{-\infty}^{\infty} \exp(-i\omega t) C_{\text{m}}(t) dt. \quad (52)$$

Experimentally,  $I_{\text{VH}}(\omega)$  and  $A^*(\omega)$  exhibit the same qualitative features. The low frequency Lorentzian<sup>[68]</sup> of light scattering corresponds to the low frequency Debye relaxation in dipolar absorption. This Lorentzian is superimposed on a broader background that extends up to ca. 100-150  $\text{cm}^{-1}$  (the far infra-red Poley absorption<sup>[16]</sup>). Beyond this, the spectrum falls exponentially with frequency.

As a consequence of this Lorentzian behaviour at low frequencies, the long-time behaviour of both  $C_{\text{m}}(t)$  and  $C_{\text{R}}(t)$  is exponential, with time constants for each exponential decay given respectively by  $\tau_{\text{m}}$  and  $\tau_{\text{R}}$ , the inverse half-width of each Lorentzian. Details of molecular motions are reflected in the deviation from the exponential at short times and give rise to an added background (or shoulder) in the depolarised scattered lineshape, and to the far infra-red Poley absorption of dipolar liquids.

A straight comparison of  $\tau_{\text{m}}$  and  $\tau_{\text{R}}$  yields information on the detailed reorientational mechanism (e.g. large rotational jumps or otherwise) of molecules in the system under study. Thus, if it has been verified that the movement about an axis can be described by a model of rotational diffusion (essentially exponential long time behaviour of  $C_{\text{m}}(t)$  and  $C_{\text{R}}(t)$ ), the Hubbard relation<sup>[69]</sup> gives the theoretical link:

$$\tau = \frac{I}{6kT\tau_{\text{R}}} = \frac{I}{2kT\tau_{\text{m}}}. \quad (53)$$

In considering the mechanism of reorientation in the low frequency (Lorentzian) region Bartoli and Litovitz<sup>[70]</sup> have considered simple idealised models of the molecular dynamics. In some liquids, which they denote as "structure-limited", a molecule will remain in a fixed position for a "residence time"  $\tau_{\text{res}}$ , and then reorient in a time of flight  $\tau_{\text{fl}} \ll \tau_{\text{res}}$ . In other liquids termed "collisional limited", a molecule reorients continuously, the individual steps being limited by collisions with its neighbours. The average duration of these individual steps is the

$\tau$  of eqn. [53].

By considering the ratio  $\tau_R/\tau_m$  and by comparing  $\tau_R$  with other characteristic times in the liquid (i.e. structural relaxation times), they suggested that liquids composed of hydrogen-bonded or strongly sterically hindered molecules are in general "structure-limited". Liquids which are spherical or small symmetric tops are categorised as "collision-limited". Among these are  $CCl_4$ ,  $CH_4$ ,  $CS_2$ ,  $CH_3CN$ ,  $C_6H_6$  and  $C_6H_2$ . The relaxation times  $\tau_R$  and  $\tau_m$  are in the rough proportions 1 : 2 or 1 : 1 if it is the "structure-limited" model which predominates, the reorientations proceeding with jumps of amplitude  $30^\circ$ - $90^\circ$ ; while the ratio is closer to 1 : 3 if the individual jumps remain [71] at less than ca.  $20^\circ$  or so.

An analysis by Ben Reuven and Gershon [63] was carried out in terms of almost uncorrelated rotational movements of individual molecules, such as the process of rotational diffusion, with which they describe the central (Lorentzian) part of the band. The wings of  $I_{VH}(\omega)$  are treated in terms of elastic collisions, or librations, (the process giving rise to far infra-red Poley absorption). These authors assume that the central (low frequency) part of the line represents the contribution of these mono-molecular rotations, while the weak multi-molecular effect at higher frequencies is treated via a tensor which generalises the well-known Kirkwood g factor (see above) [14,15].

An important aspect of studies of Rayleigh scattering (which is always meant to embody processes in which only a broadening of the spectral line about its centre is observed, in contrast to Raman processes, where frequency shifted lines are broadened) is its variation with temperature. In principle, therefrom, different contributions to the broadening process can be analysed in terms of different energies of activation, which can be compared with those obtained from viscosity and dielectric measurements.

To this end, Dardy et al. [72] have made observations of the depolarised Rayleigh line for the substituted benzenes over the range 286 - 349 K. Litovitz and co-workers [59] had previously obtained excellent experimental agreement by attributing the shape of the observed scattering spectrum of linearly anisotropic molecular systems to a single reorientational mechanism. However, it was later suggested [60] that the spectra are more accurately represented as the sum of two orientational processes due to motion of molecules about their parallel and perpendicular axes. In addition, the far wing of the Rayleigh line contains information about intermolecular

effects, since an exponential far wing can be observed [73] in a number of spherical molecules (such as  $CCl_4$ ) with scalar polarisabilities. McTague and Birnbaum [74] successfully predicted an exponential spectral profile of light scattering from noble gases by assuming a mechanism of molecular collision. Subsequently Bucaro and Litovitz [75] were able to account for the spectral shape of the depolarised Rayleigh wing in spherically polarisable molecular liquids in terms of a simple binary-collision approach. The experimental spectra of moderate and highly anisotropic liquids exhibit not only the same quasi-exponential tail as spherically polarisable molecules, but also a shoulder in the wing region ( $50 - 90 \text{ cm}^{-1}$ ) which cannot be accounted for with the distortional mechanism of Bucaro and Litovitz [75].

Dardy et al [72] used their temperature variation studies to show that a simple Lorentzian plus a background cannot account for the observed data even after a collision-induced component has been subtracted. Use of the correlation function  $C_R(t)$  reveals that considerable free-rotor (short-times) behaviour is present, a molecule such as benzene rotating about  $15^\circ$  on average between "collisions". The long time behaviour of the orientational correlation function  $C_R(t)$  is exponential, reflecting ultimate diffusional molecular behaviour. The time constant associated with this exponential is significantly greater than the average relaxation time, indicating that care must be taken in the employment of half-widths as a measure of the orientational time. Study of the short-time behaviour of the reorientational steps involved in molecular motion is greatly facilitated by analysis of the second derivative of the function  $C_R(t)$  (analogously with far infra-red band-shape analysis) which at short time is proportional to the angular velocity correlation function but which is in general [76] related to the correlation of angular momenta and angular orientation. Analysis of  $-\ddot{C}_R(t)$  allows the determination of the time between collisions,  $\tau_{BC}$ , which the authors find to follow a simple cell model of liquid structure. This correlation function shows that incomplete loss of memory occurs during a collision in benzene and thus the simple diffusion model on which the Hubbard relation is based is invalidated. (Keyes and Kivelson [77] have discussed this last point more generally). There is no need to separate the spectrum into librational and diffusional motions, but rather, it is more correct to associate the "shoulder" in the depolarised spectrum with the incomplete loss of memory after a collision. Cross-terms in orientations are neglected, but the authors feel that  $\tau_{BC}$  is not affected by their neglect.



Recently Dill et al. [78] have made a study of the effects of pressure on liquid acetone, benzene and methyl iodide, the former two being plate-like and the latter rod-like symmetric tops. From the orientational part of the Rayleigh wings they were able to extract the density dependence of  $C_R(t)$  and  $-\dot{C}_R(t)$ . They found that the mechanism of reorientation appears to be one involving molecular rotation which is randomly affected by molecular collisions. The J-diffusion model does not appear to be an accurate description of this process. The function  $-\dot{C}_R(t)$  has a negative region and oscillates (as is well-known in the far infra-red, Figs. 1 - 7), indicating that complete randomisation of the angular velocity at each collision, an assumption of the J-diffusion model, does not occur. Also, in acetone where this effect is small, the calculation of the mean time between random collisions,  $\tau_J$ , of the J diffusion model shows this to be short compared with the actual decay time of  $-\dot{C}_R(t)$ , possibly indicating non-free rotor behaviour between collisions. The fact that the oscillations in  $-\dot{C}_R(t)$  are strongest in benzene and essentially absent in acetone indicates that angular forces resulting from mechanical anisotropy lead to a tendency towards molecular librations. The effect of mechanical anisotropy is enhanced at increasing density as can be seen from the increase in oscillations in methyl iodide at the higher pressures.

The time taken for  $-\dot{C}_R(t)$  to become negative appears to be a good measure of the time between collisions ( $\tau_{BC}$ ). Its density dependence follows that of a simple cell model. It is emphasised that in general,  $\tau_{BC}$  and  $\tau_J$  are not to be identified with each other, as has often been assumed. In acetone, they are related by a density independent factor. In benzene and methyl iodide they exhibit quite different density-dependences. This results from the fact that in these liquids the efficiency of a collision for randomising the angular velocity is density dependent.

The same techniques were used by van Konynenberg and Steele [79] to study the rotational dynamics in simple fluids such as liquid nitrogen, ethane, ethylene and carbon dioxide for a number of temperatures and densities along the saturated vapour lines. These authors realised the full theoretical significance of  $-\dot{C}_R(t)$  as an angular momentum/orientation correlation function. They found that the collision-induced part may be too large relative to the scattering from permanent polarisability anisotropy to allow the extraction of reliable rotational correlation functions for ethane and ethylene. Data for nitrogen and carbon dioxide were compared with curves of the J-diffusion model which was found to describe the results

qualitatively. The authors indicate that the assumption of complete randomisation of the molecular angular momentum after collision ought to be re-examined in the light of molecular dynamics calculations of the correlation function of the angular-momentum vector which shows negative regions at intermediate times. This means that the colliding molecules are rebounding in a way that results in preferential reversals of the orientation of the angular-momentum vector. Therefore, a reversal of angular velocity is indicated which will rebuild orientational correlation as the molecule starts to return to its original orientation.

#### MODELS FOR $C_R(t)$ , THE MORI APPROXIMATION

In the case of Rayleigh depolarised light scattered from a liquid one has <sup>3,4</sup> :

$$C_R(t) = T_{\Gamma} \langle \beta_1(0) \beta_1(t) \rangle = \frac{1}{2} \langle 3[\underline{u}(0) \cdot \underline{u}(t)]^2 - 1 \rangle,$$

if the following assumptions are made:

- (i) Collision induced scattering can be treated separately <sup>[68]</sup>,
- (ii) Correlations between different molecules can be ignored.

Using eqn.(34) one has:

$$\dot{C}_R(t) = - \int_0^t K_R(t-\tau) C_R(\tau) d\tau. \quad (54)$$

It is clear from eqn.(50) that the form:

$$K_R(t) = \gamma \delta(t); \quad C_R(t) = \exp(-\gamma t) \quad (55)$$

is too simple, since the expansion of  $C_R$  has odd powers of time.

Nevertheless,  $C_R$  at long times is well approximated by an exponential <sup>[2-4, 6-8]</sup> so that at low frequencies  $I_{VH}^*(\omega)$  is given as follows <sup>[59]</sup>:

$$I_{VH}^*(\omega) \propto (\alpha_{11} - \alpha_1)^2 \int_{-\infty}^{\infty} \exp(-i\omega t) \exp(-\gamma t) dt.$$

$$\text{So that } \text{Real} [I_{VH}^*(\omega)] = I_{VH}(\omega) \propto \frac{(\alpha_{11} - \alpha_1)^2}{\gamma^2 + \omega^2}, \quad (56)$$

which is the Lorentzian bandshape used by Litovitz and co-workers <sup>[59,68, 70,72,75,78]</sup>. (The imaginary part of  $I_{VH}^*(\omega)$  describes a refringence phenomenon <sup>[53]</sup> of fluctuating refractive index). However, at higher frequencies, the experimental spectra of moderately and highly anisotropic liquids exhibit <sup>[72]</sup> a shoulder in the wing region ( $50 - 100 \text{ cm}^{-1}$ ) which no single Lorentzian can describe, although attempts have been made <sup>[80]</sup> with two Lorentzian components. The distortional mechanism of Bucaro and Litovitz <sup>[75]</sup> is incapable of accounting for the shoulder. Clearly one

needs to choose  $K_R$  so that  $C_R$ , and subsequently  $I_{VH}(\omega)$ , are better behaved at short times (or high frequencies).

The truncation:

$$K_{O,R}(t) = K_{O,R}(0) \exp(-\gamma_0 t), \quad (57)$$

of the analogous series of eqns.(39) yields the M-diffusion<sup>[28,31]</sup> scattering function as:

$$I_{VH}(\omega) \propto \frac{(\alpha_{11} - \alpha_{\perp})^2 \gamma_0 K_{O,R}(0)}{(K_{O,R}(0) - \omega^2)^2 + \omega^2 \gamma_0^2}, \quad (58)$$

which reduces to the Lorentzian:

$$I_{VH}(\omega) \propto \frac{(\alpha_{11} - \alpha_{\perp})^2 \gamma_0 K_{O,R}(0)}{K_{O,R}(0) + \omega^2 (\gamma_0^2 - 2K_{O,R}(0))},$$

at low frequencies (such that  $\omega^4 \ll \omega^2$ ). Here,  $K_{O,R}(0)$  is given by the negative of the  $t^2$  term in eqn. (50) and the finite torque  $\langle O(V)^2 \rangle$  is again ignored. So:

$$K_{O,R}(0) = \frac{3kT}{I}, \quad (59)$$

for a linear molecule, i.e. it is a single molecule property.

Although Dill et al.<sup>[78]</sup> found that the mechanism of molecular reorientation appears to be one involving rotation randomly affected by molecular interactions, the J-diffusion (and the M-diffusion) model does not appear to represent the process accurately. Figures 1 - 7 show that essentially the same is true in the far infra-red. This is because complete randomisation of the angular velocity at each collision is too drastic an assumption, consequential upon that of an instantaneous collision, with its association of the mean square torque  $\langle O(V)^2 \rangle$  becoming instantaneously infinite<sup>[8,29]</sup>. Further evidence of this comes from a recent study<sup>[81]</sup> of the Rayleigh and depolarised Raman (a  $\Sigma_g^+$  band situated near  $1386 \text{ cm}^{-1}$ ) band profiles of  $\text{CO}_2(\ell)$  obtained at 100, 1500 and 3000 bar. The J-diffusion model is adequate for the Rayleigh band at 100 bar, but fails for those at the higher pressures, where the frequency-dependence ( $\omega^{-n}$ ) of the Rayleigh line changes noticeably to a higher  $n$  at intermediate and high frequencies. The profile of the Raman band remains unaffected by pressure, so that the authors conclude that it originates from a unimolecular orientational process, whereas the depolarised Rayleigh scattering shows up both mono- and multimolecular motions. They find that cooperative behaviour increases with pressure and is appreciable at 3000 bar.

Since this type of behaviour is clearly shown by this study to be associated with a faster fall-off with frequency of the Rayleigh wing, it is going to be profitable to consider the truncation:

$$K_{1,R}(t) = K_{1,R}(0) \exp(-\gamma_2 t),$$

so that:

$$I_{VH}(\omega) \propto \frac{(\alpha_{||} - \alpha_{\perp})^2 K_{0,R}(0) K_{1,R}(0) \gamma_2}{\gamma_2^2 (K_{0,R}(0) - \omega^2)^2 + \omega^2 (\omega^2 - (K_{0,R}(0) + K_{1,R}(0)))^2},$$

which falls off as  $\omega^{-6}$  at high frequencies instead of the  $\omega^{-4}$  of the M-diffusion model, and has the finite torque term  $\langle O(V)^2 \rangle$  implicit in  $K_{1,R}(0)$ :

$$K_{1,R}(0) = a_1 - a_2/a_1$$

with  $a_1 = -3kT/I$ ;

$$4! a_2 = 4(kT/I)^2 + \langle O(V)^2 \rangle / 8I^2.$$

Equation 60 is a Lorentzian when  $\omega^4 \ll \omega^2$ .

Berne and Harp [82] plotted this kind of function and found that it peaked at  $\omega \doteq 9 \times 10^{12}$  rad s<sup>-1</sup> (ca. 50 cm<sup>-1</sup>) which is near the shoulder observed by Dardy et al [72] in anisotropic molecular liquids. Thus far the analogue of eqn. (60) in the far infra-red [34,38] has been successful in describing absorptions over three decades of frequency.

#### COLLISION-INDUCED RAYLEIGH SCATTERING

Dardy et al [72] have demonstrated that the spectrum of depolarised light can be expressed as the sum of three separate terms:

$$I_{DP}(\omega) = I_{VH}(\omega) + I_{COL}(\omega) + I_{VH-COL}(\omega) \quad (61)$$

where  $I_{COL}(\omega)$  represents the collisional part of the intensity observable [83] in molecules such as CCl<sub>4</sub> with no anisotropy of polarisability. At present, the theoretical expressions from which the sign and magnitude of the cross-term can be calculated are approximate. Although this need not be small, Dardy et al. [72] found that its neglect did not affect the consistency of their subsequent results.

In anisotropic molecules, the central term  $I_{VH}(\omega)$  (the low frequency Lorentzian) accounts for almost all of the total intensity;  $I_{COL}(\omega)$  being measurable in the wings, which Bucaro and Litovitz [75] have treated in terms of deformations of molecular polarisability during a collision, predicting:

$$I_{\text{COL}}(\omega) \propto \omega^{12/7} \exp(-\omega/\omega_0) \quad (62)$$

for  $\omega > \omega_0$ . They calculate  $\omega_0$  from available intermolecular potential data employing the expression

$$\omega_0^{-1} = \frac{\pi \Gamma_0}{6} \left( \frac{\mu}{kT} \right)^{1/2} \left[ 1 - \frac{2}{\pi} \tan^{-1} \left( \frac{2\varepsilon}{kT} \right)^{1/2} \right],$$

where  $\Gamma_0$  and  $\varepsilon$  are the Lennard-Jones parameters and  $\mu$  the reduced mass of the colliding molecules.

In isotropic molecules (e.g.  $\text{CCl}_4$ ),  $I_{\text{COL}}(\omega)$  consists of a central Lorentzian accounting for almost half the total observed intensity, together with the wing function of eqn.(62), i.e.:

$$\left. \begin{array}{l} I_{\text{COL}}(\omega) \rightarrow \text{a Lorentzian at low frequencies} \\ \rightarrow \text{eqn.(62) at high frequencies.} \end{array} \right\} \quad (63)$$

The equivalent expression<sup>[68]</sup> to eqn.(62) in the far infra-red is:

$$\alpha(\omega) \propto \omega^{26/7} \exp(-\omega/\omega_0). \quad (64)$$

Compared with the models<sup>[56]</sup> summarized in Figs. 8 and 9, eqn.(64) is much less successful (Fig.10) in fitting the experimental curves shown in these Figures but has the advantage of having fewer variables.

Bucaro and Litovitz<sup>[83]</sup> have emphasized the close similarity between  $I_{\text{COL}}(\omega)$  and  $\varepsilon''(\omega)/(1-\exp(-\hbar\omega/kT))$ , the population-corrected dielectric loss factor of non-dipolar molecules, and have shown that both are fairly well described by empirical equations of the form:

$$I_{\text{COL}}(\omega) = \frac{A}{1 + \omega^2 \tau_2^2} + Bf(\omega) \quad (65)$$

$$\frac{\varepsilon''\omega}{(1 - \exp(-\hbar\omega/kT))} = \frac{A'}{1 + \omega^2 \tau_1^2} + \frac{\omega^2 \tau_c^2}{1 + \omega^2 \tau_c^2} B'f(\omega) \quad (66)$$

where  $A$ ,  $B$ ,  $A'$ ,  $B'$ ,  $\tau_2$ ,  $\tau_1$  and  $\tau_c$  are independent of  $\omega$ , and where  $f(\omega)$ , defined for all  $\omega$ , reduces to:

$$f(\omega) \rightarrow \omega^{12/7} \exp(-\omega/\omega_0)$$

for  $\omega > \omega_0$ . Both these equations have separate high frequency and low frequency semi-empirical portions whereas generalised Langevin theory<sup>[4,7]</sup> predicts that a peak in the far infra-red or a shoulder in the Rayleigh wing should not be treated separately<sup>[84]</sup> and independently of orientational processes causing the microwave absorption or low-frequency Rayleigh scattering in both dipolar (anisotropic) or non-dipolar (isotropic, e.g.  $\text{CCl}_4$ ) liquids. Therefore it seems better to treat these collisional aspects of Rayleigh scattering on the same terms as those of Davies and Evans<sup>[56,85]</sup> for the collisional-induced microwave

(far infra-red band of non-dipolar liquids), i.e. by invoking an equation such as eqn.(60) with  $K_{O,R}(0)$ ,  $K_{1,R}(0)$ , and  $\gamma_2$  as variables.

Taking note of the similarity of eqns.(65) and (66) it seems that eqn.(60) should be nearly as successful in describing Rayleigh depolarised scattering due to molecular collisions as its equivalent in the far infra-red in describing the same fundamental dynamical process.

#### NUCLEAR MAGNETIC RESONANCE SPIN-ROTATION RELAXATION

The relaxation of nuclear spins is determined by the coupling of these spins with the rotational and translational motions of the molecules in the system. For nuclei with spin 1/2, the spin-rotation interaction of a linear molecule leads to an interaction Hamiltonian of the form  $(-c\mathbf{I}\cdot\mathbf{J})$ , where  $\mathbf{I}$  is the spin angular momentum of the nucleus,  $\mathbf{J}$  is the angular momentum of the molecule, and  $c$  is the spin rotation coupling constant [4]. When this is the only part of the Hamiltonian leading to nuclear spin relaxation, the spin relaxation time  $T_1$  is:

$$\frac{1}{T_1} = \frac{c^2}{3\hbar^2} \int_{-\infty}^{\infty} \exp(-i\omega_0 t) \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle dt, \quad (67)$$

where  $\omega_0$  is the Larmor precession frequency. In liquids, the angular momentum correlation function decays on a time scale of the order [1 - 10] of  $10^{-12}$ s, which is many orders of magnitude shorter than typical precessional periods ( $1/\omega_0 = 10^{-6}$ s). Thus:

$$\frac{1}{T_1} = \frac{c^2}{3\hbar^2} \int_{-\infty}^{\infty} \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle dt \quad (68)$$

to an excellent approximation.

For a diatomic molecule,  $\mathbf{J}$  is given by:

$$\mathbf{J} = m_1 [\mathbf{r}_1 - \mathbf{R}] \times [\mathbf{v}_1 - \mathbf{V}] + m_2 [\mathbf{r}_2 - \mathbf{R}] \times [\mathbf{v}_2 - \mathbf{V}], \quad (69a)$$

where  $m_i$ ,  $\mathbf{r}_i$  and  $\mathbf{v}_i$  are the mass, position, and velocity of the  $i$ 'th atom, respectively, and  $\mathbf{R}$  and  $\mathbf{V}$  are the position and velocity of a molecule's centre of mass; and the short time expansion of the correlation function is, for a linear molecule <sup>4</sup>:

$$C_J(t) = \frac{\langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle}{\langle \mathbf{J}^2 \rangle} = 1 - \frac{t^2 \langle O(V)^2 \rangle}{4IkT} + \frac{t^4 \langle \dot{O}(V)^2 \rangle}{4! 2IkT}, \quad (69b)$$

where  $\langle O(V)^2 \rangle$  and  $\langle \dot{O}(V)^2 \rangle$  are the mean square torque and its derivative respectively. It is seen that  $C_J(t)$  bears some resemblance to the normalised second derivative of  $C_m(t)$  (of the far infra-red) or of  $C_R(t)$  (of Rayleigh bandshapes). Gerschel et al. [37] showed that  $-\ddot{C}_m(t)$  has a negative region, and that it oscillates at short times [78], Figs. 1-7 being illustrations. Dill et al. [78], and van Konynenberg

and Steele [79] demonstrated the same properties in  $-\ddot{C}_R(t)$ . There has been very little, if anything, reported from NMR studies on the full-time dependence of  $C_J(t)$ , but Berne and Harp [4] have made some computer calculations which show that there is a negative interval [86], if the intermolecular pair potential is anisotropic (non-central). When the latter is a Lennard-Jones type, (pseudo-spherical), then  $C_J(t)$  remains positive and changes very little over the observed time interval of 1 ps.

From eqn. (69b) it is seen that in the absence of molecular interaction  $C_J(t)$  is unity, and the corresponding memory function:

$$K_J(t) = \frac{\langle O(V)^2 \rangle}{2IkT} + \frac{t^2}{2} \left[ \left[ \frac{\langle O(V)^2 \rangle}{2IkT} \right]^2 - \frac{\langle \dot{O}(V)^2 \rangle}{2IkT} \right] - \dots \quad (70)$$

is zero. Therefore,  $K_J(t)$  can be looked upon as representing the molecular memory of the interactions it has undergone. (This is different from the cases of  $C_m(t)$  and  $C_R(t)$ , (and their corresponding memory functions), which decay in the absence of intermolecular torque forces owing to the fact that there is a distribution of rotational frequencies for each molecule in the gas phase). If  $C_J(t)$  goes negative, then  $K_J(t)$  must be finite, i.e. a molecule must retain some memory of its interactions for a finite time. Berne and Harp [4] find the typical memory function behaviour to be that of quick decay almost to zero in the time interval  $0 \leq t \leq 0.3$  ps, and then a much slower decay (exhibiting a positive tail) for  $t \geq 0.3$  ps. They stress that this is approximately the average time that it would take for a molecule to travel from the centre of its cage of nearest neighbours to the "cage wall". Up to now, no attempt has been made to calculate the memory functions corresponding to  $-\ddot{C}_m(t)$  and  $-\ddot{C}_R(t)$  from far infra-red and Rayleigh scattering data respectively. It will be interesting to see how these "true" experimental functions compare with those from computer experiments on  $K_J(t)$ .

As an example of the work carried out on NMR spin-rotation relaxation, Rigny and Virlet [87] have studied the relaxation of the fluorine nuclei in the three hexafluorides of uranium, tungsten, and molybdenum, which are room temperature liquids. In contrast to what occurs in most liquids [88], the spin-rotation interaction is the dominant relaxation mechanism, even well below the critical temperature of 503 K, for  $UF_6$ , 488 K for  $MoF_6$ , and 445 K for  $WF_6$ . This means that the correlation time for the angular momentum (the mean time during which a molecule seems to retain its angular momentum) is long, probably because of the pseudo-spherical geometry of these molecules. However, the authors show that the molecules

can rotate only ca. one radian at 343K before their angular momentum changes: this shows that the rotations do not occur freely, but rather in a hindered, or "cog-wheel" fashion.

These conclusions are revealed by using the generalised rotational Langevin equation:

$$\dot{\underline{J}} = - \int_0^t \underline{\Gamma}(t-\tau)\underline{J}(\tau)d\tau + \underline{R}(t) , \quad (71)$$

with  $\underline{R}(t)$  as the stochastic torque and  $\underline{\Gamma}$  the "retarded effect of friction", or memory function, giving the Fourier-Laplace transform of  $C_J(t)$  as:

$$\begin{aligned} \tilde{C}_J(i\omega_0) &= \int_0^\infty \langle \underline{J}(0) \cdot \underline{J}(t) \rangle \exp(-i\omega_0 t) dt \\ &= \frac{\tilde{C}_J(0)}{i\omega_0 + \Gamma(\omega_0)} , \end{aligned} \quad (72)$$

where  $\omega_0$  is the Larmor frequency of the nuclear spin. This is small enough for its neglect in the denominator of eqn.(72) to be justifiable and the exponential becomes unity. In effect, this means that  $\underline{R}(t)$  will fluctuate so rapidly that its correlation function, related to  $\underline{\Gamma}(\omega)$  by:

$$\underline{\Gamma}(\omega) = \frac{1}{\langle \underline{J}^2 \rangle_{av.}} \int_0^\infty \langle \underline{R}(0) \cdot \underline{R}(t) \rangle_{av.} \exp(-i\omega_0 t) dt \quad (73)$$

becomes a delta function in time, and  $\underline{\Gamma}$  becomes frequency-independent. Therefore in eqn.(72) when  $\omega_0$  is so low that only low frequency components of the correlation function are considered one has

$$\int_0^\infty \langle \underline{J}(0) \cdot \underline{J}(t) \rangle dt = \frac{C_J(0)}{\Gamma} = C_J(0)\tau_J , \quad (74)$$

where  $\tau_J$  is the angular momentum correlation time. Thus  $\tau_J$  is related directly to  $T_1$ , the spin rotation relaxation time.

If the temperature is raised, the torque acting on a molecule fluctuates more rapidly and eqn.(73) indicates that the friction will be reduced. Thus  $T_1$  should, and is observed to, decrease as the temperature is raised, following an Arrhenius law<sup>[14]</sup>.

For spherical top molecules such as  $\text{CH}_4$ ,  $\text{CF}_4$ ,  $\text{SF}_6$  and the above, the contribution to NMR lineshape, due to spin-rotation interaction is comparable (and greater at higher temperatures) with that of spin-spin magnetic dipolar relaxation. This is the contribution to spin-resonance relaxation due to the interaction of two nuclear spins (of quantum number  $s$ ), which are identical and situated on the same molecule, separated by a distance  $b$  (a separation defined by the vector  $\underline{y}(t)$ ). The spin-spin relaxation time is given by:



$$\begin{aligned}
[T_1^{-1}(\omega_L)]_{ss} &= \frac{1}{5} \frac{\gamma^4 \hbar^2 s(s+1)}{b^6} \left[ \int_{-\infty}^{\infty} F_t(t) e^{-i\omega_L t} dt + 4 \int_{-\infty}^{\infty} F_t(t) e^{-2i\omega_L t} dt \right] \\
&= \frac{2\gamma^4 \hbar^2 s(s+1)}{b^6} \int_0^{\infty} F_t(t) dt, \quad (75)
\end{aligned}$$

since the Larmor frequency is small in practice. Here

$$F_t(t) = \frac{1}{2} \langle 3[\underline{u}(0) \cdot \underline{u}(t)]^2 - 1 \rangle, \quad (76)$$

and  $\gamma$  is the gyro-magnetic ratio. If the relaxation is due to coupling of a nuclear magnetic quadrupole moment ( $Q$ ) with the gradient of a molecular electric field whose direction is that of the vector  $\underline{u}(t)$ , one has, for a spin  $s=1$ :

$$\begin{aligned}
[T_1^{-1}(\omega_L)]_Q &= \frac{3}{8} \left( \frac{eQ}{\hbar} \frac{\partial^2 \gamma}{\partial z^2} \right)^2 \left[ \int_{-\infty}^{\infty} F_t(t) e^{-i\omega_L t} dt + 4 \int_{-\infty}^{\infty} F_t(t) e^{-2i\omega_L t} dt \right] \\
&= \frac{3Q}{8} \left( \frac{eQ}{\hbar} \frac{\partial^2 \gamma}{\partial z^2} \right)^2 \int_0^{\infty} F_t(t) dt \quad (77)
\end{aligned}$$

Using a combination of these different techniques, it is possible to describe<sup>[89]</sup> the movement of these molecules whereby the angular amplitude of a rotation before collision can seemingly reach one radian or so. If this were the case, the dynamics would no longer be those of rotational diffusion<sup>[11]</sup>, the correlation functions would not be exponential. Unfortunately, it is always difficult in NMR relaxations to extract any time-dependence of  $C_J(t)$  or  $F_t(t)$  since the  $\omega_L$  or  $\omega_0$  Larmor frequencies are so low compared with the rate of molecular reorientations. However, NMR results can be compared usefully with those of corresponding dielectric measurements<sup>[14]</sup>, in particular for temperatures approaching the triple point (diffusional rotation). For temperatures approaching the boiling point, or even higher, the mechanism of reorientation is generally interpreted with the help of the spin-rotation component of  $T_1$ , taking advantage of long periods of free molecular rotation. The principal interest in these types of studies is to investigate more closely the anisotropy of molecular rotational movement. The observed rotation is often almost free about one axis of symmetry and diffusional about the perpendicular one.

The molecule  $\text{CH}_3\text{-C}\equiv\text{N}$  has been studied in the liquid phase as a

function of temperature from the melting point to the boiling point [90,91]. The rotation is anisotropic; at 298 K it is ten times as rapid about the symmetry axis as about the perpendicular axes, and shows some characteristic properties of a damped rotational motion, with a dominant contribution to the NMR line from spin-rotation. A rotational diffusion constant is extracted which is in agreement with some calculations [92] based on "microviscosity" theory. The ratio of dielectric and NMR relaxation times is 3.7 at 298 K, compared with the rotational diffusion prediction of 3.

The same type of behaviour has been observed [93] for the molecule  $\text{CH}_3\text{-C}\equiv\text{CH}$ , studied as a function of temperature to the boiling point. Between 179 K and 304 K, the rotation about the axis of symmetry is from 30 to 8 times as fast as that about the other axes. The contribution of spin-rotation correlation time  $\tau_J$  changes from 0.1 to 1.0 times that of the spin-spin dipolar (magnetic) correlation time ( $\tau_m$ )<sub>ss</sub>. However, free rotation about the symmetry ( $C_{3v}$ ) axis is not implied, since the description of this motion by a model of rotational diffusion is more satisfactory in reproducing the observed diffusion constants. The short time behaviour of  $-\ddot{C}_m(t)$  has been obtained from the far infra-red [33,94].

The molecules  $\text{VOCl}_3$ ,  $\text{CCl}_3\text{CN}$ , and  $\text{BCl}_3$  are of smaller geometric anisotropy than the preceding molecules, and the anisotropy of rotational movement is very much less [95]. The agreement between the diffusion constants  $D_{//}$  and  $D_{\perp}$  is ca. 0.5 - 2.0. As a measure of the character of the rotation, the ratio  $X = \tau_J/\tau_f$  (where  $\tau_f$  corresponds to free rotation) is always less than 2 for  $\text{BCl}_3$ , and also for rotation perpendicular to the symmetry axis in  $\text{CCl}_3\text{CN}$ , an indication of large angles of rotation between collisions. In contrast, for  $\text{VOCl}_3$ , and the movement parallel to the  $C_{3v}$  axis in  $\text{CCl}_3\text{CN}$ ,  $\tau_J$  is large in comparison with  $\tau_f$  which suggests rotational diffusion.

Chloroform has been studied up to its boiling point [96,97]. The rotation about the symmetry axis is found to be twice as rapid as the perpendicular motion at 293 K. The ratio  $X$  suggests that this latter component of the rotational motion is diffusional in character. This is supported by the ratio of NMR to dielectric relaxation times, which is 3.5, compared with the ideal of 3.

A study of  $\text{ClO}_3\text{F}$  (perchloryl fluoride) up to the critical point [98] (368 K) has shown that a rotational diffusion mechanism is valid only below 200 K, while spin rotational relaxation becomes predominant above

this temperature. The observed mean angle between collisions increases up to 360 K, the mean angular amplitude being estimated at just less than a radian.

Asymmetric top molecules have been carefully studied with NMR relaxation techniques, the results confirming the diffusional character of their molecular rotation in liquids. The benzene derivatives:  $C_6H_5F$ ,  $C_6H_5Cl$ ,  $C_6H_5Br$ ,  $C_6H_5CH_3$ , p-xylene, mesitylene,  $C_6F_6$ , parafluorotoluene and trifluoronitrotoluene have been studied [99] up to their critical temperatures. For all these compounds, the spin-rotation interaction becomes appreciable only at high temperatures, the ratio between dielectric and NMR relaxation times being  $\geq 3$  at ambient temperatures.

Similar behaviour has been observed for certain fluoro-derivatives of methane [100] such as  $CH_2FCl$ ,  $CHF_2Cl$ ,  $CHF_3$ ; and in particular, a detailed study of the behaviour of  $T_1$  has been carried out [101] for  $CHFC_2$ . In the latter study, the effect of spin-rotation was simulated by a model of diffusion by isolated jumps of large amplitude: the observed effect being the result of a series of discrete collisions. However, Powles [88] has observed that the increase in  $\tau_j$  with temperature predicted by this model is the same as that calculated for Brownian diffusion by small jumps. Thus no conclusion can easily be reached about the detail of molecular movement from measurements of spin rotation relaxation at one Larmor frequency alone.

The main interest in these measurements stems from the unique experimental information which they give on the conservation of rotational velocity (i.e.  $\tau_j$ ) about different axes in a given molecule, e.g. they can be used to characterise a slightly perturbed rotation about the symmetry axis of stick-like molecules.

Boden et al. [102,103], give a continuing and comprehensive series of reports of the recent developments in this field, Bodens review [102] being especially useful as a guide to the developments of stochastic theories of liquids in relation to spin-rotation relaxation. For instance, the tensorial correlation time  $\tau_2$ , defined by:

$$\tau_2 = \int_0^{\infty} \left\langle \frac{3}{2} [\underline{u}(0) \cdot \underline{u}(t)]^2 - \frac{1}{2} \right\rangle dt \quad (78)$$

is related to  $\tau_j$  by Hubbard's equation 69:

$$\tau_2 \tau_j = I/6kT \quad (79)$$

in the limit of rotational diffusion, and by [104]

$$\tau_2 = \tau_j/5 \quad (80)$$

in the dilute gas, or perturbed free rotor limit for spherical top molecules.

In the intermediate region, McClung [28,105] has discussed the interrelation of  $\tau_2$  and  $\tau_J$  for spherical tops in terms of the M and J-diffusion models [3]. These models approach the above two in the limits of small and large  $\tau_J$ . Numerical calculations for the intermediate range show  $\tau_2$  that  $\tau_2$  goes through a minimum when:

$$\tau_2 \doteq \tau_J \doteq (kT/I)^{\frac{1}{2}}$$

Maryott et al. [98] have shown how values of  $\tau_2$  and  $\tau_J$  calculated from  $^{35}\text{Cl}$  and  $^{19}\text{F}$  relaxation times in liquid  $\text{C}_2\text{O}_3\text{F}$  are linked by the J-diffusion model. The  $\tau_2$  values are compared with those calculated from the Debye-Stokes-Einstein relation as modified by Gierer and Wirtz [92]:

$$\tau_2 = 4\pi a^3 \eta f / 3kT. \quad (81)$$

Here  $f$  is the microviscosity factor. As is often found,  $\tau_2$  is not a linear function of  $\eta/T$ , and the "apparent"  $f$  varied from 1/4 at the highest temperature to 1/120 at the lowest. For pure liquids, it is theoretically 0.163.

For non-spherical tops, a number of investigators [106] have described how, in the case of anisotropic rotation [107],  $\tau_2$  can, in the small-step diffusion limit, be expressed in terms of the three rotational diffusion constants for the molecule, and how these can be determined [90,91,93] by measurements of the relaxation times of three quadrupolar nuclei in geometrically non-equivalent positions in the molecule.

Sillescu [108] has extended the Debye model of Brownian motion [11] ( $\delta$ -function memory) and the random-jump model for rotation to take account of time fluctuations in their rate. In principle, this is applicable to NMR line shapes. Different shapes are given by the Debye and jump models.

Jonas et al. [109] invoke J-diffusion in explaining  $\tau_2$  and  $\tau_J$  interrelations in several NMR relaxation studies in highly pressurised liquids [78, 81]. They deal with the reorientational and angular momentum correlation times in fluorobenzene -  $d_5$ , liquid-chloroform, and internal motions in liquid benzylicyanide. Eckert et al. [110] have used spin rotation relaxation studies to measure association and anisotropic molecular orientation in liquids.

#### APPLICATION OF THE MORI APPROXIMATION

Various forms of the response function  $K$  can be used to calculate

spin-rotation and spin-spin relaxation times using eqns. [68] and [75] to give the corresponding correlations times  $\tau_J$  and  $\tau_2$ . Using equipartition of kinetic energy (two degrees of freedom) one has:

$$kT = \langle E_{\text{kin}} \rangle = \langle \underline{J}^2(o) \rangle / 2I$$

$$\text{so that } \tau_J = \int_0^{\infty} \langle \underline{J}(o) \cdot \underline{J}(t) \rangle dt / 2IkT.$$

When  $K_J$  and  $K_R$  are both delta functions one has:

$$C_J(t) = \langle \underline{J}(o) \cdot \underline{J}(t) \rangle / \langle \underline{J}^2(o) \rangle = e^{-t/\tau_J} \quad (82)$$

$$F_t(t) = \frac{1}{2} \langle 3[\underline{u}(o) \cdot \underline{u}(t)]^2 - 1 \rangle = e^{-t/\tau_2} \quad (83)$$

with  $\tau_2$  and  $\tau_J$  linked by the Hubbard relation of eqn. [79].

In many liquids, the mean field of force due to the neighbours of a given molecule tends to hold it in a fixed orientation for longer or shorter times, while superposed on this time-smoothed force field is the rapid fluctuation due to the actual molecular movements [7] (approximated in Brownian theory by a random torque of simple character superposed on the steady orienting field). If the constraining field is strong, the molecule will move, in general, as a damped gyrostatic pendulum. If the constraint is highly anisotropic the motion may approach rotation freely around a fixed axis. If the molecule is a spherical top, its component rotations behave independently [7].

These molecular angular movements are described by eqn. [44] in the case of one angular coordinate  $x$ , describing the M-diffusion process, which corresponds to:

$$K_J(t) = K_J(o) \exp(-t/\tau'_J),$$

$$K_t(t) = K_t(o) \exp(-t/\tau'_2). \quad (84)$$

Using eqns. [84] and those corresponding to eqn. [43] it is found that  $\tau'_2 \tau'_J$  does not vary in the Hubbard fashion, but goes through a minimum dependent on  $\langle O(V)^2 \rangle$  (experimental), since  $\tau_J$  depends on  $K_{o,J}(o)$ .

With the truncations:

$$K_{1,J}(t) = K_{1,J}(o) \exp(-t/\tau''_J), \quad (85)$$

$$K_{1,t}(t) = K_{1,t}(o) \exp(-t/\tau''_t),$$

one has  $(T_1^{-1})_{ss}$  and  $(T_1^{-1})_{sr}$  both dependent on  $\langle O(V)^2 \rangle$ ; and  $\langle O(V)^2 \rangle$  and  $\langle \dot{O}(V)^2 \rangle$  respectively, so that  $\tau'' \tau''_J$  behaves in a more realistic manner.

## TRANSLATIONAL MOTIONS OF MOLECULES

The above sections have all dealt with orientational, angular or rotational molecular movements, and Figs. 8 and 9 show that an extended rotational-type Langevin equation accounts for far infra-red absorptions in non-dipolar liquids very satisfactory. Furthermore, the similarity between absorptions in the far infra-red of molecules in the plastic crystalline (rotator) phases [32,33,111] and the liquid phase shows that either:

- (i) the far infra-red is totally insensitive to translational absorption; or
- (ii) the translational absorption in liquids of "typical" molecules such as t-butyl chloride or chlorobenzene is not a major contributor to the whole.

That (i) is not true was shown by Kiss et al. [112] who studied the collision-induced rotational spectrum of compressed gaseous hydrogen in the far infra-red. The absorption of a photon changes the relative kinetic energy of the colliding molecules without changing their state of internal motion. The existence of translational absorption was demonstrated conclusively by Kiss and Welsh [113], who found an absorption in mixtures of compressed rare gases in the region  $350-700 \text{ cm}^{-1}$ . Bosomworth and Gush [114] made observations down to  $20 \text{ cm}^{-1}$  on compressed He/Ar, Ne/Ar,  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{O}_2$ , and found that the far infra-red spectrum in each case consists of overlapping translational and rotational branches, except, of course, for the rare gases, where the latter is non-existent. The translational mode is easily distinguishable for  $\text{H}_2$ , but not at all so in other cases. However, Figs. 8(a) and 8(c) show that it is negligible in liquid  $\text{N}_2$  and  $\text{CH}_4$ . This is also true in liquid  $\text{CO}_2$  (Fig. 8(b)) and even in the gas [50] it is confined to  $<10 \text{ cm}^{-1}$  in a total absorption stretching up to ca.  $250 \text{ cm}^{-1}$ . The treatment of this absorption is theoretically complex even for  $\text{H}_2$ : Poll and van Kranendonk [115] have calculated the binary absorption coefficient of the translational band of hydrogen.

Bonamy and Galatry [116] have evolved a statistical theory of translational movement of atoms in a simple liquid. The latter paper contains a study of the time-evolution of the velocity correlation function

[4] of an atom (or a spherical top molecule) in a liquid, using the concept of cage potential as well as of fluctuation of the force acting on the atom. Their model, with the centre of the cage fixed, can only partially account for the average evolution of the velocity, which suggests that the position of the centre and the shape of the cage at a given time depends upon the previous behaviour of the whole system.

Their fundamental equation is:

$$\dot{\phi}(t) = - \int_0^t K_{\phi}(t-\tau)\phi(\tau)d\tau \quad (86)$$

where  $\phi(t) = \langle \underline{v}(0) \cdot \underline{v}(t) \rangle / \langle \underline{v}^2(0) \rangle$  is the velocity correlation function, and  $K_{\phi}$  the corresponding memory function, which is given the form:

$$K_{\phi}(t) = \omega_0^2 [1 + \epsilon^* A(t)] \quad (87)$$

where  $\omega_0$  is the natural frequency of "rattling" in potential wells defined by cages of neighbouring molecules, and  $A(t)$  is the correlation function of the force fluctuation upon a given atom by its surroundings. The dimensionless  $\epsilon^*$  is defined by:

$$\epsilon^* = \frac{\langle (\delta \underline{F})^2 \rangle}{\langle (\underline{F}_c - \tilde{\underline{F}}_c)^2 \rangle} = \frac{\langle (\delta \underline{F})^2 \rangle}{m^2 \omega_0^4 \tilde{x}^2} = \frac{\beta}{3m\omega_0^2} \langle \delta(\underline{F})^2 \rangle \quad (88)$$

where the random force  $\underline{F}$  is defined for atom (a) by  $m\dot{\underline{v}}(t) = \underline{F}(t)$ , so that  $\underline{F}$  describes the interaction of (a) with the (N-1) other atoms of the system. Therefore only a fluctuation  $\delta \underline{F}$  of this force is capable of dissipating the translational energy of (a) into the thermal bath, a fluctuation defined by:

$$\delta \underline{F}(\underline{x}, \underline{X}; t | \underline{x}^0, \underline{v}^0; 0) = \underline{F}(\underline{x}, \underline{X}) - \underline{F}_c(\underline{x}; t | \underline{x}^0, \underline{v}^0; 0).$$

This describes motions going from  $[\underline{x}^0, \underline{v}^0; 0]$  to  $[\underline{x}, \underline{v}; t]$  for (a), terminating in  $[\underline{X}, \underline{V}; t]$  for the thermal bath B.  $\underline{F}_c$  is thus the fluctuating force of the cage. Thus  $\epsilon^*$  is the ratio of the mean square of the fluctuations  $\delta F$  to the mean square  $\langle (\underline{F} - \tilde{\underline{F}}_c)^2 \rangle$  of the fluctuations of the cage force  $\underline{F}_c$  as displacements of (a) occur within its harmonic potential wells.

(i) If  $\langle \delta \underline{F}(0) \cdot \delta \underline{F}(t) \rangle$  is zero, then the atoms in the liquid would be fixed in energy minima (the crystal lattice), so that  $\phi(t) = \cos \omega_0 t$ , which is the equation of motion for an atom translating in a rigorously periodic fashion at the bottom of a harmonic energy well  $U_c(x) = \frac{1}{2} m \omega_0^2 x^2$ .

(ii) If the force fluctuations have a correlation time  $\tau_1$  which is very short compared with the period of oscillation within a cage, then:

$$\begin{aligned} \langle \delta \tilde{F}(0) \cdot \delta \tilde{F}(t) \rangle &= \langle \delta(F)^2 \rangle \tau_1 \delta(t) \\ &= C \delta(t) \end{aligned} \quad (89)$$

so that  $\tilde{\phi}(p)$ , the Laplace transform of  $\phi(t)$ , is given by

$$\tilde{\phi}(p) = p / (p^2 + \omega_0^2 + \frac{\beta C}{3m} p), \quad (90)$$

with  $\beta$  defined by eqn.(88). Now, if  $\omega_0 = 0$ , (no cage potential), eqn.(90) reduces to that describing the translational Brownian motion<sup>[4,7]</sup> of a particle in a liquid. In this limit, the interaction of the particle with the rest of the medium is random, and not correlated except for infinitely short times of interaction. Thus:

$$\phi(t) = \exp\left(-\frac{\beta C t}{3m}\right) \quad (91)$$

when  $\omega_0 \neq 0$ , then:

$$\begin{aligned} \phi(t) &= \left(\cos \omega t - \frac{b_1}{2\omega} \sin \omega t\right) \exp(-b_1 t/2) \\ &\quad \text{for } C < 6m\omega_0/\beta; \\ &= (1 - \omega_0 t) \exp(-\omega_0 t) \\ &\quad \text{for } C = 6m\omega_0/\beta; \\ &= \left(\cosh \omega' t - \frac{b_1}{2\omega'} \sinh \omega' t\right) \exp(1 - b_1 t/2) \\ &\quad \text{for } C > 6m\omega_0/\beta; \end{aligned} \quad (92)$$

where:

$$b_1 = \beta C / 3m; \quad \omega = \omega_0 \left(1 - \beta^2 C^2 / 36m^2 \omega_0^2\right)^{\frac{1}{2}}; \quad \omega' = \omega_0 \left(\beta^2 C^2 / 36m^2 \omega_0^2 - 1\right)^{\frac{1}{2}};$$

an expression obtained previously by Gluck<sup>[117]</sup>.

The authors compare their results (eqn.(92)) with those of Rahman<sup>[118]</sup> (computer experiment) for different values of  $C$ . The velocity autocorrelation function of eqn.(92) becomes negative at times  $t$  which became shorter as  $C$  increases. This corresponds to a reversal of the velocity vector of an atom at the instant of interaction. Because  $C$  is proportional to  $\langle \delta F^2 \rangle$ , which increases with thermal energy (i.e. with temperature), and thus with the frequency of collisions, it is natural to expect that the reversal takes place at shorter mean times as  $C$  increases. The abscissa ( $t$ ) of the minimum in  $\phi(t)$  first decreases, then increases as  $C$  increases. This is so because for the less energetic collisions (which are the most frequent when  $C$  is small), it is the form of the cage potential  $U_c(x)$  which determines the abscissa. When  $C$  is large, the cage potential no longer plays a preponderant part and  $v$  after the first collision increases with  $C$ .



Equation (92) implies that

$$\dot{\phi}(0) = -\epsilon^* \omega_0 / 3$$

so that a correlation is predicted between the acceleration and velocity of a molecule at a given time. This is due to the approximation of  $A(t)$  in eqn. (87) by the Dirac delta function,  $\delta(t)$ , which makes the fluctuating force instantaneously infinite, and thereby produces a discontinuity in the corresponding velocity. The same is true [8,29,33] of the auto-correlation function of an oscillator undergoing random and instantaneous collisions with other molecules. Equations (43) and (92) are the rotational [33,119] and translational counterparts in M-diffusion.

The translational counterpart of eqn (48) is produced if:

$$A(t) = \exp(-\omega_1 t) \quad (93)$$

with  $\omega_1 = 1/\tau_1$ . Here, the fluctuations in  $A(t)$  constitute a Markovian-Gaussian process characterised by a finite correlation time,  $\tau_1$ , so that:

$$\phi(p) = \frac{p^2 + p\omega_1}{(p^2 + \omega_0^2)(p + \omega_1) + \epsilon^* \omega_0^2 p} \quad (94)$$

corresponding to an exponential memory.

The derivative  $\dot{\phi}(t)$  at  $t = 0$  is now rigorously zero, which is a consequence of the fact that  $\delta F(t)$  is now always finite, and the time evolution of the velocity of a particle is not interrupted by discontinuities.

The above three models correspond to the three first approximations of Levi [20] developed in the context of a generalised theory of Brownian motion. Systematic use is made of the property of a random variable which allows it to be represented as the projection of a Markov process, defined in a vector space [E] containing this variable. If one considers [E] as being represented successively by the ensembles: [velocity], [velocity + acceleration], [velocity + acceleration + the derivative of acceleration] (the latter being implied in eqn. (49)), more satisfactory approximations of the statistical behaviour of the velocity itself are regained. These three spaces [E] correspond to the models described above for the velocity autocorrelation function. Similarly, there are three spaces [R] of the angular velocity and its derivatives which correspond to the Debye, M-diffusion, and Quentrec-Bezot models of rotational Brownian motion as described earlier in terms of successive Mori approximations.

The curves of eqns (90) and (94) transform into correlation functions

which resemble that of Rahman [118] only for  $\omega_0 t \lesssim 1$ . Bonamy and Galatry explain the discrepancies at longer times in terms of the failure of their model to keep track of atomic diffusion outside the cage boundary. Thus the eqns. (90) and (94) are valid to times less than those needed to traverse the cage. Outside this range, the calculated curves oscillate very slowly (with damping) compared with the computer simulation. This is because the models used imply that the velocity returns to its original value every time  $x = \omega_0 t$  changes by  $\pi$ . The damping, introduced via  $A(t)$ , is not enough to be realistic. This implies that the existence of a simultaneous transfer of energy and matter from one point in a liquid to another, situated at a distance greater than the cage diameter is desirable to explain Rahman's results properly [121]. (Cooperative, rotational molecular motion is suggested by the results of Perrot et al. [81] on compressed liquid  $\text{CO}_2$ ).

Berne and Harp [4] have evaluated a velocity correlation function  $\phi(t)$  for CO by computer simulation (with a non-central intermolecular potential) which they feel is significant below 0.4ps. They used the criteria of conservation of total energy and linear momentum as an indication that Hamilton's eqns. (1) were being integrated properly. The function  $\phi(t)$  becomes negative at  $t = 0.25\text{ps}$  and exhibits a long negative tail up to 1.0 ps and more, corresponding to transfer of energy outside the cage of immediate neighbours. The corresponding memory function decays quickly (in a Gaussian fashion), and exhibits a long positive tail. Since  $\phi(t)$  depends on changes in both direction and magnitude of the linear momentum, it is important to determine which contributes the more to the overall time dependence of  $\phi(t)$ . For CO it is the former, the correlation function of linear speed changes only by 13 % over the whole time axis, a result which can be construed as an argument for a constant linear (and, for that matter, angular) speed approximation in calculating linear (and angular) momentum correlation functions (M-diffusion in the limit of hard collisions). Several approximations to the velocity memory function are considered, and the results plotted [82] as normalised power spectra of  $\phi(t)$ .

Some factors governing the translational (rattling) mode, showing up in the far infra-red, of the guest molecule in a  $\beta$ -quinol clathrate have been investigated by Davies [122], who provided data for  $\text{N}_2$ ,  $\text{CO}_2$ , CO,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{SO}_2$  and  $\text{HCN}$  in the frequency range  $10 - 100 \text{ cm}^{-1}$  and from 4-300 K. It was found that the guest molecule "rattles" in a U---shaped

potential well the sides of which are vertical only for infinitely hard rigid atoms, which the author simulated with a Poschl Teller equation [123]. Davies's data did not provide a uniform picture of the guest molecule behaviour in quinol clathrates which is not surprising as the degree of freedom available to the guest is widely ranging variable as reflected in the range of the total linear freedom ( $d_0$ ). In many of the cases studied (HCl, SO<sub>2</sub>, HCN) there were signs of a Debye-type absorption in the GHz region [124], which is interesting since both relaxational and quantised rotational modes would not be expected for linear dipolar molecules where total dipole is involved in the quantised rotational transitions. The possible occurrence of both rotational processes in HCl and HCN quinol clathrates needs further assessment

## Appendix 1 - A Short List of Statistical Definitions [125]

## The Binomial Theorem

If an event has probability  $p$  of appearing at any one trial, the probability of  $r$  appearances in  $n$  independent trials is:

$$\frac{n!}{(n-r)! r!} q^{n-r} p^r, \text{ where } q = 1 - p.$$

This is the term involving  $p^r$  in the binomial expansion of  $(q + p)^n$ , which, since it arrays the various probabilities for  $r = 0, 1, \dots, n$ , is known as the binomial distribution.

A limiting form of the binomial distribution is the continuous frequency distribution of infinite range represented by:

$$dF = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{x-m}{\sigma}\right)^2\right) dx,$$

$-\infty < x < \infty$ , where  $m$  is the mean and  $\sigma$  the standard deviation. This is the Gaussian distribution.

## The Variate

This is a quantity which may take any of the values of a specified set with a specified relative frequency, or probability. The variate is often called a random variable. It is regarded as defined not only by a set of permissible values like an ordinary mathematical variable, but by an associated frequency (probability) function expressing how often these values appear in the situation under discussion.

## Stochastic Process

A stochastic variation is one in which at least one of the elements in a variate, and a stochastic process is one wherein the system incorporates

an element of randomness as opposed to a determinate system. [στοχος - a target].

### Correlation

In general, the interdependence between quantitative or qualitative data. In a narrower sense, the relationship between measurable variates.

### Autocorrelation function

The internal correlation between a number of series of observations ( $\mu$ ) in time or space. The autocorrelation of a stationary, stochastic process is defined by:

$$p(\tau) = \frac{1}{(b-t-a)} \int_a^{b-t} \mu(t)\mu(t+\tau)dt \Big/ \frac{1}{(a-b)} \int_a^b \mu^2(t)dt$$

for a series with zero mean and range  $a < t < b$ , defined at each point in time. The numerator above is called the autocovariance of the process, and the denominator its variance. The limits  $a$  and  $b$  may be infinite, subject to the existence of the integrals or sums involved.

### The Spectral Function

A necessary and sufficient condition for  $p(\tau)$ ,  $\tau = 0, 1, 2, \dots$  to be an autocorrelation function of a discrete stationary, stochastic process is that it is expressible in the form:

$$p(\tau) = \int_0^{\infty} \cos \omega \tau dF(\omega)$$

with  $F(0) = 0$ ,  $F(\infty) = 1$ ,  $F(\omega)$  is a spectral function which is therefore a probability distribution function.

### Markov's Hypothesis

Only the last state occupied by a process is relevant in determining its future behaviour.

If the probability that each state will be occupied after the  $(n+1)$ th transition, given the entire trajectory of history of state occupancies

through time  $n$  is:

$$P[s(n+1) = j \mid s(n) = i, s(n-1) = k, \dots, s(0) = m]$$

where  $s(n)$  is the state at time  $n$ , then the Markov assumption reduces this to:

$$P[s(n+1) = j \mid s(n) = i]$$

i.e. the probability of making a transition to each state of the process depends only on its present state. If a process is not Markovian, the history of the system before the last state occupied does influence future behaviour.

## Appendix 2

### The Central Limit Theorem

In its simplest form, the theorem states that if  $n$  independent variates have finite variances then their sum will, when expressed in standard measure, tend to be normally distributed as  $n \rightarrow \infty$ . It is a necessary and sufficient condition for the validity of the theorem that the variances obey a condition which may be roughly expressed by saying that no single one is so large as to be comparable with their total.

A normal distribution is a binomial, or Gaussian distribution in the limit of  $n \rightarrow \infty$ . If  $x$  is a variate with mean  $\mu$  and standard deviation  $\sigma$ , the transformed variate  $y = (x - \mu)/\sigma$  is said to be in standard measure (with zero mean and unit standard deviation).

### Stationary Processes

The necessary and sufficient conditions for a random, Gaussian process  $x(t)$  to be stationary are:

$${}^1f_x(t_1) = {}^1f_x(t_2) = \text{constant} = {}^1f_x$$

$${}^2f_x(x_1, t_1; x_2, t_2) = {}^2f_x(\tau)$$

with  $\tau = t_2 - t_1$ .

Here,  ${}^n f_x$  is the joint distribution function of order  $n$  of the

variate  $x$ . So that:

$$\begin{aligned}\langle X(t') \rangle &= \int X(p, q) f_x(p, q, t) dp dq \\ &= \langle X(t + t') \rangle \\ &= \langle X \rangle.\end{aligned}$$

Defining the autocovariance of  $X$  by:

$$C_{xx}(t) = \langle [X(t) - \langle X(t') \rangle][X(t + t') - \langle X(t + t') \rangle] \rangle,$$

then

$$\begin{aligned}C_{xx}(t'; t') &= C_{xx}(t + t'; t + t') \\ &= \sigma_x^2,\end{aligned}$$

where  $\sigma$  is the standard deviation, and

$$C_{xx}(t'; t + t') = C_{xx}(t)$$

i.e. the point in time at which one starts the exercise of correlating  $X$  at  $t = t$  and  $X$  at  $t = t'$  is of no consequence.

#### Ergodicity and Khinchin's Theorem

A stochastic, stationary process  $X(t)$  is ergodic if:

$$y(t) = \frac{1}{t} \int_0^t X(t') dt' \rightarrow \langle a \rangle \text{ as } t \rightarrow \infty.$$

Using probability theory, this can be stated as:

$$\lim_{t \rightarrow \infty} \langle \left| \frac{1}{t} \int_0^t [X(t') - \langle X \rangle] dt' \right|^2 \rangle$$

is  $\langle \epsilon \rangle$  for  $\epsilon \rightarrow 0$  where  $\epsilon$  is arbitrarily small. Therefore:

$$\lim_{t \rightarrow \infty} \left| \frac{1}{t^2} \int_0^t (t - \tau) C_{xx}(\tau) d\tau \right|$$

is  $\langle \epsilon \rangle$  for  $\epsilon > 0$ ,  $\epsilon \rightarrow 0$ . This is a form of Khinchin's theorem, which states

that a sufficient condition for a system of  $n$  stationary, stochastic processes to be ergodic is that all correlation functions  $C_{PQ}(t) \rightarrow 0$  as  $t \rightarrow \infty$ .

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