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Correlation and Memory Function Analysis of Molecular Motion in Fluids

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1 Introduction

The foundations and framework of this review have been established in two previous articles of this series, the first by Wyllie,[1] who discussed the broad theoretical concepts necessary for the interpretation of far i.r. and lower frequency spectroscopic data; and the other by Brot,[2] whose main contribution lay in annotating and evaluating the recent attempts at solving the problem of the dynamic internal field.[3] In both these articles several models of fluid dynamics were discussed on the molecular scale, and related to bulk properties such as the dielectric loss and dispersion with classical fluctuation–dissipation theory.[4] This third report on advances within six years aims to be selective and complementary rather than comprehensive. The natural complement is found in fields of work covering the dynamical processes in fluids that give rise to absorption in the far i.r. region[5] of the electromagnetic spectrum and which represent different kinds of experimentally observable phenomena.

The past twenty years have seen the emergence of Kubo's generalizations[6] of classical fluctuation–dissipation theory, enabling a coherent analysis of superficially different bulk transport properties to be made in terms of the motions of vectors defined in the molecular frame. Zwanzig,[7] Gordon,[8] and Berne[9] have made significant advances in isolating some fundamental statistical theorems pertaining to the fluid state, as well as in emphasizing the role of the most

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[1] G. Wyllie, in this series, 1972, Vol. 1, p. 21.

[2] C. Brot, in this series, 1975, Vol. p. 1.

[3] (*a*) J. L. Rivail, *J. Chim. Phys.*, 1969, **66**, 981; (*b*) D. D. Klug, D. E. Kranbuehl, and W. E. Vaughan, *J. Chem. Phys.*, 1969, **50**, 3904; (*c*) T. W. Nee and R. Zwanzig, *ibid.*, 1970, **52**, 6353; (*d*) M. Titulaer and J. M. Deutch, *ibid*, 1974, **60**, 1502; (*e*) J. L. Greffe, J. Goulon, J. Brondeau, and J. L. Rivail, in 'Molecular Motions in Liquids', ed. J. Lascombe, Reidel, Dordrecht, 1973, p. 151.

[4] For a list of references to six or more different derivations of the fluctuation–dissipation theorem see J. S. Rowlinson and M. Evans, *Ann. Reports (A)*, 1975, **72**, 5.

[5] K. D. Müller and W. G. Rothschild, 'Far Infra-red Spectroscopy', Wiley-Interscience, New York, 1971. This contains a bibliography by Palik of 1512 papers on the far infra-red up to 1970.

[6] (*a*) R. Kubo, 'Lectures in Theoretical Physics', Interscience, New York, 1959; (*b*) 'Statistical Mechanics of Equilibrium and non-Equilibrium, North-Holland, Amsterdam, 1965.

[7] R. Zwanzig, 'Annual Review of Physical Chemistry', ed. H. Eyring, Annual Reviews Inc., Palo Alto, 1965, Vol. 16, p. 67.

[8] R. G. Gordon, *Adv. Mag. Resonance*, 1968, **3**, 1.

[9] B. J. Berne, 'Physical Chemistry – an advanced treatise', ed. H. Eyring, D. Henderson, and W. Jost, Academic Press, New York, 1971, Vol. 8B, Chapt. 9 p. 539; (*b*) B. J. Berne and G. D. Harp, *Adv. Chem. Phys.*, 1970, **17**, 63.

important concept of the correlation function. This is formally the ratio of the covariance of stationary (time independent) random process to its variance.[10,11] Here 'correlation' takes on the narrow statistical sense of being the relationship between two or more measurable random events occurring in a temporal sequence. The frequencies of such events brings us into the domain of spectroscopy, since a spectral function, being a distribution of probabilities of events occurring with given frequencies, is itself statistical in nature. Fourier[12] provided the link between temporal and frequency domains in his integral theorem, so that the correlation and spectral functions, $C(t)$ and $\tilde{C}(\mathrm{i}\omega)$ respectively, are Fourier transform pairs.

Molecular fluctuations in phase space may be correlated statistically and related to many different kinds[9] of absorptions and dispersions, the former being the real and the latter the imaginary parts of the Fourier transform of $C(t)$. The correlated random variable is conveniently a vector, or tensor trace, whose magnitude and direction may be evolving in time. To discuss the absorption of energy by molecules from an electromagnetic field (a stream of photons), it is sufficient[8] to define such a vector u in the molecular frame (x, y, z). The direction may be that of the permanent dipole (μ) if this exists, so that u may be normalized to unity ($u = \mu/|\mu|$). It is generally true that any molecule (i), whether dipolar or not, in a fluid of finite density, made up of a finite ensemble of N molecules, will experience the resultant electrostatic field of the $(N-1)$ others at the instant t. This means that (i) will carry a small interaction-induced, temporary dipole $[{}^{(i)}M]$. To correlate its value at an initial instant $t = 0$ with that at time t later it is sufficient to take the projection ${}^{(i)}\boldsymbol{M}(0)\cdot{}^{(i)}M(t)$. This can be repeated for all the $(N-1)$ other molecules [by making the cross-correlations $\Sigma^{(i)}_{j\neq i}M(0)\cdot{}^{(j)}M(t)$] so that the spectrum of induced dipolar fluctuations is the Fourier transform of all such projections averaged over phase space. The spectrum from the permanent dipole is similarly a Fourier transform of auto- and cross-correlation functions of u, which unlike $\boldsymbol{M}$, does not fluctuate in magnitude. The total spectrum is a sum of these two parts, with a contribution from correlations between u and M.

The far i.r./microwave spectrum of a fluid is composed mainly of such orientational contributions, but collision-induced dipole moments are dependent also on the centre-of-mass co-ordinates of a molecule in the external (laboratory) frame, that is, on the relative positions of the interacting molecules. Consequently, part of the energy of the photon which is absorbed may be converted into molecular translational energy after collision, and it is possible to observe pure translational absorption in such cases as binary mixtures of rare gas atoms.[13] The separated translational and rotational components can be observed[13] in the spectrum of compressed or liquid hydrogen, but for heavier

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[10] A. Papoulis, 'Probability, Random Variables and Stochastic Processes', McGraw Hill, New York, 1965.

[11] J. Goulon, 'Theories Stochastiques des Phenomenes de Transport, Cas des Mouvements de Reorientation Moleculaires', Thèse D'Etat (deuxième), Univ. of Nancy, 1972.

[12] M. J. Lighthill, 'Introduction to Fourier Analysis and Generalised Functions', Cambridge Univ. Press, 1958.

[13] (*a*) D. R. Bosomworth and H. P. Gush, *Canad. J. Phys.*, 1965, **43**, 751; (*b*) J. D. Poll and J. van Kranendonk, *ibid.*, 1961, 39, 189.

molecules such as oxygen and nitrogen the translational component is not separable, and the broad bands observed[13] are roto-translational in origin. In fluids such as CH_4 and CD_4 the induced far i.r. bands peak at frequencies which indicate[14] $I^{1/2}$ (rotational) rather than $M^{1/2}$ (translational) dependence. In what follows, we treat the far i.r. absorptions of molecular fluids exclusively in terms of orientational correlation functions since the translational intensity is so much weaker.

The scattering of electromagnetic[15] or neutron[16] radiation can be related to correlations of the vectors $\boldsymbol{u}$ and $\boldsymbol{r}$, respectively, the latter being the position of the i'th nucleus in the fluid. In principle, the inelastic scattering of neutrons, being much heavier than photons, can be analysed for change of angle and speed. An incoming wave of length λ is characterized by a vector $\boldsymbol{k}_0$ which specifies its direction. The wave scattered with a vector $\boldsymbol{k}_1$ has an intensity proportional to $S(\boldsymbol{k}, \omega)$, where $\boldsymbol{k} = \boldsymbol{k}_0 - \boldsymbol{k}_1$ and ω is the change in angular frequency. The structure factor $S(\boldsymbol{k}, \omega)$ is the three-dimensional Fourier transform of the van Hove correlation function.[17] The scattering can be either incoherent (from one centre) or coherent (from a pair of centres) according to the nature of the atomic nuclei in the molecule. The former arises from the 'self' part of the correlation function and the latter from the distinct. Thermal neutrons have a wavelength of about 10 nm, and so k is comparable with the intermolecular spacing, and the coherently scattered beam yields the distinct part of the van Hove correlation function upon Fourier transformation.[18]

Visible light (nowadays from a laser[15]) is scattered coherently with negligible change of momentum, and the spectrum is thus nearly $S(\boldsymbol{0}, \omega)$. The change of frequency is small, but observable if the incident light is from a laser and so highly monochromatic. Measurement of the intensity and angle, but not the spectrum of the scattered light tells us only about the static properties: in particular, $S(\boldsymbol{k} = \boldsymbol{0})$ is related to the compressibility, and so such scattering is intense near the critical point in a fluid, where this tends to infinity.[19] The spectrum of scattered light is a more useful observable and it has three distinct peaks,[20] a Rayleigh line centred at $\omega = 0$ (the zero frequency displacement) and two Brillouin lines at $\omega = \pm W\bar{\nu}_\omega$, where W is the speed of sound and $\bar{\nu}_\omega$ the wavenumber of the particular phonon mode responsible for the scattering. The Rayleigh line arises from density (or more immediately refractive index) fluctuations corresponding to local entropy fluctuations at constant pressure. Such fluctuations do not propagate through the fluid and so the Rayleigh

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[14] R. Savoie and R. P. Fournier, *Chem. Phys. Letters*, 1970, 7, 1.

[15] P. N. Pusey and J. M. Vaughan, in this series, 1975, Vol. 2, p. 64.

[16] W. Marshall and S. W. Lovesay, 'Theory of Thermal Neutron Scattering', Clarendon Press, Oxford, 1971.

[17] L. van Hove, *Phys. Rev.*, 1954, 95, 249.

[18] J. G. Powles, 'Chemical Applications of Thermal Neutron Scattering', ed. B. T. M. Wills, Clarendon Press, Oxford, 1973.

[19] (*a*) H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, 'Physics of Simple Liquids', North Holland Amsterdam, 1968; (*b*) C. A. Croxton, 'Liquid State Physics', Cambridge Univ. Press, 1974; (*c*) A. F. M. Barton, 'The Dynamic Liquid Statė', Longmans, London, 1974.

[20] (*a*) D. McIntyre and J. V. Seagers, in ref. 19*a*; (*b*) H. L. Strauss, in 'Chemical Applications of Lasers', ed. C. B. Moore, Academic Press, New York, 1974.

feature is centred on $\omega = 0$. It contains a depolarized component of significant breadth centred on the incident frequency and known as the Rayleigh wings.[21-25] In molecular fluids such as benzene the spectrum is thus composed of a relatively narrow diffuse superimposed on a much broader background. High-resolution, high-power measurements[25] have disclosed some additional features, notably a very narrow central doublet: in its general contour and dependence on the scattering angle and polarizations, the diffuse band and central doublet fit the theory of Rytov,[26] which phenomenologically associates the diffuse band with scattering by transverse shear waves. However, the absolute integrated intensities, which can be obtained by comparison with intensities of the polarized Rayleigh and Brillouin spectrum (see below), are very close[27] to those predicted from theoretical expressions[8] obtained for the reorientations of single vectors (such as u). Furthermore, the inverse half-width of the diffuse band (the rotational relaxation time), fits reasonably well in magnitude, temperature dependence, and activation energy into the broad scheme of fluctuation–dissipation theory mentioned above,[1,2,6-9] in which other phenomena such as far i.r. and microwave absorption/dispersion, nuclear spin–rotation relaxation, Raman scattering, and near i.r. vibration–rotation absorptions are described by temporal correlations of selected vectors. The close relation between induced and permanent far i.r. absorptions and the Rayleigh bands are described below in some detail, and the conclusions obtained on the same fluid by different authors using some of the different experimental techniques described above, are checked for consistency.

The Brillouin lines arise from fluctuations of density due to fluctuations of pressure at constant entropy. These form the acoustic mode spectrum of the condensed phase and they are present in all liquids at equilibrium, and they diffract light at the appropriate Bragg angle. The frequency shift is a Doppler effect of the moving 'grating', and, since the sound wave of appropriate length and orientation can be moving in either direction, a pair of lines is produced, one on each side of the incident frequency. Polarized Brillouin bands can be described in terms of a molecular correlation function related to the trace of the polarizability tensor. Depolarized bands are Fourier transforms of correlation functions related to its xy'th (off-diagonal) elements.[9] The total intensity of the Rayleigh and Brillouin lines yields the compressibility, the ratio of intensities yields the ratio of specific heats at constant pressure and constant volume, the width of the Rayleigh line yields the thermal diffusivity, and the displacement and width of the Brillouin lines yield the speed and coefficient of absorption of sound at frequencies above 10 GHz, *i.e.* above the range of mechanically generated sound waves.

Correlations of the vector u are involved also in the determination of n.m.r.

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[21] H. Z. Cummings and R. W. Gammon, *J. Chem. Phys.*, 1966, **44**, 2785.
[22] A. Szöke, E. Courtens, and A. Ben Reuven, *Chem. Phys. Letters*, 1967, **1**, 87.
[23] D. A. Pinnow, S. J. Candau, and T. A. Litovitz, *J. Chem. Phys.*, 1968, **39**, 347.
[24] H. C. Craddock, D. A. Jackson, and J. G. Powles, *Mol. Phys.*, 1968, **14**, 373.
[25] G. I. A. Stegemann and B. P. Stoicheff, *Phys. Rev. Letters*, 1968, **21**, 202.
[26] S. M. Rytov, *Soviet Phys. J. E. T. P.*, 1958, **6**, 401, 513.
[27] A. Ben Reuven and N. D. Gershon, *J. Chem. Phys.*, 1969, **51**, 893.

lines broadened by spin–spin coupling and relaxation[28] and the only currently known experimental source of information about fluctuation of J, the total molecular angular momentum vector, is spin–rotation relaxation.[29] In a linear molecule, u and J are related by: $J = I\omega$, $\dot{u} = u \times \omega$, where ω is the total angular velocity vector, perpendicular to u.

2 General Formalism in Classical Mechanics: Memory Functions

The major problem in building up an analytical description of the dense fluid is that of describing the complex many-body interactions in a realistic fashion. To do this the intermolecular potential must be defined. On the one hand, recent articles[30] have exposed the shortcomings of the classical Lennard-Jones potential even for rare-gas atomic interactions, but on the other several recent numerical solutions[4,31] of the Newton equations for groups of up to 864 basically Lennard-Jones potentials have had a marked degree of success in reproducing macroscopic equilibrium properties[32] and also their corresponding spectra.[33–35]

This section describes the recent attempts[36] at bypassing the intermolecular potential problem by using the very general statistical properties of a canonical ensemble of particles to derive a series of integro-differential equations[37] linking the correlation function of u or other vectors to that of its n'th derivatives ($u^{(n)}$) or memory function. It is hoped that the latter might have a simpler analytical dependence upon time, and so might be simulated empirically with a reasonable

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[28] N. Boden, in 'Nuclear Magnetic Resonance', ed. R. K. Harris, (Specialist Periodical Reports), The Chemical Society, London, 1972, Vol. 1, p. 115.

[29] See ref. 28 and papers in 'Molecular Motions in Liquids', ed. J. Lascombe, Reidel, Dordrecht, 1974.

[30] (*a*) G. C. Maitland and E. B. Smith, *Chem. Soc. Rev.*, 1973, **2**, 181; (*b*) T. B. MacRury, W. A. Steele, and B. J. Berne, *J. Chem. Phys.*, 1976, **64**, 1288.

[31] (*a*) B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 1959, **31**, 459; (*b*) B. J. Alder, W. G. Hoover, and W. W. Wood, ref. 19*a*; (*c*) J. Barojas, D. Levesque, and B. Quentrec, *Phys. Rev.*, 1973, **7A**, 1092; (*d*) P. S. Y. Cheung, and J. G. Powles, *Mol. Phys.*, 1975, **30**, 921; (*e*) B. J. Berne and D. Forster, *Ann. Rev. Phys. Chem.*, 1971, **22**, 563.

[32] (*a*) A. Rahman, *Phys. Rev.*, 1964, **136**, A405; (*b*) J. Naghizadeh and S. A. Rice, *J. Chem. Phys.*, 1962, **36**, 2710.

[33] (*a*) D. Levesque and L. Verlet, *Phys. Rev.*, 1970, **2A**, 2514; (*b*) B. J. Alder and T. E. Wainwright, *ibid.*, 1970, **1A**, 18; (*c*) T. E. Wainwright, B. J. Alder, and D. M. Gass, *ibid.*, 1971, **4A**, 233; (*d*) R. Zwanzig, in 'Statistical Mechanics – New Concepts, New Problems, New Applications', ed. S. A. Rice, K. F. Freed, and J. C. Light, Univ. of Chicago Press, Chicago, 1972, p. 241; (*e*) Papers by B. J. Alder and J. M. Deutch, in 'Transport Phenomena – 1973', ed. J. Kestin, American Inst. Phys., 1973.

[34] R. T. Bailey, in 'Molecular Spectroscopy', ed D. A. Long, D. J. Millen, and R. F. Barrow (Specialist Periodical Reports), The Chemical Society, London, 1974, Vol. 2, p. 200. This review also covers the far infrared and related fields comprehensively up to 1973/1974.

[35] (*a*) D. Tildesley and W. B. Street, *Proc. Roy. Soc.*, 1976, **348**, 485; (*b*) J. Kushick and B. J. Berne, *J. Chem. Phys.*, 1973, **59**, 3732; (*c*) C. Brot and I. Darmon, *ibid.*, 1970, **53**, 2271.

[36] (*a*) T. Keyes and D. Kivelson, *J. Chem. Phys.*, 1972, **56**, 1057; **57**, 4599; (*b*) B. Quentrec and P. Bezot, *Mol. Phys.*, 1974, **27**, 839; (*c*) P. Madden and D. Kivelson, *ibid.*, 1975, **30**, 1749.

[37] (*a*) H. Mori, *Prog. Theor. Phys.*, 1965, **33**, 423; (*b*) P. Schofield, in 'Statistical Mechanics', ed K. Singer, (Specialist Periodical Reports), The Chemical Society, London, 1975, Vol. 2.

degree of success. A straightforward derivation of these equations was given in classical mechanics by Berne, Boon, and Rice,[38] and the same theorem was later proven by Berne[9] in quantum notation. The classical derivation is briefly recalled here in order to emphasize how generally applicable is this formalism. Subsequently, several currently popular models of the fluid state can take their place in this scheme (Table 1), which is essentially an expression in Laplace space as a quotient of polynomials whose coefficients are equilibrium averages having the units of s^{-2}, s^{-4}, and so on, for example zero-time averages of derivatives of u. This is consistent with the fact that any classical auto-correlation function has a series expansion (1), where the brackets $\langle\,\rangle$ denote the canonical average (2) in N particle phase-space Γ_N. Here $H^{(N)}$ and Z_N are the hamiltonian and the canonical partition function. Therefore, in general, $u(\Gamma_N)$ may be any vector property of phase space. (In quantum mechanics, correlation functions have a real, even part and an odd, imaginary part, so that a quantum correction is made by replacing t with $[t - \mathrm{i}h/2kT]$.)

$$C(t) = \langle u(0) \cdot u(t) \rangle = 1 - \langle \dot{u}(0)^2 \rangle \frac{t^2}{2!} + \langle \ddot{u}(0)^2 \rangle \frac{t^2}{4!} - \cdot \cdot \cdot \tag{1}$$

$$\langle u \rangle = Z_N^{-1} \int u \exp(-H^{(N)}/kT)\, \mathrm{d}\Gamma_N \tag{2}$$

$$C(t) = Z_N^{-1} \int u(\Gamma_N) \exp(\mathrm{i}t\mathscr{L}^{(N)}) u(\Gamma_N) \exp(-H^{(N)}/kT)\, \mathrm{d}\Gamma_N \tag{3}$$

The classical auto-correlation function, $C(t)$, may be written[38] as equation (3), where $\mathscr{L}^{(N)}$ is the Liouville operator. It is assumed that $\langle u \rangle = 0$ and $\langle u \cdot u \rangle = 1$. Differentiation of equation (3) twice, followed by partwise integration, leads directly to equation (4), the Laplace transform of which, together with an algebraic identity for $\tilde{C}(p)$, yields the fundamental relation (5), where the kernel K is the memory function, defined in Laplace space by equation (6).

$$\ddot{C}(t) = -\langle \dot{u}(0) \cdot \dot{u}(t) \rangle = \phi(t) \tag{4}$$

$$\dot{C}(t) = -\int_0^t K(t-\tau) C(\tau)\, \mathrm{d}\tau \tag{5}$$

$$\tilde{K}(p) = \tilde{\phi}(p)/(1 - \tilde{\phi}(p)/p) \tag{6}$$

It is important to note that equation (5) embodies no assumptions other than those of equation (3), that is that the N particle ensemble is canonical, and obeys the Liouville equation of motion. Equation (5) is true for any vector whose expectation vanishes and whose auto-correlation function is even under time reversal. In ref. 38 it is shown how it can be rederived using linear regression theory[6] and by means of the properties of transport coefficients. It is a fundamental theorem of molecular statistical mechanics.

[38] B. J. Berne, J. P. Boon, and S. A. Rice, *J. Chem. Phys.*, 1966, **45**, 1086.

Defining a projection operator[7,9] $\hat{P}$ onto a well-behaved function, $G(\Gamma_N)$, of the phase space as in (7), where $f_{\mathrm{eq}}^{(N)} = Z_N^{-1}\exp(-H^{(N)}/kT)$, equation (8) can be written, showing that the kernel K is related to the dynamical coherence (or memory) of the N particle ensemble. It is possible subsequently to define a set of kernels, or memory functions, $K_0(t), \ldots, K_n(t), \ldots$ giving[37] equation (9), where the dynamical quantities f_n are defined so that $f_0 = u$ and $f_n = (1-\hat{P}_{n-1})\mathrm{i}\,\mathscr{L}_{n-1}u_{n-1}$. This leads directly to the sequence (10) first derived by Mori. In Laplace space, this is a continued fraction; linking $\tilde{C}(p)$ to $\tilde{K}_n(p)$ as in equation (11).

$$\hat{P}G(\Gamma_N) = u(\Gamma_N)\, f_{\mathrm{eq}}^{(N)} \int \Gamma'_N u(\Gamma'_N) G(\Gamma'_N)\, \mathrm{d}\Gamma'_N \tag{7}$$

$$K(t) = \langle \dot{u} \exp[\mathrm{i}t(1-\hat{P})\mathscr{L}^{(N)}]\, \dot{u} \rangle \tag{8}$$

$$K_n(t) = \langle f_n \exp[\mathrm{i}\,\mathscr{L}_n(t)] f_n \rangle \tag{9}$$

$$\frac{\partial}{\partial t} K_{n-1}(t) = -\int_0^t K_n(t-\tau) K_{n-1}(\tau)\, \mathrm{d}\tau \tag{10}$$

$$\tilde{C}(p) = \frac{\tilde{C}(0)}{p + \tilde{K}_0(p)} = \frac{\tilde{C}(0)}{p + \dfrac{\tilde{K}_0(0)}{p + \tilde{K}_1(p)}} = \frac{\tilde{C}(0)}{p + \dfrac{\tilde{K}_0(0)}{\vdots \atop \dfrac{\tilde{K}_{n-1}(0)}{p + \tilde{K}_n(p)}}} = \ldots \tag{11}$$

If a property $F(t)$ is defined[9] as in equation (12), then we can write equation (13). This is widely known as the generalized Langevin equation, since it reduces to the classical equation[39,40] when K is a delta function, that is when the system for Brownian motion lacks dynamical coherence and has no memory for past events, so that $F(t)$ is a Gauss/Markov random variable.[11] It is important to note that equation (13) may be derived (as above) with the assumptions inherent in equation (3), but without any about the nature of Brownian motion as such. Equations (14) and (15) hold by definition; the latter is generally known[9] as the second fluctuation–dissipation theorem of Kubo.

$$F(t) = ([\exp \mathrm{i}(1-\hat{P})\mathscr{L}t]\,\mathrm{i}\mathscr{L})\, u \tag{12}$$

$$\frac{\partial u}{\partial t} = -\int_0^t K(t-\tau) u(\tau)\, \mathrm{d}\tau + F(t) \tag{13}$$

$$K(t) = \langle F(0) \cdot F(t) \rangle \tag{14}$$

$$\langle u(0) \cdot F(t) \rangle = 0 \tag{15}$$

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[39] P. Langevin, *J. Phys.*, 1905, **4**, 678.

[40] (*a*) R. A. Sack, *Proc. Phys. Soc.*, 1957, **70B**, 402; (*b*) J. T. Lewis, J. McConnell, and B. K. Scaife, *Proc. Roy. Irish Acad.*, 1976, **76A**, 43; (*c*) G. W. Ford, J. T. Lewis, and J. McConnell, *ibid.*, p. 117, 1976, **76A**, 117.

Table 1 *Some dynamical models in Mori's formalism.* $K_n(t)$ *is the n'th memory function of the dipole unit vector*

$K_n(t)$	$\tilde{K}_n(p)$	*Model and references*	*Description and comments*	$C(t)$
$K_0(t) = D\delta(t)$	$\tilde{K}_0(p) = D$	Debye 11, 41	Infinitesimal angular displacements in infinitely short time. Inertia neglected, used to describe dielectric absorption at low frequencies, but leads to a Debye plateau in the far i.r.	$\exp(-t/\tau_D)$ where τ_D is the Debye relaxation time.
$K_0(t) = K_0(0)e^{-\gamma_1 t}$	$\tilde{K}_0(p) = \dfrac{\tilde{K}_0(0)}{\gamma_1 + p}$	Gordon *M*-diffusion 1, 2, 7–9, 34, 40, 42	Instantaneous elastic collisions perturb the rotation at random times. Angular momentum vector (*J*) is randomized in direction but not magnitude; torque is infinite at impact since *J* changes instantly. A slow return to transparency in the far i.r. for polar liquids.	Taylor expansion $1 - at^2 + O(t^3)$ and so starts as an even function of t.
$K_0(t) = \mathrm{FR}\,K_0(t)e^{-\gamma_j\lvert t\rvert}$ where $K_0(t)$ is the memory function of a free rotor	see ref. 42	Gordon *J*-diffusion 1, 2, 7–9, 34, 42, 43	As for *M*-diffusion except that angular momentum is randomized in both magnitude and direction, onto a Boltzmann distribution. An inertia corrected Debye model. Far i.r. return to transparency slower than observed for polar liquids.	A complicated, but analytical, function whose Taylor series has a term in t^3.
$K_0(t) = K_0(0)e^{-\gamma t}\cos\omega_0 t$	$\tilde{K}_0(p) = \dfrac{\tilde{K}_0(0)(p+\gamma)}{(p+\gamma)^2 + \omega_0^2}$	Damped libration in one plane 41b, 44	The calculated loss factor ϵ'' has a high frequency asymptotic fall-off of ω^{-3}, compared with ω^{-1} for Debye behaviour. This asymptotic behaviour is also that of *M* and *J* diffusion. ω_0 is the libration frequency – an adjustable parameter.	$A_1e^{-\gamma_1 t} + A_2e^{-\gamma_2 t} + A_3e^{-\gamma_3 t}$ with $A_1, A_2, A_3, \gamma_1, \gamma_2, \gamma_3$ determined by cubic eqns. Oscillates at short times, has a term in t^3.
$K_0(t) = K_0(0)e^{-\gamma^2 t^2}$ where:	Not analytic, but can be expressed as a series	Harp and Berne 45	Here $\psi(t) = \langle \boldsymbol{\omega}_\perp(0)\cdot\boldsymbol{\omega}_\perp(t)\rangle$ where $\boldsymbol{\omega}_\perp$ is the angular velocity component perpendicular to u.	Not analytic, but there are no odd powers of time in

			libration frequency – an adjustable parameter.	short times, has a term in t^3.
$K_0(t) = K_0(0)e^{-\gamma^2 t^2}$ where: $\gamma = \left(\frac{\pi}{4}\right)^{1/2} K_0(0) \times \int_0^{\infty} \psi(t)\, dt$	Not analytic, but can be expressed as a series	Harp and Berne 45	Here $\psi(t) = \langle \boldsymbol{\omega}_\perp(0) \cdot \boldsymbol{\omega}_\perp(t) \rangle$ where $\boldsymbol{\omega}_\perp$ is the angular velocity component perpendicular to $\boldsymbol{u}$. This is the form of memory function obtained by maximizing the information entropy of an N particle system. Its far i.r. spectrum is too sharp compared with experimental data and is less realistic than the exponential memory for $\psi(t)$ thus far used.	Not analytic, but there are no odd powers of time in its $K_0(t)$, thus all the latter's moments are finite.
$K_0(t) = {}^{\mathrm{FR}}K_0(t)\psi(t)$ ${}^{\mathrm{FR}}K_0(t)$ describes the distribution of frequencies. $\psi(t)$ depends upon interactions. There is no coupling.	Not analytic in general.	Desplanques 44	In this model ${}^{\mathrm{FR}}K_0(t)$ is replaced by the short time approximations: (i) ${}^{\mathrm{FR}}K_0(t) = K_0(0) \exp[-K_0(0)t^2/2]$ for a linear molecule; (ii) ${}^{\mathrm{FR}}K_0(t) = K_0(0) \exp[-K_0(0)(1 + I_A/2I_B)t^2/2]$ for a symmetric top $\psi(t)$, defined as in the Harp/Berne model, is calculated by choosing the Gaussian form: $k(t) = \frac{\langle N_\perp^2 \rangle}{I^2 K_0(0)} \exp\left[-\left[\frac{\langle \dot{N}_\perp^2 \rangle}{\langle N_\perp^2 \rangle} - \frac{\langle N_\perp^2 \rangle}{I^2 K_0(0)}\right]\frac{t^2}{2}\right]$ for its memory function $k(t)$. Here $N_\perp$ is a torque component and $\dot{N}_\perp$ its derivative	This is even in its Taylor expansion. The corresponding spectrum is compared with some experimental data in Figure 1 for the far i.r./microwave region. However, in general, the theoretical spectrum is too sharp. i.e. there is an insufficient distribution of frequencies.
$K_1(t) = \beta^{\mathrm{FR}}K_1(t)e^{-\|t\|/\tau}$	$\beta^{\mathrm{FR}}\tilde{K}_1\left(p + \frac{1}{\tau}\right)$	Bliot and Constant 43b, c, 46	${}^{\mathrm{FR}}K_1(t)$ is the second memory of the free rotor. β and τ are purely stochastic parameters, the former being proportional to the mean square torque. This may be described as a more realistic *J*-diffusion model since there are no singularities in the torque. However, this model does not give a realistic picture of far i.r. absorptions, the theoretical curves being too sharp.	This is even up to t^4 in its Taylor expansion, but contains an a-physical t^5 coefficient.

Table 1 *continued*

$K_n(t)$	$\tilde{K}_n(p)$	*Model and references*	*Descriptions and comments*	$C(t)$
$K_1(t) = K_1(0)e^{-\gamma t}$	$\tilde{K}_1(p) = \dfrac{\tilde{K}_1(0)}{p+\gamma}$	31c, 36b,c, 47	Assumes that $K_1(t)$, the second memory of $C(t)$, is an exponential. Does not describe the free rotor $C(t)$ well except at short times. Describes the cross-correlation function of collision-induced far i.r. absorption and Rayleigh bands very well. Less successful for far i.r. dipolar absorptions in dense liquids.	Analytical and even up to t^4. Contains a term in t^5.
$K_1(t) = K_1(0)f(t)$ and $K_2(t) = K_2(0)e^{-\gamma t}$	Not analytic for the general $f(t)$	Evans *et al.* (to be published)	Here $f(t)$ is any differentiable function of time. It is found that Gaussian and Lorentzian second memories, when fitted to lower frequency data, give five unrealistically sharp absorptions in the far i.r. The exponential third memory is sometimes satisfactory.	Analytical and even up to t^6 for the exponential third memory. Otherwise even if $f(t)$ is even.

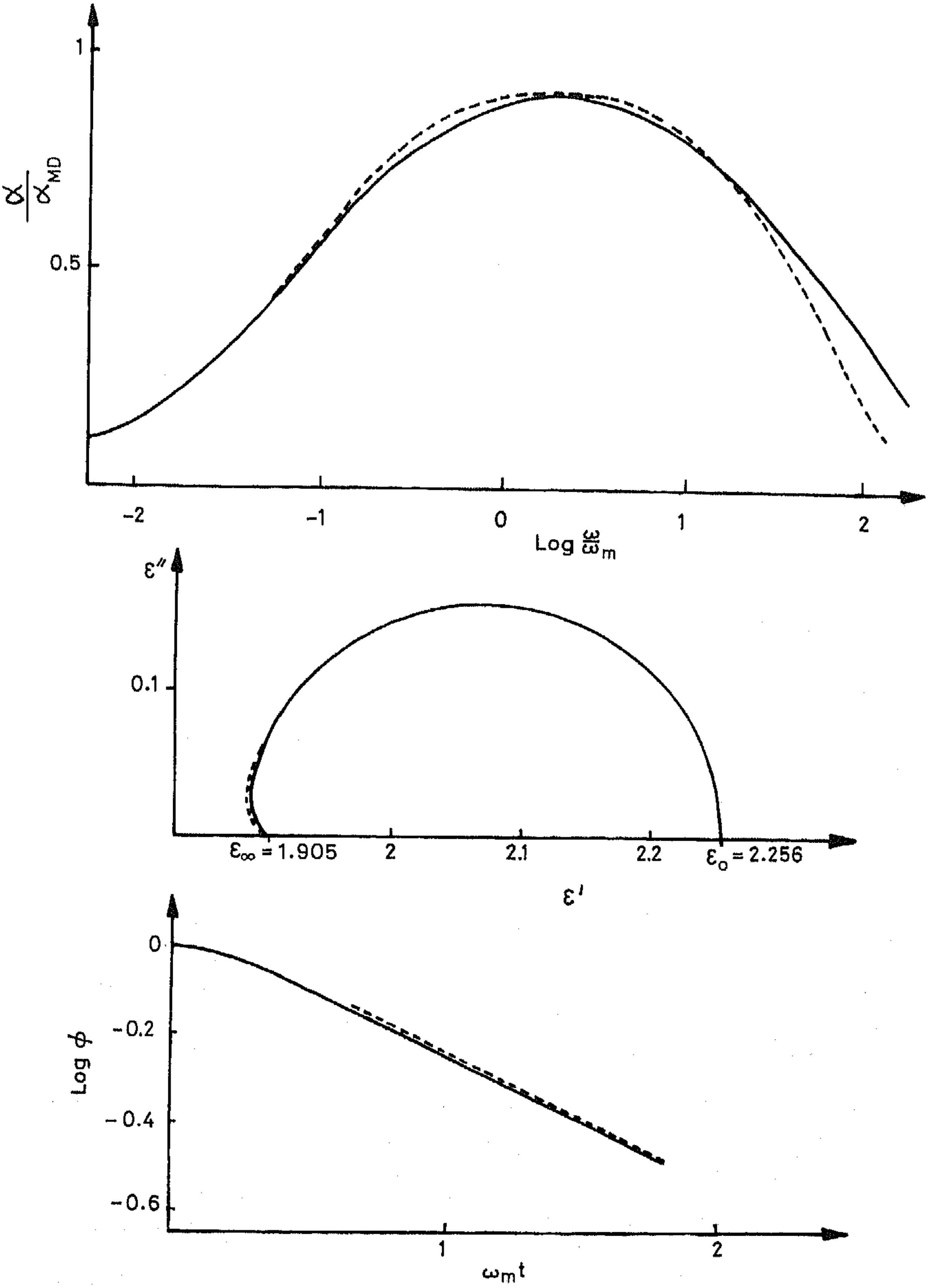

Figure 1 *Comparison between experimental (solid line) and model (dashed line) curves for trichloroethane in hexane at* 298 K. *Top: power absorption coefficient* (neper cm^{-1}) vs. *frequency. Centre: Cole–Cole plot. Bottom: orientational correlation function*
(Reproduced by permission from P. Desplanques, these d'Etat, 1973, p. 117)

Table 1 summarizes the way equations (5) and (10) have been used in recent publications. The especial concern has been to find a coherent representation of the total rotational mode spectrum of polar molecules in the liquid state. This spectrum typically extends from 10^8 to 10^{12} Hz and (in arbitrary descriptions[41d]) has two components: the Debye-type absorption centred on $\epsilon''_{\max}$ in the microwave region and the Poley librational mode peaking at $\alpha_{\max}$ in the far i.r. (near 50 cm^{-1}). The aim of the correlation functional representation is to provide a quantitative match to the observed contours based on $\langle u(0) \cdot u(t) \rangle$. The series formulation, for example equation (11), can be truncated with a suitable function either for $K_0(t)$, the memory function of $C(t)$, or for $K_1(t)$, the memory function of $K_0(t)$ itself. Most investigations to date are for autocorrelation functions, but Davies and Evans[47e] have used the Mori series to describe the cross-correlations of the fluctuating dipole $^{(i)}M$ (see Table 1) to calculate the induced far i.r. spectrum of non-dipolar liquids.[34] The only models of this series widely used to date outside the far infra-red,[42-44,47] are the M and J diffusion mechanisms of Gordon,[42] which fit into the Mori formalism (see Table 1). Whilst useful in all the fields of relaxation study mentioned in the introduction, they are sternly tested when pitted against $\alpha(\omega)$, the power absorption coefficient (neper cm^{-1}) of the i.r. since this is exceptionally sensitive at submillimetre frequencies to the short-time behaviour of the dipole autocorrelation function. In comparison, the far wings of the Rayleigh depolarized spectrum, for example, would measure the power spectrum $\alpha(\omega)/\omega^2$, or to a good approximation, $\epsilon''(\omega)/\omega$, where ϵ'' is the dielectric loss; and consequently any deviation from the low-frequency Lorentzian in light scattering is much more difficult to observe than the corresponding changes from classical Debye behaviour (see Table 1) in the far i.r.

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[41] (*a*) P. Debye, 'Polar Molecules', Dover, New York, 1954; (*b*) B. Keller and F. Kneubühl, *Helv. Phys. Acta*, 1972, **45**, 1127; (*c*) G. Williams, *Chem. Rev.*, 1972, **72**, 55; (*d*) M. Davies, *Ann. Reports (A)*, 1970, **67**, 65.

[42] (*a*) R. G. Gordon, *J. Chem. Phys.*, 1966, **44**, 1830; (*b*) R. E. D. McClung, *ibid.*, 1972, **57**, 5478; (*c*) I. W. Larkin, *Faraday Symp.*, 1972, **6**, 112; (*d*) R. Haffmanns and I. W. Larkin, *J. C. S. Faraday II*, 1972, **68**, 1729; (*e*) M. W. Evans, M. Davies, and I. W. Larkin, *ibid.*, 1973, **69**, 1011; (*f*) I. W. Larkin, *ibid.*, 1973, **69**, 1278; (*g*) I. W. Larkin and M. W. Evans, *ibid.*, 1974, **70**, 477; (*h*) I. W. Larkin, *ibid.*, 1974, **70**, 1457; (*i*) M. W. Evans, *ibid.*, 1975, **71**, 843, 2051; 1976, **72**, 727.

[43] (*a*) F. Bliot, C. Abbar, and E. Constant, *Mol. Phys.*, 1972, **24**, 241; (*b*) F. Bliot and E. Constant, *Chem. Phys. Letters*, 1973, **18**, 253; 1974, **29**, 618; (*c*) F. Bliot, 'Etude de la Dynamique des Molecules Toupies Symetriques en Phase Gazeuse Comprimée. Application à l'Interpretation des Spectres d'Absorption Dipolaire dans le Domaine Hertzien et Infrarouge Lointain', Thèse d'Etat, Univ. of Lille, 1973.

[44] P. Desplanques, 'Absorption Dipolaire et Dynamique Moleculaire en Phase Liquide', Thèse d'Etat Univ. of Lille, 1974.

[45] G. Harp and B. J. Berne, *Phys. Rev.*, 1970, **2A**, 975.

[46] G. J. Evans, G. H. Wegdam, and M. W. Evans, *Chem. Phys. Letters*, 1976, **42**, 331.

[47] (*a*) A. Gerschel, *Mol. Phys.*, 1976, **32**, 679; (*b*) G. J. Evans and M. W. Evans, *J. C. S. Faraday II*, 1976, **72**, 1169; (*c*) M. W. Evans, *Spectrochim. Acta*, 1976, **32A**, 1259; (*d*) M. W. Evans, *ibid.*, p. 1253; (*e*) G. J. Davies and M. W. Evans, *J. C. S. Faraday II*, 1976, **72**, 1194, 1206; *Chem. Phys. Letters*, 1976, **41**, 521; (*f*) G. J. Davies, G. J. Evans, and M. W. Evans, *J. C. S. Faraday II*, 1976, **72**, 1901; (*g*) G. J. Davies, G. J. Evans and M. W. Evans, *ibid.*, p. 2138; (*h*) M. W. Evans, *J. C. S. Faraday II*, 1976, **72**, 2138. (*i*) G. J. Evans and M. W. Evans, *J. C. S. Faraday II*, 1977, **73**, 285.

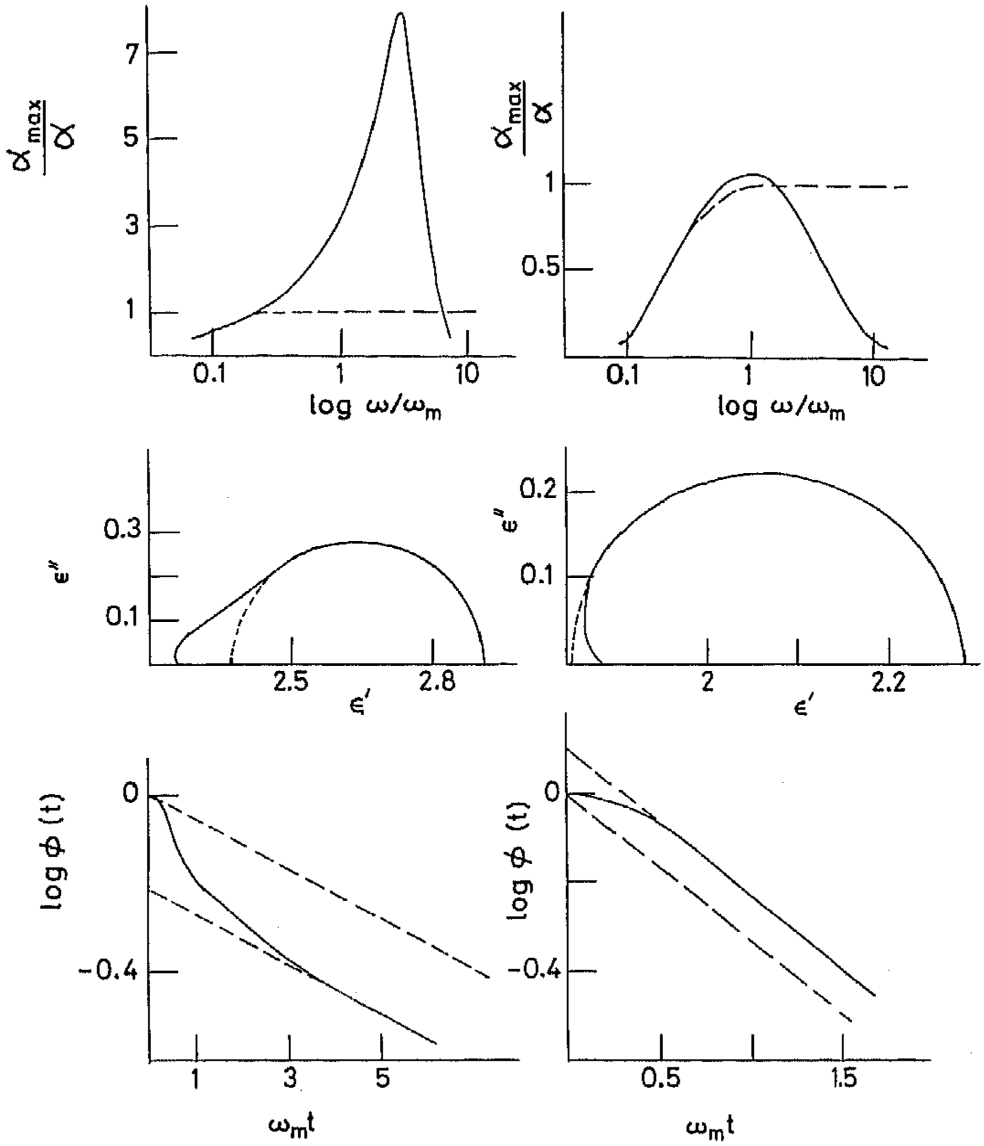

Figure 2 *As for Figure 1 in two extreme cases where the Poley absorption is pronounced (l.h.s. column, a solution of* CH_3CN *in* CCl_4*, 5% mole fraction), and small (r.h.s. column, 20% mole fraction* $(CH_3)_3CCl$ *in hexane at* 298 K). *The dotted curve is the theoretical absorption according to the Debye model of rotational diffusion*
(Reproduced by permission from P. Desplanques, these d'Etat, 1973, p. 45)

Cole[48] has given a careful account of how the Debye equations for ϵ'' and ϵ' result from an exponential correlation function. This is ill-behaved at short times[11] (not differentiable); thus by implication the Debye relations are unacceptable at high frequencies. Figure 2 shows that the spectral function becomes asymptotic at the so-called Debye plateau,[1,2,34] whilst experimentally $\alpha(\omega)$ is a broad band of finite half-width (*ca.* 50 cm^{-1}) appearing above the asymptote and there described as the Poley absorption,[49] as it is in no part envisaged in the Debye process.

[48] R. H. Cole, *J. Chem. Phys.*, 1965, **43**, 637.
[49] J. P. Poley, *J. Appl. Sci.*, 1955, **4B**, 337.

3 *M* and *J* Diffusion Models and Rayleigh/Raman Scattering

It is clear that $\alpha(\omega)$ in classical Debye theory does not have a high-frequency decay (or equivalently does so as ω^0, infinitely slowly), but considering the *M*-diffusion equation (16),[31c] one obtains, by Fourier–Laplace inversion, equation (17), which is asymptotic as ω^{-2}. The same high-frequency behaviour is true of *J*-diffusion, and transparency is not regained quickly enough at liquid-like densities (Figure 3). Neither can this model reproduce oscillations (Figure 4) in the dipole autocorrelation function which are often observed due to torsional oscillations of the dipole trapped in energy wells formed by the potentials of surrounding molecules.

$$K_0(t) = K_0(0)\exp(-\gamma_0 t) \tag{16}$$

$$\alpha(\omega) \propto \frac{\omega^2\gamma_0 K_0(0)}{(K_0(0)-\omega^2)^2+\omega^2\gamma_0^2} \tag{17}$$

An analytical equation for $C(t) = \langle u(0)\cdot u(t)\rangle$ of the *M* diffusion limit was evaluated by Brot,[50] who extended the Gordon model to describe the two-dimensional librator in a multi-well potential formed by neighbouring molecules. Libration or torsional oscillation, of a permanent dipole within a potential well, is 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. The theoretical absorption curves therefrom were compared with far i.r. and microwave data in the dense fluid and rotator crystalline phases of a wide range of differently shaped molecules by Larkin *et al.*[42c–i] The fit was not

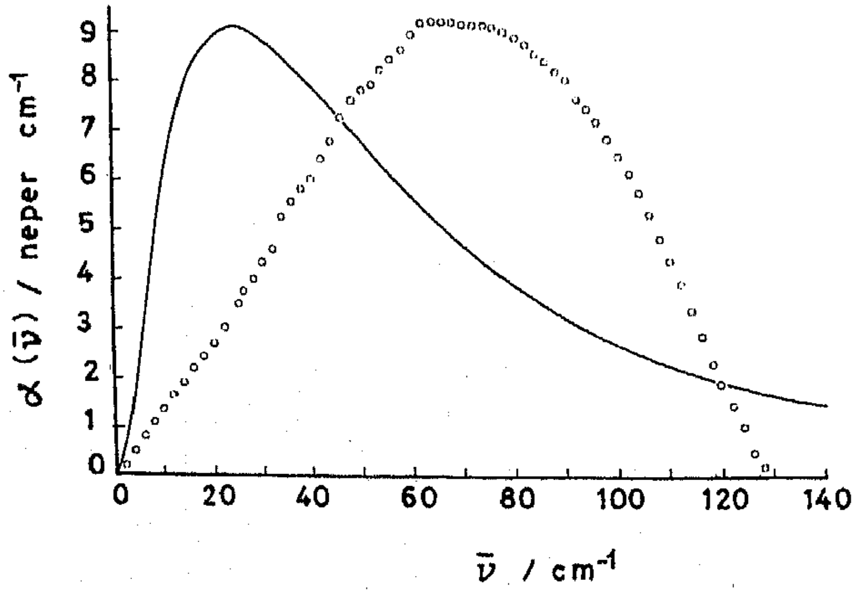

Figure 3 ○ *Absorption of* $(CN)_2(l)$ *at* 301 K. —— *J diffusion broadening of the individual quadrupole-induced* $J \rightarrow J+2$ *lines. Ordinate:* $\alpha(\bar\nu)$/neper cm^{-1}; *abscissa:* $\bar\nu$/cm^{-1}
(Reproduced by permission from *Spectrochim. Acta*, 1976, **32A**, 1253)

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[50] C. Brot, *J. Phys. Rad.*, 1967, 28, 789.

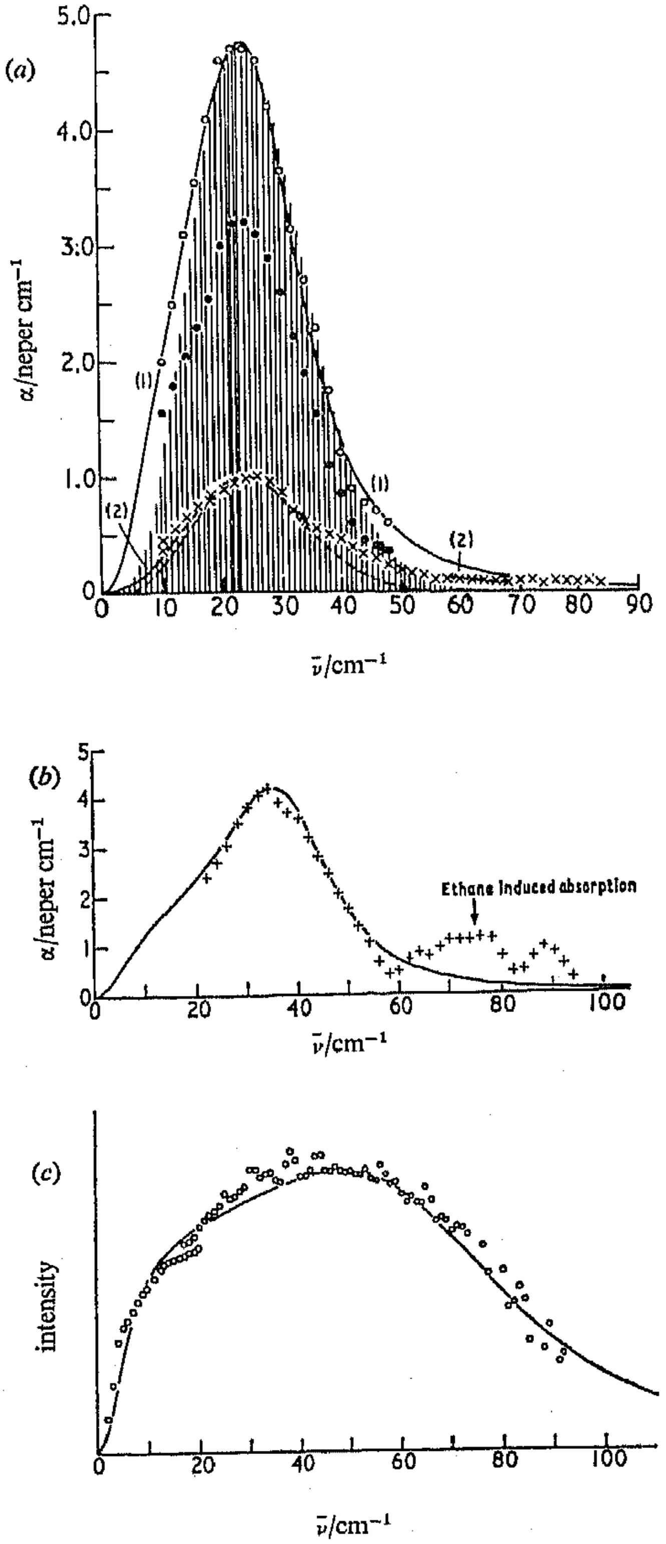

Figure 4 (*a*) ○ *Absorption of* CH_3Cl *at* 5.8 bar, 296 K; ● *absorption of* CH_3Cl *at* 4.4 bar, 296 K; × *absorption of* CH_3Cl + *ethane at a total pressure of* 33.5 bar, 296 K; *the vertical lines are a set of* $\Delta J = 1$ *lines for quantum free rotation. The* $\Delta K = 0$ *lines are not drawn in.* (1) *Three-variable Mori formalism, best fit;* (2) *best, least mean squares, fit to the data.* --- *Contour of the* $J \rightarrow J+1$ *lines.* (*b*) + *Absorption of* CH_3Cl + *ethane (liquid) at* 296 K. —— *Mori theory, best fit.* (*c*) ⊙ *Absorption of liquid* CH_2Cl_2 *at* 296 K. —— *Mori theory, best fit.*

(Reproduced from *J. C. S. Faraday II*, 1976, 72, 1901) satisfactory either at low or high frequencies since the autocorrelation function has a term in t^3 in its Taylor expansion. The itinerant oscillator model developed and described by Wyllie[1] behaved very similarly since it is also asymptotic as ω^{-2}. Often in these papers the authors made misguided attempts at fitting the whole microwave/far i.r. broad-band absorption with a model for the absorption of permanent dipoles alone, while it had been known[51] that as much as 60% of $A = \int_{\text{band}}\alpha(\omega)d\omega$ could arise from the collision induced absorption of the dipoles denoted ${}^{(i)}M$ above. It is acceptable to fit the total profile only for dilute solutions of very strongly dipolar solutes, although collision-induced absorption becomes negligibly small in comparison with that of the permanent dipole below about 1 cm^{-1}. The autocorrelation function of the permanent dipole alone should (in principle) be investigated with data below 1 cm^{-1} (loss and dispersion), and the high-frequency absorption predicted therefrom.

The far wings of Rayleigh bands contain information about intermolecular effects, since an exponential fall-off can be observed[52] for spherical molecules[53] with scalar polarizabilities, so that here too one must separate molecular from intermolecular effects before evaluating M and J diffusion models. Bucaro and Litovitz[54] were able to account for the contours of the depolarized Rayleigh wing in spherically polarizable molecular liquids in terms of a simple binary-collision approach, but the experimental Rayleigh bands of moderately and highly anisotropic molecular fluids exhibit not only the same quasi-exponential tail as spherically polarizable molecules, but also a shoulder in the wing region (50–90 cm^{-1}) which cannot be accounted for with the binary collision model.

There are numerous other assumptions made in the theory of light scattering which must be clarified before the validity or otherwise of any variant of the Mori formalism (and in particular M and J diffusion) can be tested. Briefly, these are:

(i) The light is incident upon a fluid of N identical point molecules characterized by a tensor polarizability α, diagonal in a body-fixed co-ordinate frame (x', y', z').

(ii) The radiation is characterized by a field E_0 along the z axis of the laboratory frame (x, y, z) and a wave vector k_0 lying in the x–y plane; and the scattered light by E and k.

(iii) k makes an angle θ_0 with the z axis (or E_0) and an angle ϕ_0 with E. The angle θ_0 determines the direction of the scattering and ϕ_0 its polarization after passing through the sample.

The analysis proceeds by first transforming the incident field E_0 from the laboratory frame to the body-fixed frame, then computing the scattering and finally transforming back to the laboratory frame. Euler angles (α, β, γ) are used for the transformations. Therefrom the relative intensity of light scattered into (θ_0, ϕ_0) and shifted in angular frequency from Ω_0 to Ω is:

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[51] G. W. F. Pardoe, Thesis, Univ. of Wales, 1969.

[52] W. S. Gornall, H. E. Howard Lock, and S. P. Stoicheff, *Phys. Rev.*, 1970, **A1**, 1288.

[53] (*a*) J. P. McTague and G. Birnbaum, *Phys. Rev. Letters*, 1968, **21**, 661; (*b*) S. C. An, C. J. Montrose, and T. A. Litovitz, *J. Chem. Phys.*, 1976, **64**, 3713, and refs therein.

[54] J. A. Bucaro and T. A. Litovitz, *J. Chem. Phys.*, 1971, **55**, 3846.

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$$\frac{I(\Omega)}{I_0}\mathrm{d}\Omega = \left[\frac{\Omega_0^2}{4\pi R_0 c^2}\right]\int_{-\infty}^{\infty} \mathrm{e}^{-\mathrm{i}(\Omega-\Omega_0)t}$$

$$\times\left\langle \sum_{j,l} \mathrm{e}^{\mathrm{i}q\cdot r_j(0)} X_j(\theta_0, \phi_0, 0)\mathrm{e}^{-\mathrm{i}q\cdot r_l(t)} X_l^*(\theta_0, \phi_0, \tau)\right\rangle \mathrm{d}t\,\frac{\mathrm{d}\Omega}{2\pi}$$

where X_j and X_l^* are complicated functions of the time dependent Euler angles α, β, γ and the polarizability components of the molecule: $\alpha_{x'}, \alpha_{y'}, \alpha_{z'}$.

(iv) In the case $\theta_0 = \phi_0 = \pi/2$ (depolarized light) for a symmetric top molecule we have a certain simplification.

(v) It is also frequently assumed that the angular motions of different molecules are uncorrelated and that the translation and orientation of a given molecule are likewise uncorrelated.

Then we have:

$$\frac{I(\Omega)}{I_0} = \left[\frac{\Omega_0^2\alpha_2}{4\pi R_0 c^2}\right]\int_{-\infty}^{\infty} \mathrm{e}^{-\mathrm{i}\omega\tau}\left\langle \sum_j \mathrm{e}^{\mathrm{i}q\cdot[r_j(0)-r_j(t)]}\right\rangle$$

$$\times\left\langle \frac{2\pi}{15}\left[Y_{2,1}(\theta_j, \phi_j; 0) + Y_{2,-1}(\theta_j, \phi_j; 0)\right]\right.$$

$$\left.\times\left[Y_{2,1}(\theta_j, \phi_j; \tau) + Y_{2,-1}(\theta_j, \phi_j; \tau)\right]^*\right\rangle \frac{\mathrm{d}\tau}{2\pi}$$

with

$$Y_{2,\pm 1}(\theta, \phi) = \mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cos\theta\sin\theta\exp(\pm\mathrm{i}\phi)$$

and

$$\alpha_2 = \alpha_z' - (\alpha_{x'} + \alpha_{y'})/2$$

The dynamics of reorientation of a single particle may be described by the conditional probability:[11]

$$f(\theta_\tau, \phi_\tau; \theta_0, \phi_0) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_{lm}(\theta_0, \phi_0)Y_{lm}^*(\theta_\tau, \phi_\tau)f_{l,m}(\tau)$$

where $f_{l,m}(\tau)$ is a time autocorrelation function expressed in spherical harmonic form.[9] For rotational diffusion of a symmetric top we have:

$$f_{l,m}(\tau) = \exp\{-[D_1 l(l+1) + (D_3 - D_1)m^2]\tau\}$$

and assuming that reorientation takes place on time scales when small values of q are involved ($q \approx 10^5$ cm^{-1}), we have equation (18). Here D_1 and D_3 are the components of the rotational diffusion tensor and N_0 is the molecular number density. The Rayleigh band for molecules with tensor polarizability is theoretically a Lorentzian only on assuming that $I(\Omega)$, the scattered intensity, is independent of q, the change in wave vector of the scattered light.

$$\frac{I(\Omega)}{I_0} = \left[\frac{\Omega_0^2\alpha_2}{4\pi R_0 c^2}\right]\frac{4N_0}{15}\cdot\frac{5D_1 + D_3}{(5D_1 + D_3)^2 + \omega^2} \tag{18}$$

Almost a decade ago it was reported by Zaitsev *et al.*[55] that this is true for liquids such as CS_2 and CCl_4, even for the viscous benzophenone and salol, but $I(\Omega)$ is dependent upon q for benzene and toluene.[56] Even by using the M and J diffusion models for $f_{l,m}(\tau)$ as evaluated by McClung,[42b] this q dependence must be accounted for separately, since $f_{l,m}(\tau)$ deals only with the orientational part of the total equation for $I(\Omega)/I_0$. It is clear that Gordon's relation[57] between the correlation function of the polarizability trace and the Rayleigh bandshape must be applied after subtraction in some way of the induced part of the spectrum. Particularly in its simplest form, that is when the autocorrelation function reduces, for a linear molecule, to equation (19),[57] no account is taken of any dependence there may be on q.

$$\begin{aligned} C_{\mathrm{R}}(t) &= \frac{1}{2}\langle 3[u(0)\cdot u(t)]^2 - 1\rangle \\ &= 1 - \frac{3kT}{I}t^2 + \left[4\left(\frac{kT}{I}\right)^2 + \frac{\langle T_{\perp}^2\rangle}{8I^2}\right]t^4 - \dots \end{aligned} \tag{19}$$

Recently there have been a number of studies of the effect of kilobars of external pressure on the depolarized Rayleigh bands of liquids. Dill *et al.*[58] examined acetone, benzene, and methyl iodide, the former two representing 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 $C_{\mathrm{R}}(t)$ and its second derivative (which they wrongly assumed to be the angular velocity autocorrelation function). The mechanism of reorientation appeared to be one involving molecular rotation which is randomly affected by collisions; the J-diffusion model did *not* appear to be an accurate description of its mechanism. The second derivative has a negative region and oscillates (as is well known in the far i.r.[41i]) indicating that complete randomization of the angular velocity at each collision (an assumption of the J-model) does not occur.

The equivalent M-diffusion function for the i.r. that is $\langle \dot{u}(0)\cdot\dot{u}(t)\rangle = -\ddot{C}(t)$ has been evaluated by Evans.[41i] It has a negative region, as it must mathematically, but cannot exhibit oscillations. The negative overshoot has no particular physical significance, and since $\dot{u} = u \times \boldsymbol{\omega}$, $-\ddot{C}(t)$ is a combinatorial orientation/angular velocity autocorrelation function. However, for acetone, the mean time between random, elastic collisions of the J-diffusion model is very small compared with the observed decay time of $-\ddot{C}_{\mathrm{R}}(t)$, possibly indicating non-free-rotor behaviour between collisions. The oscillations in this function are strongest in benzene and nearly absent in acetone, and become more pronounced at higher number densities. The authors take the time at which $-\ddot{C}_{\mathrm{R}}(t)$ becomes negative as a measure of the time between collisions (τ_{BC}), which is not τ_{J}, since in benzene and methyl iodide these two factors exhibit

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[55] (*a*) G. I. Zaitsev and V. S. Starunov, *Optika i Spektroskopiya*, 1967, **22**, 409; (*b*) G. I. Zaitsev, *Ibid.*, 1967, **23**, 325; (*c*) G. I. Zaitsev, Yu I. Kyzylasov, V. S. Starunov, and I. L. Fabelinskii, *Zhur, Eksp. Teor, Fiz., Pis'ma Redaktsiyu*, 1967, **6**, 505, 695.

[56] R. D. Mountain, 'Critical Reviews, Solid State Science', Chem. Rubber Co., Cleveland, Ohio, 1970, Vol. 1, p. 5.

[57] R. G. Gordon, *J. Chem. Phys.*, 1965, **43**, 1307.

[58] J. F. Dill, T. A. Litovitz, and J. A. Bucaro, *J. Chem. Phys.*, 1975, **62**, 3839.

quite different density dependences so that the efficiency of a collision for randomizing the angular velocity is density-dependent.

The same techniques were used by van Konynenburg and Steele[59] to study the rotational dynamics of liquid nitrogen, ethane, ethylene, and carbon dioxide for a number of temperatures and densities along the saturated vapour pressure lines. These authors realized the full meaning of $-\ddot{C}_R(t)$ as an angular momentum/orientation correlation function. They found that the collision-induced part of the Rayleigh band was too large relative to the scattering from permanent polarizability anisotropy to allow the extraction of reliable information for ethane and ethylene. This immediately throws into doubt the conclusions of Dill *et al.*, who assumed that the induced bandshape is that of rare gas liquids,[60] whose spectra they characterized using the empirical methods of Dardy *et al.*[61] with the binary interaction model[54] mentioned earlier. The implication is that the oscillations in $-\ddot{C}_R(t)$ upon which Dill *et al.* base their discussion may well be merely a consequence of the way they corrected for induced scattering. The induced scattering for nitrogen and carbon dioxide[61] seems to be small, and the Rayleigh band can only be approximated with the J-diffusion model which was *not* able to match the data satisfactorily. The authors indicate that the assumption of complete randomization of the molecular angular momentum after collision is not compatible with those computer calculations[31–33] which show up negative parts to the angular momentum autocorrelation function 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. Essentially the same conclusions were reached by Bruining and Clarke[62] in a Raman and Rayleigh scattering study on liquids CO, N_2, and O_2 at 77 K; they also discussed the forms of the reorientational cross-correlation functions determined from their Raman data in comparison with the total Rayleigh correlation function. However, these authors also used a comparison with rare-gas liquids to estimate the induced anisotropy scattering intensity. This was ~10% for CO, ~2.5% for N_2 and ~1% for O_2. They ignore its effect on spectral forms.

Another study of CO_2(l) up to 3 kbar has been carried out[63] using Rayleigh depolarized scattering and the depolarized wings of the Σ_g^+ Raman mode at 1386 cm^{-1}. The J-diffusion model is adequate for the Rayleigh band at 100 bar, but fails for those at higher pressures, where the frequency dependence of the intensity changes form, falling off very sharply. The profile of the Raman band remains unaffected by pressure, so that the Rayleigh scattering reflects both mono- and multi-molecular motion.

The information obtained from measuring the shape of a fully depolarized vibrational Raman line[56] is, in Fourier transform space, strictly an autocorrelation function of vibration modulated by orientation, since the vibrational states of molecules are not correlated. Here truly single particle motion is observed[34]

[59] P. van Konynenberg and W. A. Steele, *J. Chem. Phys.*, 1975, **62**, 2301.
[60] J. P. McTague, P. A. Fleury, and D. B. DuPré, *Phys. Rev.*, 1969, **188**, 303.
[61] H. D. Dardy, V. Volterra, and T. A. Litovitz, *J. Chem. Phys.*, 1973, **59**, 4491.
[62] J. Bruining and J. H. R. Clarke, *Mol. Phys.*, 1976, **31**, 1425.
[63] M. Perrot, J. Devaure, and J. Lascombe, *Mol. Phys.*, 1975, **30**, 97.

$$\hat{I}(\omega) = \lambda^4 \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\omega}\right|_{\perp} \Big/ \int_{\mathrm{band}} \lambda^4 \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\omega}\right|_{\perp} \mathrm{d}\omega$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} \langle Y_{2,0}(\theta,\phi,0) Y^{*}_{2,0}(\theta,\phi,t)\rangle \exp(-\mathrm{i}\omega t)\,\mathrm{d}t \qquad (20)$$

unlike depolarized Rayleigh scattering. Reorientational motion modulates the vibrational motion so that the Raman line is broadened into a band. In the case of totally symmetric vibrations of a linear or symmetric top molecule, and the totally symmetric vibration in a spherical top, we have equation (20),[8] where (θ, ϕ) specify the orientation of the molecular co-ordinate system with respect to a laboratory frame of co-ordinates; λ is the wavelength of the scattered light, and $\lambda^4\ \mathrm{d}\sigma/\mathrm{d}\omega$ is the scattering cross-section. However, vibrational relaxation processes (the loss factor in the vibrational excitation) among modes of the same symmetry species vary greatly, whereas the orientational mobility of a given molecular axis is the same, and, in general, the Raman wings are convolutions of vibrational and orientational autocorrelation functions when these are uncorrelated. For example, the carbon–hydrogen stretch absorption (ν_1) of chloroform[64] contains a very large contribution from vibrational relaxation, so that the evaluation from it of a 'pure' rotational correlation function would be inexact with presently available Raman techniques. However, the carbon–chlorine stretch (ν_2) dissipates its vibrational energy much more slowly, so that the vibrational and rotational motion are virtually uncorrelated. When this is the case the separation of the two autocorrelation functions is effected as follows: denoting by $\langle u(0)u(t)\rangle$ the a.c.f. of the vibrational transition dipole u,

$$\langle u(0)u(t)\rangle = \int_{-\infty}^{\infty} [I_{VV}(\omega) - \tfrac{4}{3}I_{VH}(\omega)]\,\mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}\omega \qquad (21)$$

$$\langle u(0)u(t)\rangle \langle P_2\,[u(0)\cdot u(t)]\rangle = \int_{-\infty}^{\infty} I_{VH}(\omega)\mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}\omega \qquad (22)$$

where $\langle P_2\,[u(0)\cdot u(t)\rangle$ denotes the orientational c.f. of equation (19), and $I_{VV}(\omega)$ and $I_{VH}(\omega)$ respectively the intensities of the totally polarized and depolarized scattered light. Here ω is measured from the band centre. The wings of i.r. vibration–rotation lines[64] are similarly described by equation (23), if it is assumed again that vibrational and rotational relaxation are uncorrelated. The difficulties of this kind of study are fully described by Bailey.[34]

$$\langle u(0)u(t)\rangle \langle u(0)\cdot u(t)\rangle = \int_{-\infty}^{\infty} \alpha^{\mathrm{IR}}(\omega)/\omega(1-\mathrm{e}^{-\hbar\omega/kT})\mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}\omega \qquad (23)$$

Rothschild, Rosasco, and Livingston[64] give many reference publications on the characteristics of the vibrational, rotational, and translational motions in liquid chloroform using such techniques as i.r. and Raman spectroscopy; dielectric, far i.r.; quadrupole, spin echo, and spin–lattice n.m.r. spectroscopy. Results and claims in the literature are in serious disagreement. Whereas earlier

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[64] W. G. Rothschild, G. J. Rosasco, and R. C. Livingston, *J. Chem. Phys.*, 1975, **62**, 1253.

i.r. correlation functions indicated that the molecular axes traverse large angles in individual 'jumps', subsequent Raman work has shown that this is only an upper limit, a possibility rather than a probability. Raman and i.r. results indicate that the orientational motion of the symmetry axis of chloroform in the liquid phase consists of very small jumps of 1–4°. Rothschild *et al.*, themselves obtain vibrational and rotational (dipole and second-order tensor) c.f.'s from three parallel and one perpendicular fundamentals of liquid $CHCl_3$, $CDCl_3$, and $CH^{35}Cl_3$. All these are exponential at long but not at short times. They find that J diffusion is too fast beyond 1 ps and that M diffusion fits the data up to 4 ps and is thereafter too slow. The symmetry axis reorients by 'free' jumps of about one-third radian. The Raman correlation time is about equal to the n.m.r. quadrupolar correlation time (both techniques involving the same tensor a.c.f. of u), but the i.r. rotational correlation time is only about three-quarters of the corresponding dielectric relaxation time.

The underlying assumptions in this paper are clearly delineated by the authors themselves. These include one that induced absorption, that is the band-broadening due to a dipole moment which persists during the time of collision, does not affect their conclusions, although they actually observe the experimental rotational second moment to become larger than that expected theoretically for the ν_3 mode of $CHCl_3$ and $CH^{35}Cl_3$. However, they conclude that only a certain amount of rotational energy is exchanged between the molecules during an effective collision, which is not elastic as in M or J diffusion. The motion up to 6 ps is an 'end-over-end rotation' in a fluctuating liquid cage whose average molecular positions persist but whose angle-dependent forces are 'averaged-out' by the very motions of the molecules. They feel that molecular shape rather than polarity is the dominant factor.

A few months later Rosenthal and Strauss[65] published data on the i.r. and Raman ν_1 and ν_3 modes of liquid chloroform along with some on the depolarized Rayleigh wing. The forms of the vector and tensor cross-correlation functions were deduced: the former can be predicted by fitting in the other results with the theory of Keyes and Kivelson,[36a] which is a truncation of the Mori series one step up from that which produces the M and J diffusion mechanism. As predicted by the theory, the cross-correlation function decays much more slowly than either the autocorrelation function *or the total correlation function*. The tensor cross-correlation function (Rayleigh wing) is less well described.

G. J. Evans[66a] later obtained improved far i.r. data for liquid chloroform and demonstrated that in terms of $\alpha(\omega)$, more than half of the observed intensity is collision induced and *must not* be included as due to the total correlation function of the *permanent* dipole. To obtain the latter, Rosenthal and Strauss Fourier-transformed the whole band, distorted as it is by the absorption of temporary dipoles. It is well known that the intensity check used by them:

$$\epsilon_0 - \epsilon_\infty = \frac{2}{\pi}\int_0^\infty \frac{\epsilon''}{\omega}\,d\omega$$

[65] L. C. Rosenthal and H. L. Strauss, *J. Chem. Phys.*, 1976, **64**, 282.

[66] (*a*) G. J. Evans, *Spectrochim. Acta*, to be published; (*b*) J. P. Riehl and F. S. Richardson, *Chem. Phys. Letters*, 1976, **42**, 501.

is especially insensitive to induced absorption; the latter is a high-frequency process which, owing to the frequency factor in the relation $\epsilon'' \propto \alpha\,(\text{optical})/\bar{\nu}$, never appears as more than a slight increase in the very high frequency tail of $\epsilon''(\omega)$. Fortunately, the orientational c.f., being effectively the Fourier transform of $\epsilon''/[1 - \exp(-\hbar\omega/kT)]$, is almost totally determined in liquids such as chloroform by data below the far i.r. frequency region, and as such, is insensitive to induced absorptions.

Vibrational and rotational time-correlation functions for Brownian motion have been derived by Riehl and Richardson[66b] using *circularly* polarized vibrational Raman spectra. These correlation functions can be obtained from $I(\omega) = I_L + I_R$ and $\Delta I(\omega) = I_L - I_R$ spectra, where I_L and I_R are, respectively, the intensities of the left and right circularly polarized components of the Raman scattered light. However, the authors are not clear at present what advantages there will be in using this technique as opposed to linear polarization (vertical and horizontal). Preference for one technique over the other would be determined entirely by whichever will yield the best resolved spectra with well-defined contours for a particular system.

There have been a few attempts[67,68] to modify the simple M and J diffusion models and to make them more realistic. These make it possible to vary the amount of angular momentum transferred during a collision and the distribution of the intervals in between (Figure 5).[46] However, the modified formalism still

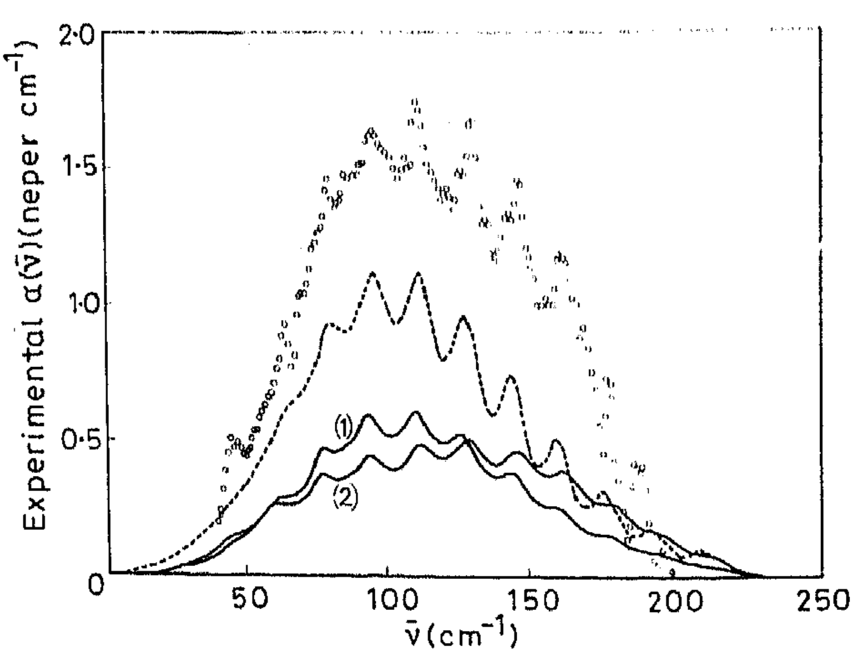

Figure 5 *Experimental absorption of* HBr/SF$_6$ *liquid mixture at* 296 K. ––– *Frenkel/Wegdam formalism*[68] ordinate scale unnormalized. —— (1) *Truncated Mori formalism of Bliot* et al.[42] *Both curves* (1) *and* (2) *are unnormalized to the experimental data on the ordinate scale* (*see ref*)
(Reproduced by permission from *Chem. Phys. Letters*, 1976, **42**, 331)

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[67] M. Constant R. Fauquembergue, and P. Descheerder, *J. Chem. Phys.*, 1976, **64**, 667.

[68] (*a*) D. Frenkel, G. H. Wegdam, and J. van der Elsken, *J. Chem. Phys.*, 1972, **57**, 2691; (*b*) D. Frenkel and G. H. Wegdam, *ibid.*, 1974, **61**, 4671.

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produces an autocorrelation function with an a-physical t^3 term in its Taylor series, and delayed regain of far i.r. transparency. Denoting by $\cos[\gamma(J)]$ the average cosine of the angular momentum vector, before and after a collision, it is found[68] that the Poley absorption cannot be reproduced in the M-diffusion limit unless it is assumed that collisions are correlated and that at the same time the angular momentum is such that $\cos[\gamma(J)] < 0$. The same is true for J diffusion, and, in fact, the most conspicuous feature of the far i.r. spectrum, its shifted maximum of absorption compared with that of a free-rotor ensemble, *demands* the assumption of correlated collisions, since the simple models of M and J diffusion can move $\omega_{\max}$ only very slightly, for example Figure 3. The power spectrum of the dipole correlation function, obtained from $\alpha(\omega)/\omega^2$, is a very useful means of differentiating between the M-diffusion and J-diffusion limits of the extended model. This diverges logarithmically around $\omega = 0$ in the elastic limit for M-diffusion but remains finite for J-diffusion.

Frenkel and Wegdam[68b] compare the use of a binary collision model for a dense system with approximating to a sine wave with a square wave, so that many details of the molecular motion are neglected or distorted but the dominant features are retained. The situation is similar to the application of a hard-sphere model for the description of the equilibrium properties of monatomic liquids. Chandler[69] has discussed the translational and rotational diffusion of rough hard spheres, starting from the Liouville equation, and found that the deviation from Poisson behaviour in dense systems means that the first term in the cumulant expansion of the memory kernel is insufficient to describe the dynamics of the system. This happens when the rotational motion couples strongly to collective modes[70] in the medium. The amount of rotational energy and momentum transfer during a collision roughly corresponds, for dense systems, to the average change in these quantities during a time of the order of the interval between collisions. Correlated collisions mean that the angular momentum correlation function becomes oscillatory, which is found in molecular dynamics studies[7] where the intermolecular potential is strongly anisotropic. These modified M, J diffusion models have been extended to symmetric top geometry by Constant *et al.*[67] The original Gordon concept of M and J diffusion appears to have received its final blow from O'Dell and Berne[71] who collected molecular dynamics data on rough sphere ensembles. The Gordon models dictate certain criteria, as does any other: the rough sphere meets *almost all* of these criteria, yet there is an enormous disparity between prediction and observations of correlation functions from the numerical solution of the equations of motion. However, part of the discrepancy seems to be in the fact that collisions in the body frame can randomize only two of the three components of momentum.[72] Gordon wrongly assumed that all three are randomized.

[69] D. Chandler, *J. Chem. Phys.*, 1974, **60**, 3500.

[70] (*a*) G. D. Enright and B. P. Stoicheff, *J. Chem. Phys.*, 1976, **64**, 3658; (*b*) F. Garisto and R. Kapral, *ibid.*, p. 3826; (*c*) T. Yamaguchi, *ibid.*, p. 1555; (*d*) J. Kushick and B. J. Berne, *ibid.*, p. 1362; (*e*) H. J. Coles and B. R. Jennings, *Mol. Phys.*, 1976, **31**, 571.

[71] J. O'Dell and B. J. Berne, *J. Chem. Phys.*, 1975, **63**, 2376.

[72] C. S. Pangali, personal communication.

4 Higher Order Truncations of the Mori Continued Fraction

The physical meaning of truncating this series with an empirical form for $K_1(t)$, say, instead of $K_0(t)$, may be explained in the context of generalizing the simple equation for Brownian motion.[73] 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 vector space E as being represented successively by the ensembles: velocity (zeroth order truncation); velocity + acceleration [truncating with a form for $K_0(t)$]; velocity + acceleration + derivative of acceleration [empirical form for $K_1(t)$]. Similarly there are three spaces P of the angular momentum and its derivatives which correspond to the Debye, M and J diffusion, and the other models of Table 1 which can be described in terms of successive Mori approximations.

Kivelson and Keyes have developed[36a] a theory of light scattering based upon the above ideas, and the formalism was applied to bypass successfully the problem of the dynamic internal field by Kivelson and Madden.[36c] A statistical theory of depolarized laser light-scattering was developed by assuming that the autocorrelation function of the dielectric tensor is proportional to that of a 'primary' variable which is slowly varying and which is associated with molecular orientations, and the time evolution of this a.c.f. is calculated by means of a pair of coupled linear transport equations in which the primary variable is 'coupled' to a 'secondary' variable. This is a rapidly varying quantity dependent upon intermolecular forces. In this way the sharp and broad depolarized Rayleigh lines which dominate the scattered spectrum can be explained, but the theory ignores some of, the k-dependent fine structure mentioned above. It was concluded, contrary to numerous theories, that the observed spectra cannot be explained in terms of a single primary variable. (This is analogous to saying that the far i.r. spectrum may not be explained by simple Debye theory.) The sharp line arises from molecular reorientations in the role of primary variable and the broad wings depend on a 'distinct primary' variable such as the one describing local field fluctuations. An important point to emerge from this paper is that although auto- and cross-correlation functions may have different time dependences, the total anisotropic polarizability still decays with a *single time*, giving rise to a single line in the scattered spectrum. These results may be used to explain the difference between correlation times measured by n.m.r. spin–spin or quadrupole relaxation which measure an autocorrelation function, and those obtained from the width of the sharp depolarized Rayleigh line, which are those of the total anisotropic polarizability dependent upon auto- and cross-correlations (single- and two-particle correlations).

To link this formalism with the Gordon models, Kivelson and Keyes considered the hydrodynamic coupling of molecular reorientation with the molecular angular velocity about the principal axes. The dielectric fluctuations are assumed to be proportional to the fluctuations in molecular reorientation (primary variable), and the correlation times for the torques are assumed to be very short. This corresponds to an extended diffusion model, similar to that of Gordon, where the 'jump' between orientations may be large or small, but the

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[73] A. C. Levi, *Physica (Utrecht)*, 1967, **36**, 324.

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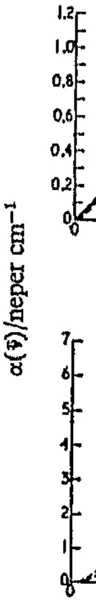

Figure 6 (*a*
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[74] (*a*) B. D.
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collision durations are infinitesimal. It is found that this mechanism cannot explain the observed spectra because t does not give enough intensity to the broad line, which in theory has a negative intensity! (Of course the net intensity at any given frequency is positive because of the wings of the sharp line.) The autocorrelation function in this case consists of just two exponentials.

Later the same authors developed a unified theory[74] of orientational relaxation which is expressed in terms of Mori's formalism for generalized hydrodynamics, which embodies the continued fraction discussed above. The formalism is developed with three orientational variables interrelated by three coupled linear transport equations. The three variables are D, $\mathrm{d}D/\mathrm{d}t$, and $\mathrm{d}^2D/\mathrm{d}t^2$, where D is a relevant Wigner rotational transformation function. (Compare the relations: $C(0) = \langle u(0) \cdot u(0) \rangle$; $K_0(0) = \langle \dot{u}(0) \cdot \dot{u}(0) \rangle / \langle u(0) \cdot u(0) \rangle$, $K_1(0) = \langle \ddot{u}(0) \cdot \ddot{u}(0) \rangle / \langle \dot{u}(0) \cdot \dot{u}(0) \rangle - \langle \dot{u}(0) \cdot \dot{u}(0) \rangle$.) In appropriate limits the theory reduces to that for rotational diffusion, extended diffusion, and libration. It exhibits most of the intensity features of these models, Steele's inertial effects, and Ivanov's jump theory, and furthermore predicts rotational or torsional side bands in the frequency spectrum of the molecular orientational autocorrelation function. In the far wings there is an ω^{-6} dependence [see equation (19)]. The variable $\mathrm{d}^3D/\mathrm{d}t^3$ is Markov (meaning that $K_1(t) = K_1(0)\exp(-\gamma t)$ or that $K_2(t)$ is a delta function in our notation).

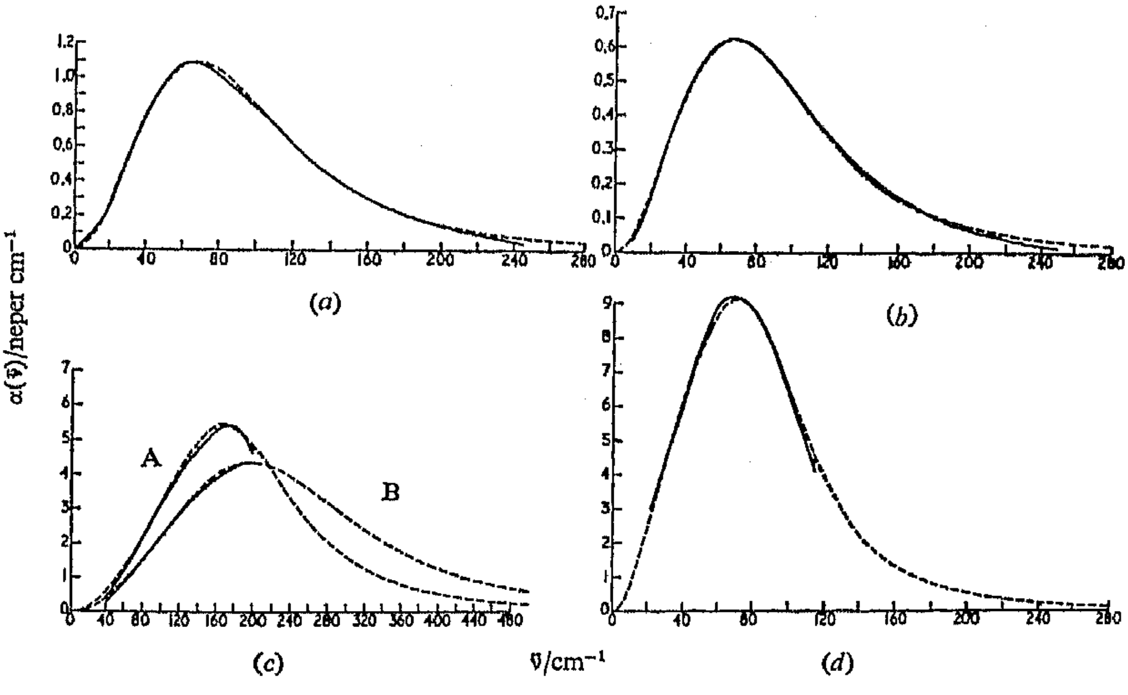

Figure 6 (*a*) —— *experimental absorption for* N_2 (l) *at* 76.4 K; ––– *three-variable Mori formalism, best fit;* (*b*) —— *experimental absorption for* CO_2 (l) *at* 273 K, –––– *theory;* (*c*) —— *experimental absorption for:* A, *methane* (*rotator phase I*) *at* 76 K, B, *methane* (*liquid*) *at* 98 K, –––– *theory;* (*d*) —— *experimental absorption for* $(CN)_2$ (l) *at* 301 K, ––– *theory*
(Reproduced from *J. C. S. Faraday II*, 1976, 72, 1194)

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[74] (*a*) B. D. Ladanyi and T. Keyes, *Mol. Phys.*, 1976, **31**, 1685; (*b*) D. Kivelson, T. Keyes, and J. Champion, *ibid.*, p. 221.

Table 2 *Recent uses of three-variable Mori formalism in the far i.r.*

System	*Molecules*	*Comments and References*
Dipolar liquid	Furan, chloroform at different temperatures	[36b]. Exponent for $K_1(t)$, a three-variable formalism. Authors made the mistake of trying to fit the observed $\alpha(\omega)$ band without allowing for induced absorption. Autocorrelation used. Cross-correlation allowed for with a static g factor.
Dipolar solutes	$CH_3I–CCl_4$; $CHBr_3–CCl_4$	[42b]. $K_1(t) = \beta^{FR}K_1(t)\exp(-\gamma\,\lvert t\rvert)$. Three variable formalism. Fair fit at low (microwave) frequencies, computed curve at far infra-red frequencies too sharp. Discrepancies in the high wings attributed to induced absorption.
Dipolar solutes	$CH_3I–CCl_4$; $CHBr_3–CCl_4$; $CHBr_3$–hexane, cyclohexane; $CHCl_3–CCl_4$, hexane, cyclohexane; $(CH_3)_3CCl$–hexane; tetradecane, hexane. At different temperatures	Desplanques [43]. Effectively a three-variable formalism with the equations displayed in Table 1. Far i.r. curves generally too narrow. Original method employed to account for the influence of induced absorption. This method can be used without introducing supplementary parameters, and can be applied to other studies without difficulty. As yet unused by other authors.
Dipolar liquids and nematogen	CHF_3, $CClF_3$, $CBrF_3$, propyne(l), MBBA	[47b]. Empirical γ and $K_1(0)$ with $K_1(t)$ an exponential. A study of the effect on $K_1(0)$, effectively the mean square torque, of increasing molecular anisotropy. Fit to far i.r. data good but behaviour with microwave data not investigated, except for the nematogen MBBA. Here a fit to the microwave data[75] produces a very sharp far i.r. librational curve[76] at a frequency commensurate with observation.[41e]
Dipolar compressed gas and liquid	CH_3Cl; $CH_2{\cdot}CF_2$ up to 40 bar	[47*f*]. Exponential for $K_1(t)$. This model does not reduce to the correct free rotor behaviour in the limit of vanishing torque. However, compressed gas bandshapes reproduced well, $K_1(0)$ increases with pressure. Care taken to minimize effects of induced absorption by choosing highly dipolar molecules.
Induced absorption in non-dipolar liquids	N_2, CO_2, CH_4, CCl_4, $(CN)_2$, CS_2 cyclohexane, benzene, *trans*-decalin, 1,4-dioxan	[47*e*]. Exponential $K_1(t)$. $K_0(0)$ and $K_1(0)$ now torque dependent. Both increase steadily as molecular anisotropy increases. Excellent fit to experimental data in the far i.r. (Figures 6 and 7). Mori formalism used with the two-particle cross-correlation function.
Non-dipolar liquids Effect of kbars of external pressure and temperature	CS_2, CCl_4	[47*e*]. γ, $K_0(0)$, and $K_1(0)$ empirical, the latter two torque dependent. Far i.r. absorption of CS_2 up to 11.5 kbar described very well. $K_0(0)$ and $K_1(0)$ increase with number density. Increase with temperature for CS_2. Decrease

Induced absorption in non-dipolar liquids	N_2, CO_2, CH_4, CCl_4, $(CN)_2$, CS_2 cyclohexane, benzene, *trans*-decalin, 1,4-dioxan	[47*e*]. Exponential $K_1(t)$. $K_0(0)$ and $K_1(0)$ now torque dependent. Both increase steadily as molecular anisotropy increases. Excellent fit to experimental data in the far i.r. (Figures 6 and 7). Mori formalism used with the two-particle cross-correlation function.
Non-dipolar liquids Effect of kbars of external pressure and temperature.	CS_2, CCl_4	[47*e*]. γ, $K_0(0)$, and $K_1(0)$ empirical, the latter two torque dependent. Far i.r. absorption of CS_2 up to 11.5 kbar described very well. $K_0(0)$ and $K_1(0)$ increase with number density. Increase with temperature for CS_2. Decrease slightly for CCl_4. Formalism also applied to non-dipolar mixtures.
Induced absorption in non-dipolar compressed gas	Ethylene up to 55.8 bar	[77]. Fit to data much better than quantum theory of quadrupole-induced dipole absorption.[78] γ, $K_0(0)$, $K_1(0)$ go through a minimum with pressure (Figures 8 and 9).
Induced absorption in the plastic crystalline and liquid phases	CBr_4	[47*g*]. Three-variable formalism for the cross-correlation function. Mean square torque found actually to be *smaller* in the crystal. Seems to support the deduction[71] that rotational motion is freer in the solid just below the melting point in rough hard sphere ensembles.*
Dipolar solute	H_2O in cyclohexane, benzene and CCl_4.	[47*h*]. Three-variable formalism with exponential $K_1(t)$ used to simulate the far i.r. absorption of dilute solutions of water in organic solvents. The motion is not rotational diffusion, but large amplitude reorientations, exhibiting solvent dependence.
Nematogen	4-n-heptyl-4′-cyanobiphenyl	[47*i*, 79]. Exponential $K_1(t)$. Theory produces two linked peaks separated by six decades of frequency, a sharp, liberational peak at 137 cm^{-1}, and a Debye curve at MHz frequencies, fitting the data of Moutran *et al.*
Dipolar liquids	Monohalogenobenzenes $(CH_3)_3CCl$	[80]. Theory tested out over the whole microwave/far i.r. region, fitting at low frequencies and extrapolating through the far i.r. Three forms used for $K_1(t)$, exponential, Gaussian, and Lorentzian. Whereas all three fit at low frequencies only the first is satisfactory in the far i.r.: where the predicted intensity is only *ca.* 50% of that observed, the rest being collision induced.

*See C. Clemett and M. Davies, *Trans. Faraday Soc.*, 1962, 58, 1718

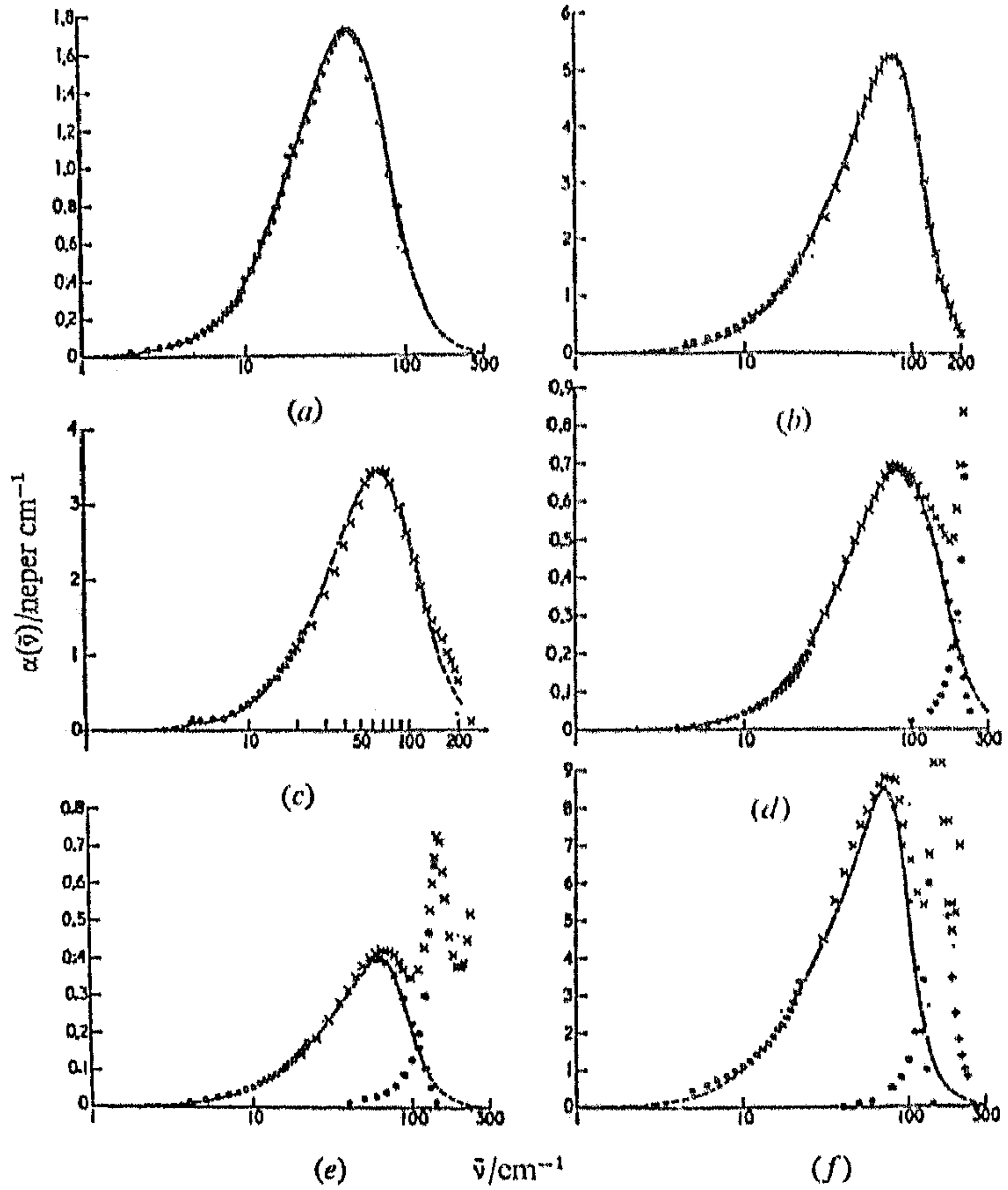

Figure 7 (*a*) ⊙*Experimental absorption for* CCl_4(l) *at* 296 K, ——— *three-variable Mori theory, best fit;* (*b*) ⊙*absorption of benzene (liquid) at* 296 K, ——— *theory;* (*c*) ⊙*absorption of* CS_2(l) *at* 296 K, ——— *theory;* (*d*) ⊙*absorption of cyclohexane at* 296 K. *The high-frequency proper mode is extrapolated using a model of collision disturbed vibrators. This technique is also used in* (*e*) *and* (*f*), ——— *theory;* (*e*) ⊙ *absorption of* trans-*decalin at* 296 K, ——— *theory;* (*f*) ⊙*absorption of 1,4-dioxan at* 296 K, ——— *theory*

(Reproduced from *J. C. S. Faraday II*, 1976, **72**, 1194)

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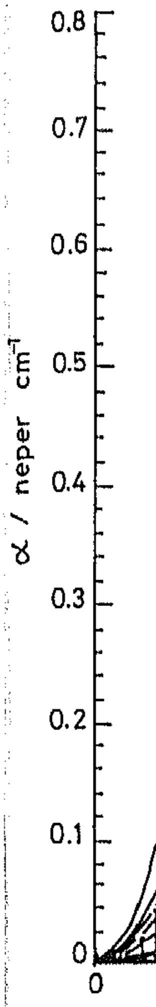
[75] P. Maurel and A. H. Price, *J. C. S. Faraday II*, 1973, **69**, 1486.

[76] W. T. Coffey, T. Ambrose, and J. H. Calderwood, *J. Phys. (D)*, 1976, **9**, L115; W. T. Coffey, personal communication – such a peak is also observed with a model of the two-dimensional itinerant oscillator.

[77] G. J. Evans and M. W. Evans, *Adv. Mol. Relax. Processes*, 1976, **9**, 1.

[78] (*a*) G. J. Davies and M. W. Evans, *J. C. S. Faraday II*, 1975, **71**, 1275, 1976, **72**, 40; (*b*) M. W. Evans, *Mol. Phys.*, 1975, **29**, 1345; (*c*) M. W. Evans, *J. C. S. Faraday II*, 1975, **71**, 1255; 1973, **69**, 763; *Spectrochim. Acta*, 1974, **30A**, 79.

[79] M. Davies, R. Moutran, A. H. Price, M. S. Beevers, and G. Williams, *J. C. S. Faraday II*, 1976, **72**, 1447.



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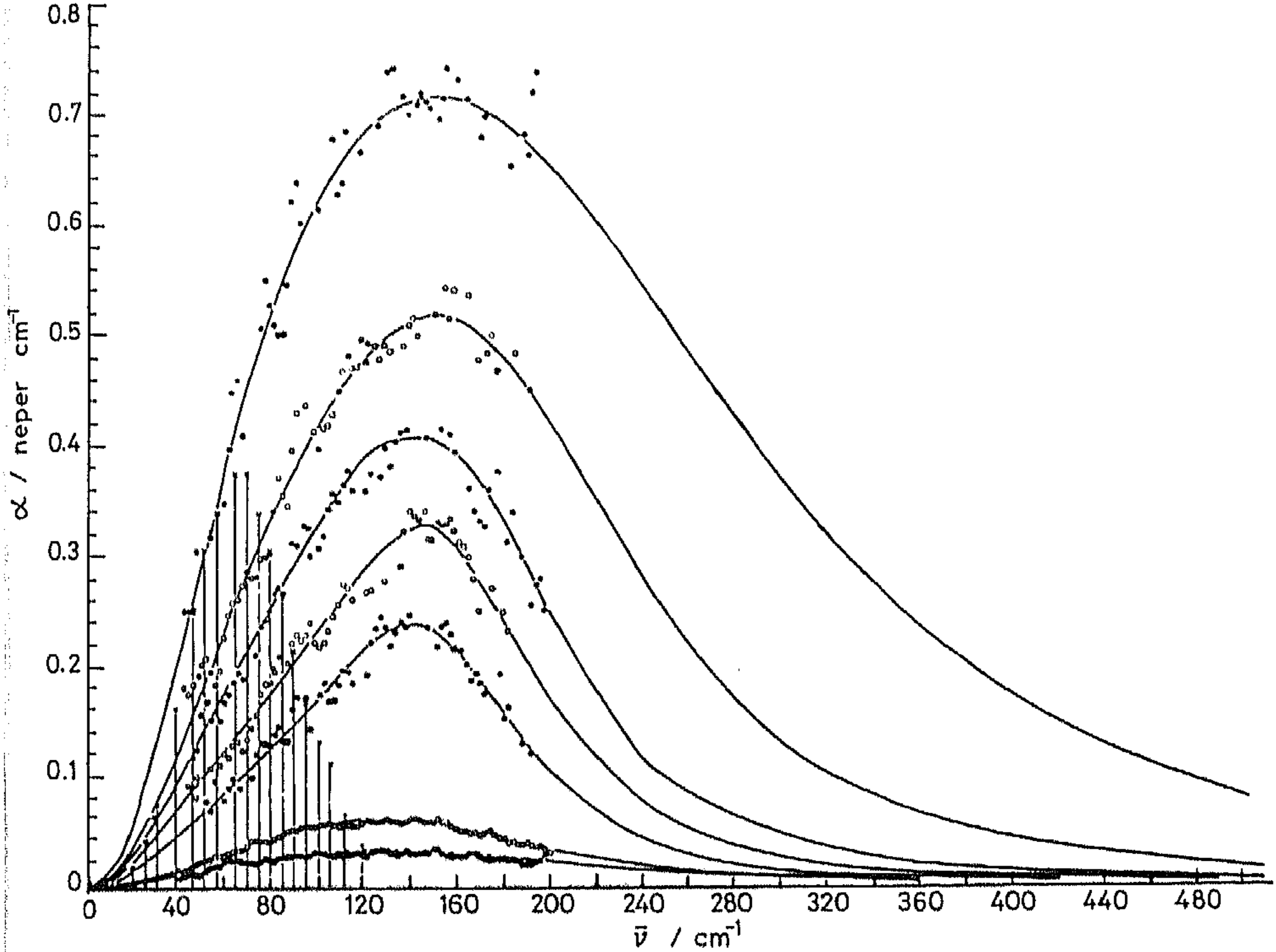

Figure 8 *Far i.r. absorption of ethylene (gas) at* 296 K. *Experimental data, from top to bottom,* 55.8 bar, 48.9 bar, 42.1 bar, 35.2 bar, 28.4 bar, 21.5 bar, 14.7 bar. —— *Truncated Mori expansion. The vertical lines are the set of* $J \rightarrow J+2$ *lines from quantum theory*
(Reproduced by permission from *Adv. Mol. Relax. Processes*, 1976, 9, 1)

Unfortunately, very little use of this theory has been made by experimentalists in fields other than the far i.r.,[46,47] where it was first applied by Bliot *et al.*[42,43] and by Quentrec and Bezot.[36b] Its validity has been investigated systematically by Evans *et al.*[47] for a range of dipolar and non-dipolar fluids, and also in the rotator crystalline phase, where rotational freedom is conserved but translational diffusion is restricted. The recent work in this context is summarized in Table 2. The most stringent test is applied by fitting data below about 1 cm^{-1}, where these are available, since here the problem of induced absorption is minimized. This has been done for the monohalogenobenzenes by Evans *et al.*[80] and the far i.r. theoretical absorption estimated therefrom. A fairly realistic result is obtained only from an exponential $K_1(t)$ (Figure 10), which gives an integrated absorption intensity A (see above) of about half that observed in the far i.r.[81] The excess is due mainly

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[80] G. J. Evans, G. J. Davies, and M. W. Evans, *J. C. S. Faraday II*, in press.
[81] M. N. Afsar, J. B. Hasted, and J. Chamberlain, *Infrared Phys.*, 1976, **16**, 301.

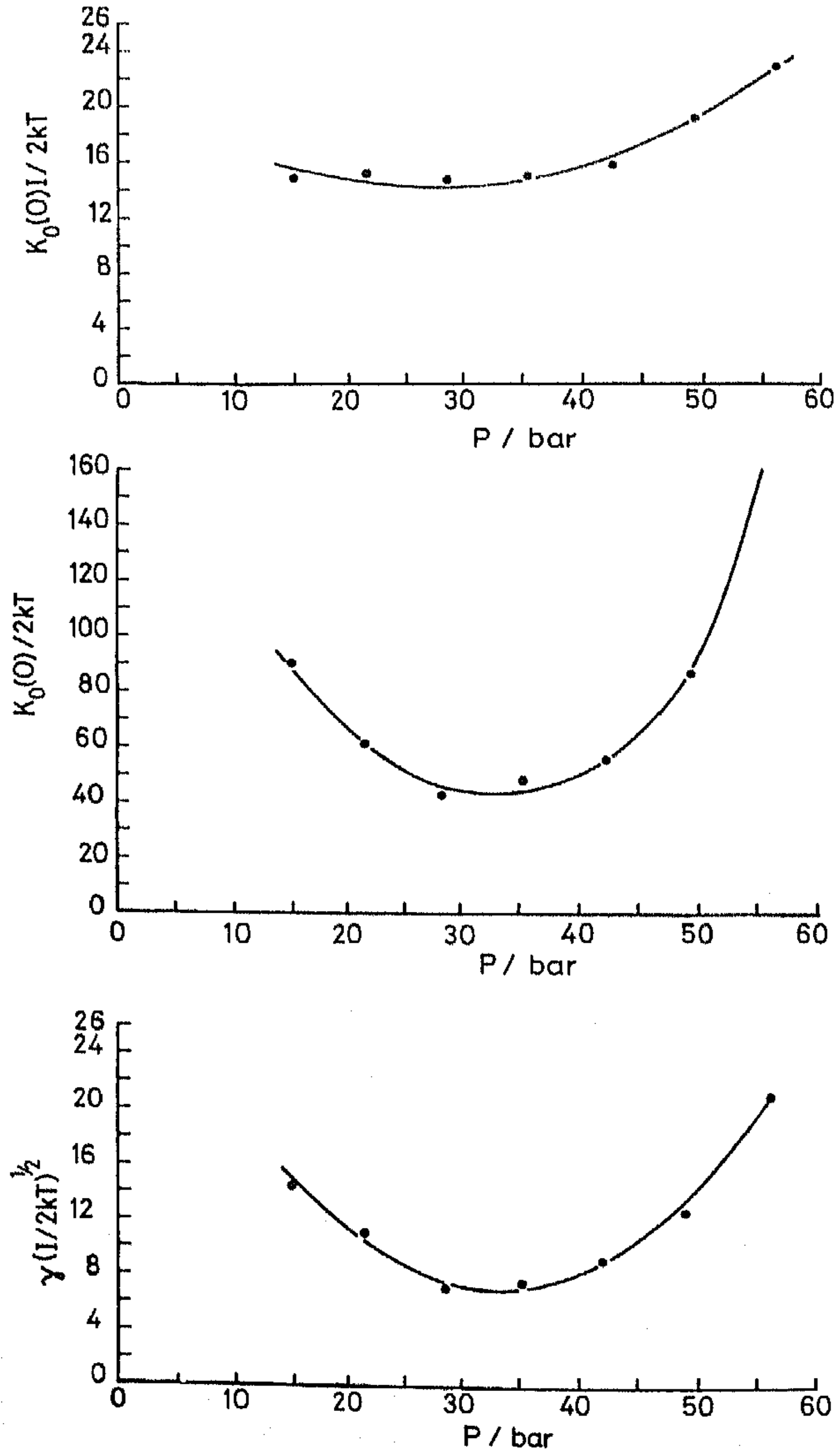

Figure 9 *Top to bottom: variation of* $K_0(0)$, $K_1(0)$, *and* γ *of three-variable theory with pressure for ethane gas*
(Reproduced by permission from *Adv. Mol. Relax. Processes*, 1976, 9, 1)

to intermolecular collision-induced absorption, but also in part to the difference between the dynamic internal field and the Maxwell field and to the fact that in the liquid, the molecular dipoles are partially aligned and coupled for times greater than the Debye. For pure liquid t-butyl chloride at 295 K (Figure 11) even the exponential produces a very unsatisfactory result, but taking another

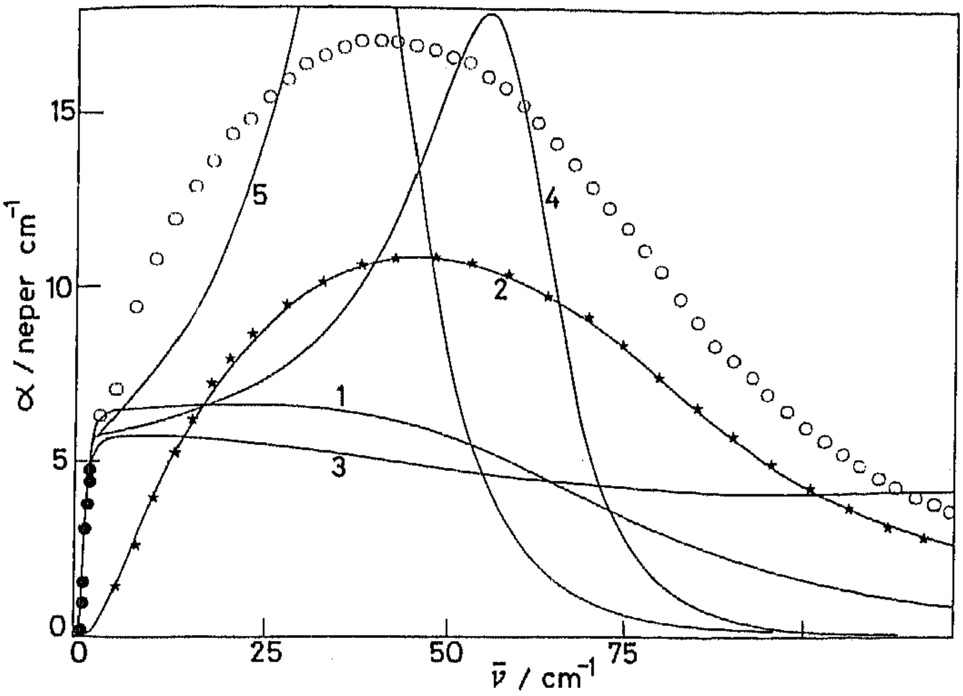

Figure 10 *Absorption of liquid chlorobenzene at room temperature.* ○ *Far i.r. results of M. N. Afsar (personal communication).* (1) *Three-variable theory, best fit to microwave data.* **Experimental data with curve* (1) *subtracted.* (2) *Three-variable theory best fit to the induced absorption**. (3) *Four-variable theory best fit to microwave data.* (4) *Gaussian second memory.* (5) *Lorentzian second memory*

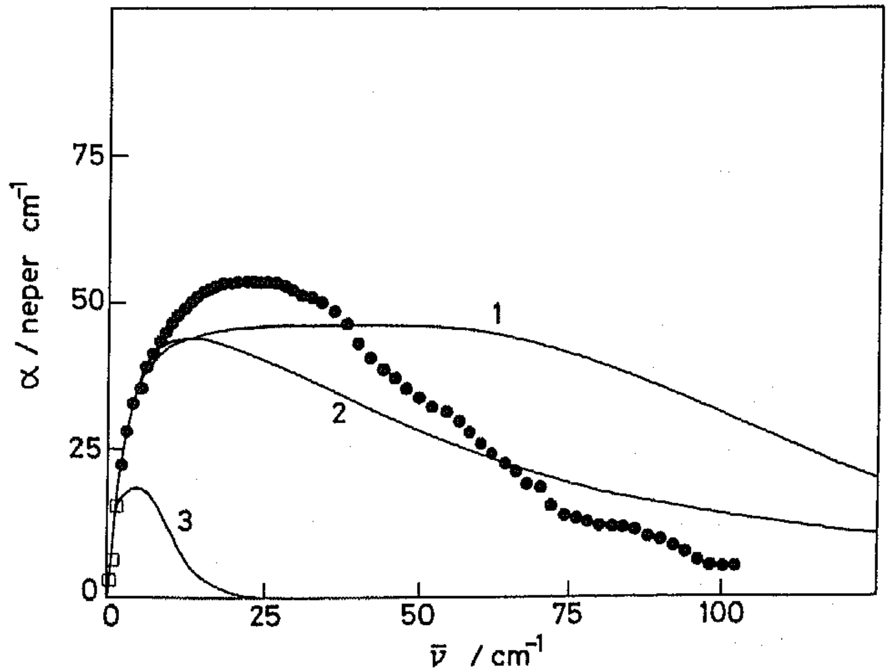

Figure 11 *Absorption of t-butyl chloride liquid at room temperature.* ● *Experimental, polarizing interferometer.* □ *Poley's microwave data.* (1) *Three-variable theory, best fit to microwave data.* (2) *Four-variable theory, best fit to microwave data.* (3) *Lorentzian memory* K_2(t)

term in the Mori series[47b] by way of equation (24), iterating on $K_2(0)$, $K_1(0)$, γ, is a significant improvement. Nonetheless, there is a disappointing lack of convergence in a liquid such as chlorobenzene, where the use of equation (24) produces a *more unrealistic* curve than that from the exponential $K_1(t)$ itself (Figure 10).

$$K_2(t) = K_2(0)\exp(-\gamma t) \tag{24}$$

The only experimental source of information about correlation functions with the same units as $K_2(t)$ (*e.g.* $\langle \dot{\boldsymbol{\omega}}(0)\cdot\dot{\boldsymbol{\omega}}(t)\rangle$ where $\boldsymbol{\omega}$ is the angular velocity), is the numerical technique of molecular dynamics, where the Newton equations are solved numerically for a group of the order of 10^2 molecules with a given intermolecular potential. Using the atom–atom potential of Tildesley and Street,[35a] Evans *et al.*[82a] have computed $\langle \dot{\boldsymbol{\omega}}(0)\cdot\ddot{\boldsymbol{\omega}}(t)\rangle$ for a range of interatomic separations and number densities, some of the results of which are shown in Figure 12. The form is complicated and oscillatory at short times, the function showing negative regions at long times in some instances. The whole curve in general is a long way from the assumed delta function of three-variable theory, although it may for instance decay very quickly compared with the angular momentum autocorrelation function.

Bossis and Quentrec[82b] point out that rotation/translation coupling is neglected in the three-variable theory of Kivelson and Keyes discussed above, and feel that this may have an effect on microwave/far i.r. spectra, although this reporter is of Wyllie's opinion[47b] that any coupling with hydrodynamic modes, for instance, would show up on the low-frequency side of the Debye absorption at frequencies of kHz or low MHz. Pure translational absorption, even in small gaseous molecules such as CO_2 is confined to below 10 cm^{-1}.

At a recent Faraday Symposium, Gerschel[82c] has reported much careful measurement in the far i.r. and microwave of simple organic fluids such as OCS, $CHCl_3$, CH_3F, and CH_3Cl at densities and temperature ranging from near the triple point up to the vicinity of the critical point, and all along the liquid–gas coexistence curve. Using this data *experimental* memory functions corresponding to our $K_0(t)$ and $K_1(t)$ are obtained from analytical expressions developed using the Cole–Glarum and Fatuzzo–Mason theories relating the spontaneous fluctuations of orientation to the frequency-dependent absorption. Despite some vagueness about the corrections used for induced dipole absorption for $CHCl_3$ and OCS (the others being extremely dipolar), it was established that both $K_0(0)$ and $K_1(0)$ are complicated, oscillating functions of time, the latter displaying a slowly decaying plateau out to quite long times at the lower temperatures. A tentative interpretation of this new feature is its ascription to an accompanying motion of the medium, which may reduce or enhance the self motion. A very important conclusion is that the underlying physical processes associated with successive memory functions become increasingly intricate in

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[82] (*a*) M. W. Evans, G. H. Wegdam, and G. J. Evans, paper in preparation; (*b*) G. Bossis and B. Quentrec, *Mol. Phys.*, 1976, **32**, 591; (*c*) 'Newer Aspects of Molecular Relaxation Processes', Faraday Symposium No. 11, The Chemical Society, London, 1977; (*d*) P. W. Atkins and D. S. Broomhead, *Mol. Phys.*, 1976, **32**, 487; (*e*) 'Advances in Chemical Physics', ed. I. Prigogine, and S. A. Rice, Wiley, New York, 1976, Vol. 34; (*f*) P. G. de Gennes, *Mol. Crystals Liquid Crystals*, 1971, **12**, 193.

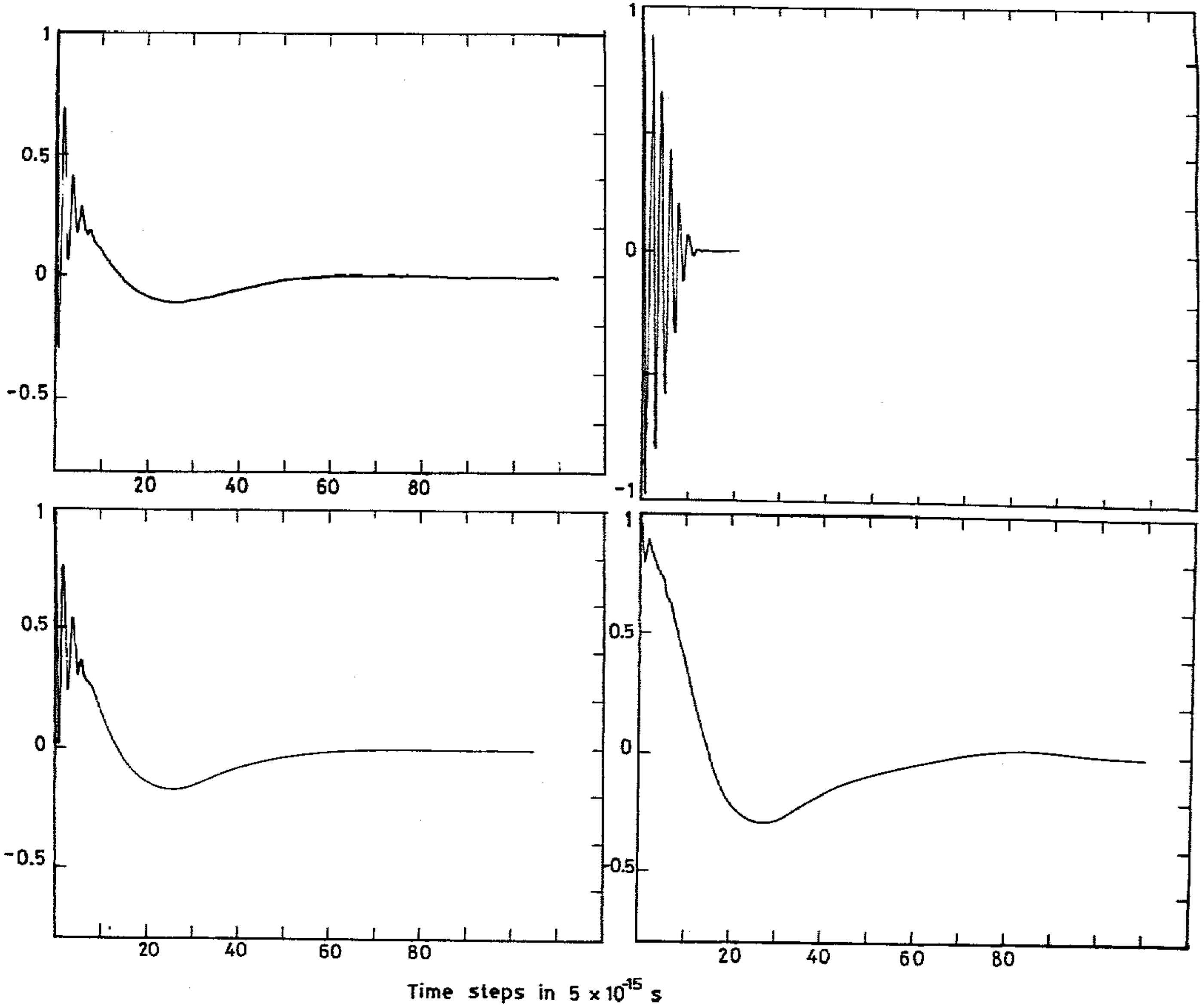

Figure 12 *Examples of* $\langle \dot{\omega}(0) \cdot \dot{\omega}(t) \rangle$ *computed by integrating the equations of motion for two-centre, atom–atom, Lennard-Jones intermolecular potentials: see references in text*

nature. Furthermore, a detailed analysis of the motion does not reveal a white noise of molecular interactions, and here memory functions are very useful in that knowledge of only their short-time details is sufficient to establish the complete time dependence of the auto- or cross-correlation functions.

The dissipation of restricted rotation is the subject of a clearly written implementation of Mori formalism by Atkins and Broomhead.[82d] The decay of a classical hindered rotor over the whole domain of motion from almost free overall rotation to harmonic vibration in a well is examined. This paper contains a particularly useful summary of the ideas behind projection operators. By a modification of this formalism involving the separation of dynamical and lattice time-scales, it goes on to describe the decay with a canonical transformation into a hindered rotating frame that rotates and oscillates in accord with the unperturbed equation of motion of two coaxial dipoles. The results conform to a skeletal reality in that 'real' fluids are more complicated but their rotational molecular behaviour is well described by this simplest of potentials.

Volume 34 of *Advances in Chemical Physics*[82e] published in August 1976, contains some reviews relevant to this report. In Steele's article virtually all the relaxation work up to 1974 is described for three selected fluids, CH_4, C_6H_6 and CH_3I, although a consensus between the different techniques available has not been achieved to any satisfactory degree. van Kampen presents the mesoscopic approach to statistical problems and roots out many of the basic misconceptions and misuses in recent literature, but confines himself to Markovian problems which is time-graining on too coarse a scale for most modern spectroscopists. Anderson, Chandler, and Weeks review the equilibrium structure of dense fluids, which is determined, except for H-bonded systems, by repulsive forces.

At the Faraday Symposium of Dec. 1976,[82c] Deutch reviewed critically the theory of dielectric relaxation in rigid dipolar fluids and emphasizes the need for work on the same systems with different techniques, *cf*. Steele (*loc. cit.*). It is apparent that the ability of dielectric measurements to resolve different models of molecular orientational dynamics is limited.

In the same meeting, Searby, Bezot, and Sixou provided a very useful, incisive review of many light-scattering theories which will be mentioned briefly below. They studied the behaviour of I_{VH} for liquids of small molecules with low viscosity, 'ordinary' liquids (such as chlorobenzene), supercooled liquids, and liquid crystals in the isotropic phase. The coupling parameters from *VH* and *HH* spectra, that is those between molecular orientation and transverse or longitudinal shear waves in the liquid, are assessed. The former are strongly propagative at low temperatures in a viscous medium, but as the viscosity is decreased these waves become progressively 'softer' and eventually become purely diffusive. The *VH* spectra for supercooled liquids are difficult to fit with the existing 'two-variable' microscopic theories, since a very weak depolarized doublet appears on the wings of the central line, indicating the presence of well-defined propagating shear waves. This observation suggests that a third variable is needed in the microscopic theories, that is one of the so-called 'fast' variables can no longer be averaged out of the equations of motion, and the authors suggest this should be one describing the translational correlations of molecules.

Quentrec[82b] has recently constructed a new set of hydrodynamics equations for a dense fluid using a more generalized version of the approach made by de Gennes.[82f] He introduced two microscopic variables into his equations of motion. The first is the tensor used by de Gennes and describes the local orientational order, and the second is an analogous tensor describing the local translational order of the molecules. However, the calculations have yet to be applied to depolarized light scattering.

It seems on the slender experimental evidence available that the empirical exponential form for $K_1(t)$ reproduces far i.r. *induced* absorption bands in non-dipolar fluids satisfactorily (but what this means on the molecular scale in some cases is still obscure); but satisfactorily only for *some* of the data available for dipolar liquids, even after allowing for induced absorption. However, one pleasing facet of the formalism is its behaviour in the limit of very high torque $[K_1(0)]$ which is found in the nematic mesophase of a molecule such as 4-n-heptyl-4′-cyanobiphenyl (HCB). With a dipole moment aligned in the long axis, rotational absorptions can be confined to torsion about the mutually perpendicular short axes, a process which can, energetically, be simulated (see Table 2) with a very high $K_1(0)$. The theoretical result is a good fit to Moutran's MHz data[79] where the low-frequency process occurs. The far i.r. spectral consequence of this fit is found by extrapolating the theoretical curve six decades higher to submillimetre (THz) frequencies. This results in a narrow librational peak at 137 cm^{-1} which is 11 cm^{-1} short of the observed band assigned on general spectroscopic evidence to an intermolecular origin. This suggests the general principle that every sharply distinct far i.r. librational mode is linked to a low-frequency loss process (Figure 13), and that the two absorptions are part of the same overall dynamical process, and are describable by the same, continuous mathematical function of frequency the presence of one being an inevitable consequence of the other.

The simplest form for the intensity $I_{VH}(\omega)$ of depolarized light scattered in

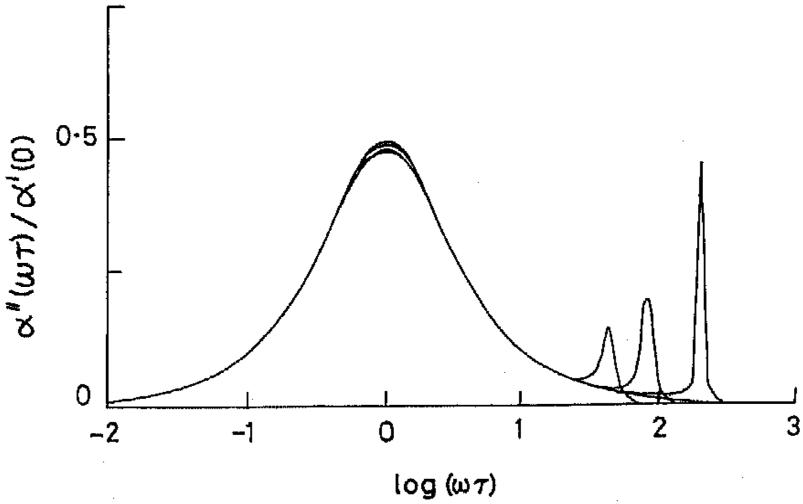

Figure 13 *Loss curves for the itinerant oscillator model of molecular motion, corrected for inertial effects*
(Reproduced by permission from a personal communication by W. T. Coffey and J. H. Calderwood, to be published)

three-variable theory [exponential $K_1(t)$] is equation (25), where $\alpha_\parallel$ and $\alpha_\perp$ are components of the polarizability anisotropy. This falls off as ω^{-6} at high frequencies, and analogously with the far i.r. such an equation has been used[83a] to describe both the intra- and inter-molecular contributions to the total scattered intensity in 'computer argon'[84] and for real acetone, methyl iodide, and benzene up to several kbar, using the results of Dill *et al.*[58] In general, the depolarized Rayleigh spectral intensity is the Fourier transform of a correlation function which can be written as equation (26), where $C_{\text{ind}}(t)$ is the contribution from intermolecular collisions which alone exists in molecules such as CCl_4 with scalar polarizabilities. $C_{\text{ip}}(t)$ accounts for cross-correlation between permanent and induced polarizability components. In the specific case of autocorrelation in linear molecules, $C_{\text{perm}}(t)$ is given by equation (19), but cross-correlations of $C_{\text{perm}}(t)$ and the last two terms of equation (26) are much more difficult to derive explicitly in terms of vectors such as $\boldsymbol{u}$. The computer simulation of Alder *et al.*[84] produced the characteristic exponential decay of the interaction-induced Rayleigh band in argon by assuming a dipole-induced dipole interaction mechanism for $C_{\text{ind}}(t)$ for which $\beta(r) = 6\alpha_0^2/r^3$, where α_0 is the atomic polarizability and r the interatomic distance. This gives $C_{\text{ind}}(t)$ as equation (27); here u_{ij} is a unit vector along the line joining the pair ij.

$$I_{VH}(\omega) \propto \frac{(\alpha_\parallel - \alpha_\perp)K_0(0)K_1(0)\gamma}{\gamma[K_0(0) - \omega^2]^2 + \omega^2\{\omega^2 - [K_0(0) + K_1(0)]\}^2} \tag{25}$$

$$C(t) = C_{\text{perm}}(t) + C_{\text{ind}}(t) + C_{\text{ip}}(t) \tag{26}$$

$$C_{\text{ind}}(t) = \sum_{k\neq l}\sum_{i\neq j} \langle \beta[r_{ij}(0)]\beta[r_{kl}(t)]P_2[u_{ij}(0)\cdot u_{kl}(t)]\rangle \tag{27}$$

The $C_{\text{ind}}(t)$ estimated by the best fit[83] of the Fourier transform of equation (27) to the computer data all have exponential tails which are significantly positive at fairly long times (Figure 14). This could be indicative of those long hydrodynamic tails[85] whose origin is in the collective, shearing motions of many molecules over a significant range of molecular diameters. Long tails such as this can be seen in computer simulations[7] of $K_0(t)$ and were an original objective in Alder's investigation, but seem to have a more involved dependence on time than $t^{-3/2}$ or e^{-t}. Indeed the vortex motion of which they are a manifestation has long-range implications which indicate that cross-correlations form a very important part of any correlation function observable by depolarized Rayleigh scattering. The results of this fit are shown in Table 3, where it is shown that $\gamma, K_0(0)$, and $K_1(0)$ are proportional to temperature and to amagat density; this makes physical sense since these are torque dependent parameters: the correlation time γ^{-1} of the dynamical process for which $K_1(t)$ is the exponential (Markovian) cross-correlation function is becoming much shorter.

In the case of $C_{\text{perm}}(t)$ in liquid acetone (Figure 15), the fit to the data of Dill *et al.* as corrected by them for induced absorption (see the previous caveat)

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[83] M. W. Evans, *J. C. S. Faraday II*, 1977, **73**, 484.

[84] B. J. Alder, H. L. Strauss, and J. J. Weiss, *J. Chem. Phys.*, 1973, **59**, 1002.

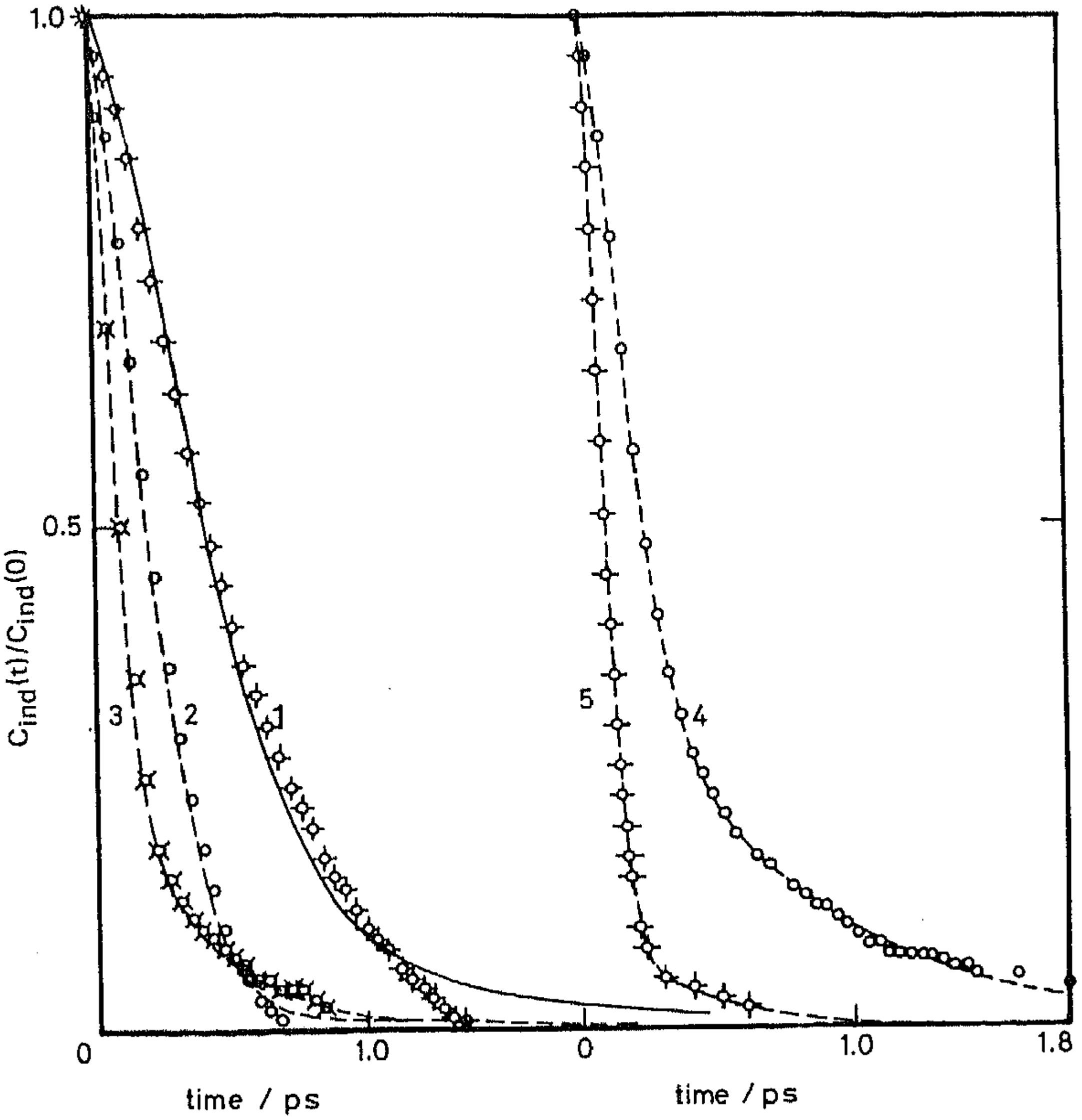

Figure 14 (1) *The points are derived from the computed correlation function* [equation (27)] *for argon at* 300 K, 67 amagat. *The solid line is the least mean squares best fit using three-variable Mori theory.* (2) 300 K, 473 amagat; (3) 300 K, 905 amagat; (4) 960 K, 757 amagat; (5) 90 K, 795 amagat

is again good, and it is encouraging to see from Table 3 that $K_0(0)$ for l.m.s. best fit this time does not vary significantly under free iteration over the pressure range up to a few kilobars, while $K_1(0)$ and γ increase a great deal. Why this should be so theoretically can be seen from equation (19) where the coefficient of t^2 [which is $K_0(0)$] is a single molecule property. For benzene and methyl iodide, the agreement with experiment is poorer, only some of the observed oscillations being followed theoretically. Possible reasons are: (i) they are artefacts caused by the method used to estimate the induced absorption; (ii) accepting the experimental data as accurate, an improvement is needed in the theoretical $C(t)$ which could come either by using a more realistic truncation for $K_1(t)$:

$$K_1(t) = K_1(0)f(t)$$

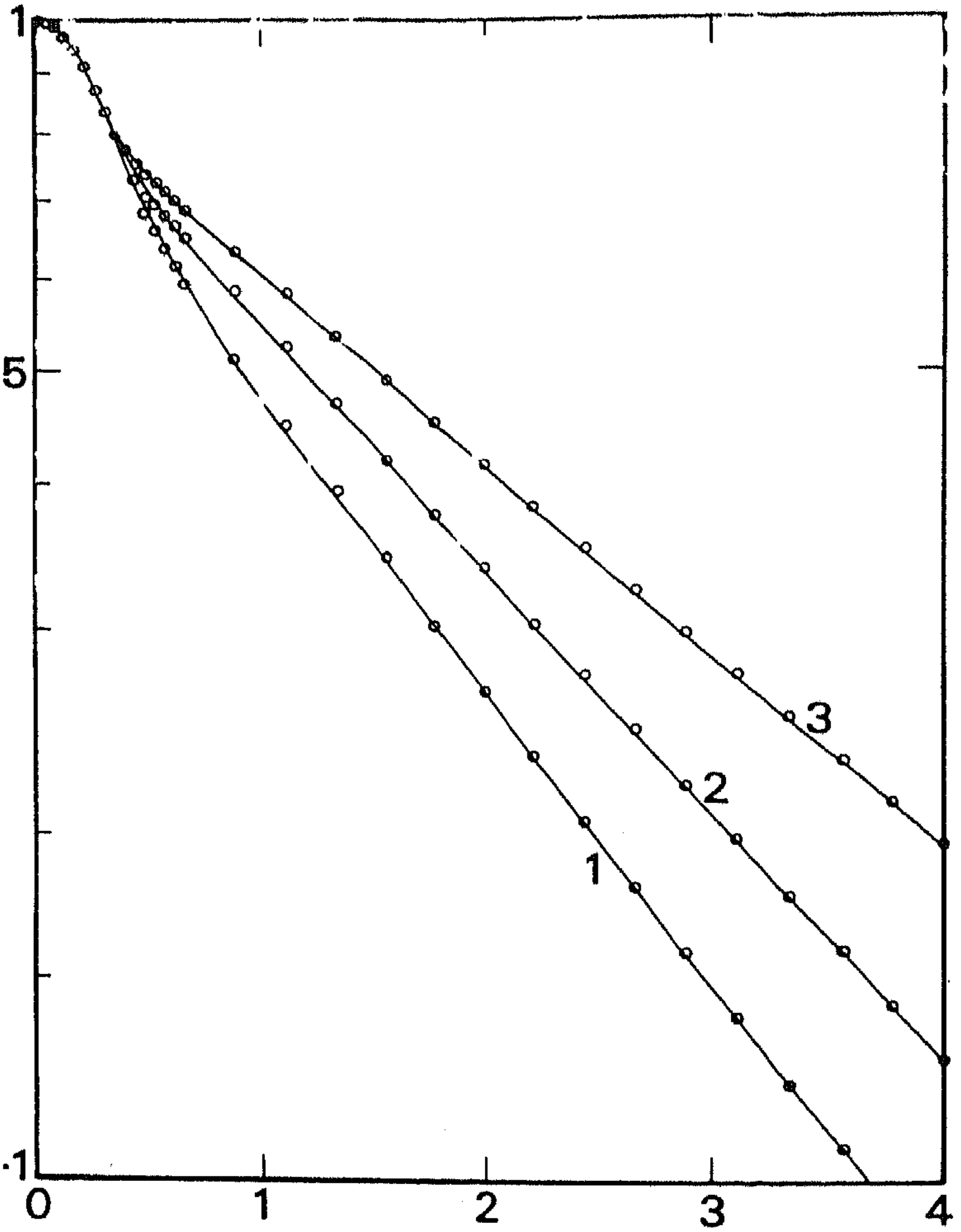

Figure 15 *Rayleigh scattering autocorrelation function of orientation corrected for induced absorption, for liquid acetone. The lines are the best fit with tabulated parameters,* (1) 1 bar, 296 K; (2) 1 kbar, 296 K; (3) 2 kbar, 296 K

where $f(t)$ is, for example, a damped oscillating function; or by using a multi-parameter model based upon truncating the series at higher order.

It is important to note that the form of equation (25) was determined by Berne and Harp and found to *peak*; thus it is capable of reproducing the central dip in the depolarized Rayleigh band observed originally by Stegemann and

Table 3 *Best fit of equation (25) to some experimental*[58] *and computer argon*[84] *data*

System	T/K	P/amagat	$10^{-24}K_0(0)/s^{-2}$	$10^{-24}K_1(0)/s^{-2}$	$10^{-12}\gamma/s^{-2}$
Computer argon	300	67	2.8	22.0	7.7
Computer argon	300	473	8.9	72.0	14.1
Computer argon	300	905	29.0	306.0	28.5
Computer argon	90	795	8.5	101.3	16.2
Computer argon	960	757	35.7	394.6	32.7

System	T/K	P/kbar	$IK_0(0)/kT$	$IK_1(0)kT$	$\gamma(I/kT)^{1/2}$
Acetone (l)	296	0.001	1.8	24.5	7.3
Acetone (l)	296	1.0	1.9	36.3	8.8
Acetone (l)	296	2.0	1.5	41.1	9.7
CH_3I (l)	296	0.001	1.15	21.8	7.2
CH_3I (l)	296	1.00	1.1	23.6	7.5
CH_3I (l)	296	2.50	1.2	42.5	9.8
Benzene (l)	296	0.001	2.1	92.9	14.4
Benzene (l)	296	0.601	1.7	156.3	19.1

Stoicheff,[25] and lately subject to intense theoretical study by, for example, Gershon *et al.*[85] using variants of Mori hydrodynamic theory.

5 Laser Light Scattering and Related Studies

The extensive role of dynamic light scattering in the fields of chemistry, biology, and physics is discussed fully in a recent book by Berne and Pecora.[86] In this section we will concentrate on some of the numerous papers on this topic which appeared from January to October 1976.

The subject of fluorescence correlation spectroscopy (FCS) which may give some information on the fluctuations of the vector u, has been developed considerably in an article by Aragon and Pecora,[87] where a general theory is presented to include the fluorescent intensity consequences of translation and rotational motions and also of chemical reactions in ideal solutions. The principle of the method is to excite fluorescent molecules in dilute solution with a suitable continuous laser source and to analyse the fluctuations of fluorescent intensity by means of an auto-correlator or wave analyser. Apart from fluctuations due to the corpuscular nature of light (photon noise), the emitted

[85] (*a*) N. D. Gershon and I. Oppenheim, in 'Molecular Motions in Liquids', ed. J. Lascombe, Reidel, Dordrecht, 1973, p. 553; (*b*) N. D. Gershon, *Chem. Phys. Letters*, 1974, **27**, 451, 132, 153; 1976, **37**, 589; (*c*) J. Rouch, J. P. Chabrat, L. Letamendia, C. Vaucamps, and N. N. D. Gershon, *J. Chem. Phys.*, 1975, **63**, 1383; (*d*) N. D. Gershon and I. Oppenheim, *Physica*, 1972, **62**, 198; 1973, **64**, 247, 625; 1974, **71**, 131, 134, 527; *J. Chem. Phys.*, 1973, **59**, 1337.

[86] B. J. Berne and R. Pecora, 'Dynamic Light Scattering with Applications to Chemistry, Biology and Physics', Wiley, New York, 1976.

[87] S. R. Aragon and R. Pecora, *J. Chem. Phys.*, 1976, **64**, 1791.

fluorescent intensity varies according to the instantaneous number and orientation of the members of each fluorescent species in the observed sample volume. The number of fluorescers changes owing to diffusion in and out of the observed volume, and by chemical reactions. Since fluorescence is an incoherent process, translational diffusion within the observed volume does not affect the emitted intensity, rotational diffusion does, since the intensity depends on the angular relation between the absorption (emission) transition moment and the polarization vector of the incident beam. Thus the random molecular reorientations introduce fluctuations into the observed intensity.

An exploratory theoretical paper by Titulaer and Deutch[88] looks at the scattering of light by anisotropic impurities at a fluid interface. Two other theoretical papers by Kielich *et al.*[89] deal with interaction effects on the lineshape of hyper-Rayleigh scattered light in molecular liquids and on the second-order intensity correlation tensor of Rayleigh scattered light. In a paper[90] concerning the type of relaxation responsible for sound velocity dispersion at GHz frequencies, determined by light scattering measurements, quite different predictions for the spectrum are obtained, depending on the type of relaxation of the internal variable considered (that is, structural, thermal, or mixed). The theory is applied to glycerol, for which both ultrasonic and light scattering data are available.

A valuable paper by Beysens[91] deals with entropy fluctuations in the medium, differentiated from a multitude of other contributions by appropriate spectral analysis of the scattered light. He points out that the numerous theories[91] put forward to express the ratio of scattered to incident power (the Rayleigh factor) of pure fluids predict quite different refractive index variations. His results for liquids ranging on refractive index from 1.3 to 1.6 show good agreement with some formulations, but others show consistent discrepancies. In reaching these conclusions the use of absolute intensity measurement is avoided because this depends on so many factors since the total light 'scattered' involves Raman lines, relaxation lines, depolarized lines, stray light, *etc.*

Three papers on Rayleigh/Raman scattering[92] deal with the molecular motions of CH_2Br_2, CH_3I, and 1,2,5-thiadiazole over ranges of concentration and temperature. Combining the results yields significantly more information than can be obtained from either technique alone. In pure CH_2Br_2 liquid the classical Stokes–Einstein relation for rotational diffusion does not apply, despite the fact that the Rayleigh relaxation time (τ_R) is linear in η/T, where η is the viscosity. The authors edit out cross-correlation effects in τ_R by extrapolating to zero CH_2Br_2 concentration and obtain τ_s, the single particle reorientational relaxation time. According to Keyes and Kivelson, using two variable Mori

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[88] U. M. Titulaer and J. M. Deutch, *J. Chem. Phys.*, 1976, **64**, 1895.

[89] (*a*) T. Bancewicz and S. Kielich, *Mol. Phys.*, 1976, **31**, 615; (*b*) M. Kozierowski, R. Tanás, and S. Kielich, *ibid.*, p. 529.

[90] C. Allain-Demoulin, P. Lallem, and N. Ostrowsky, *Mol. Phys.*, 1976, **31**, 581.

[91] D. Beysens, *J. Chem. Phys.*, 1976, **64**, 2579.

[92] (*a*) C. H. Wang, D. R. Jones, and D. H. Christensen, *J. Chem. Phys.*, 1976, **64**, 2820; (*b*) C. K. Cheung, D. R. Jones, and C. H. Wang, *ibid.*, p. 3567; (*c*) D. R. Jones, C. H. Wang, D. H. Christensen, and O. F. Nielson, *ibid.*, p. 4475.

formalism, these are related by equation (28),

$$\tau_{\mathrm{R}}^{-1} = \tau_{\mathrm{s}}^{-1}(1 + gn)(1 + fn)^{-1} \tag{28}$$

where f and g are respectively the measures of average static and dynamic pair orientational correlations and n is the molecular number density of the solute, CH_2Br_2. In general, τ_{R} is 'slowed down' by cross-correlations. They obtain the Raman auto-correlation function by dividing our equation (22) by equation (21), the area under which gives the correlation time τ_{Ram}. The time τ_{s} appears larger than τ_{Ram} extracted from the ν_2 band (symmetric H–C–H bend) but is smaller than those from the ν_3 or ν_4.

A paper by Jones and Wang[93] uses depolarized Rayleigh scattering to study the backbone motion of poly(propylene glycol) as a function of polymer molecular weight, concentration, and temperature. The difference from dielectric results[94] indicates that dielectric relaxations are almost exclusively dependent on the reorientation of polymer segments, whereas the light- and neutron-scattering experiments are also sensitive to local overdamped torsional oscillations.

Transverse collective modes in liquid pyridine have been studied in a useful paper by Searby *et al.*[95] The *HH* (polarized) fine structure is particularly well resolved and is visible over a wider temperature range than the *VH* fine structure.[96] Both are analysed in terms of the Keyes–Kivelson development of hydrodynamic Mori formalism.

Tsay and Kivelson[97] have recently calculated an expression for the *VH* spectrum with a finite coupling constant R, and which contains terms of higher order in k, the wave vector; but this seems to be erroneous since it contains terms of different dimensions.

A number of gases have been studied by Rayleigh–Brillouin scattering,[98] namely those with internal relaxation (CO, N_2, C_2F_6, and C_2H_6 at 302 K in both kinetic and hydrodynamic regions) and mixtures of rare gases (He–Kr and Ar–Kr). For N_2 and CO_2 the Mountain theory for a fluid with a relaxing bulk viscosity fitted the data adequately over the whole pressure range. In the hydrodynamic regime the approach of Weinberg, Kapral, and Dasai gives a good fit to the C_2F_6 and C_2H_6 data as long as only one relaxation frequency is comparable to the Brillouin frequency.

6 Recent Relevant Papers

Some new ground has been covered in the application of the dynamic Kerr effect[99] to the reorientational motions of molecules. The dielectric and

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[93] D. R. Jones and C. H. Wang, *J. Chem. Phys.*, 1976, **65**, 1835.

[94] S. Yano, B. R. Rahalkar, S. P. Hunter, C. H. Wang, and R. H. Boyd, *J. Polymer Sci.*, (to be published).

[95] G. M. Searby, P. Bezot, and P. Sixou, *J. Chem. Phys.*, 1976, **64**, 1485.

[96] G. R. Alms, D. R. Bauer, J. I. Braunan, and R. Pecora, *J. Chem Phys.*, 1973, **59**, 5304.

[97] S. J. Tsay and D. Kivelson, *Mol. Phys.*, 1975, **29**, 1.

[98] Q. H. Lao, P. E. Schoen, and B. Chu, *J. Chem. Phys.*, 1976, **64**, 3547; (*b*) Q. H. Lao, P. E. Schoen, B. Chu and D. A. Jackson, *ibid.*, p. 5013.

[99] M. S Beevers, J. Crossley, D. C. Garrington, and G. Williams, *J. C. S. Faraday II*, 1976, **72**, 1482.

Kerr-effect relaxations are considered for the models of rotational diffusion and 'defect' diffusion. Kerr-transient data and dielectric data, when combined, are useful means of discriminating between different mechanisms of molecular reorientation.

At the Faraday Symposium, Beevers, Crossley, Garrington, and Williams presented[82c] further joint studies of dielectric relaxation and dynamic Kerr effects in the frequency range 10^4 to 10^{-2} Hz in supercooled fluorenone/*o*-terphenyl and tri-n-butyl ammonium picrate/*o*-terphenyl solutions. The single process observed is due to the reorientational motions of the dipolar solute molecules. The dielectric relaxation times τ_D and the Kerr effect decay times $\tau_{K,d}$ were found to be the same for the fluorenone/*o*-terphenyl system, which is inconsistent with small angle rotational diffusion. The data are discussed in terms of models of cooperative reorientation in viscous liquids. At the same meeting, Madden reviewed the theory of resonance scattering of light to clarify the relation between the lineshape and various relaxation processes. Experimental points are fully discussed in terms of a novel spinning cell system for scattering studies. Dorfmüller, Fytas, Mersch, and Samios presented a polarized light scattering study of relaxation in simple liquids based on the sound velocity dispersion in the ranges 1.1–1.4 ps and 10–100 ps respectively.

In a paper by Fury and Jonas[100] the viscosity dependence of n.m.r. and Raman single particle correlation times is developed further in terms of the hydrodynamic slip limit theory of Hu and Zwanzig[101] and the K parameter of Kivelson *et al.*[102] These theories emphasize the importance of molecular shape (see Anderson *et al.* in ref. 82*e*) in determining the viscosity dependence of reorientation. The analysis of much high-pressure data shows K to be independent of pressure and temperature; and, importantly, the coupling between translational and rotational motions as characterized by K is dominated by the molecular shape (the repulsion part of the interaction potential). This viewpoint is endorsed in a theoretical paper by Berne and Montgomery[103] on such coupling in a fluid of rough spheres; using Mori formalism they calculated the correlation functions for thermal neutron and laser light scattering in the binary collision approximation. The maximum deviation between the coupled and uncoupled results occur for wavenumbers commonly found in thermal neutron scattering, and translation–rotation is, in the authors' opinion, clearly important in the calculation of correlation times in certain regions. They make the point that the deviation will become increasingly important the *larger* the separation in the time scales characterizing the linear and angular momentum decays, that is in dense fluids of the more anisotropic molecules.

Rotation–translation Fokker–Planck equations have been developed recently by Glen Evans[104] in order to study, among other things, the hydrodynamic

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[100] M. Fury and J. Jonas, *J. Chem. Phys.*, 1976, **65**, 2206.

[101] C. Hu and R. Zwanzig, *J. Chem. Phys.*, 1974, **60**, 4354.

[102] (*a*) R. E. D. McClung and D. Kivelson, *J. Chem. Phys.*, 1968, **49**, 3380; (*b*) D. Kivelson, M. G. Kivelson and I. Oppenheim, *ibid.*, 1970, **52**, 1810; (*c*) J. Hwang, D. Kivelson, and W. Placky, *ibid.*, 1973, **58**, 1753.

[103] B. J. Berne and J. A. Montgomery, *Mol. Phys.*, 1976, **32**, 363.

[104] Glen Evans, *J. Chem. Phys.*, 1976, **65**, 3030.

coupling. In dense fluids the streaming part of the Liouville operator (that part between collisions), can be treated perturbatively owing to the dominance of the collision operator, and only a few terms in the cumulant expansion used need be calculated. Using the second cumulant alone is equivalent to a two-variable Mori theory. The most interesting and immediately significant result of this exposition is that for Brownian particle in a continuous fluid, the hydrodynamic part of the coupling tensor (the torque-force autocorrelation function) which measures the effect of the coupling on the orientational correlation function and the orientational time is minimal, even for a propellor-like molecule such as biphenyl. In Brownian rods of $C_{\infty v}$ or $D_{\infty h}$ symmetry this coupling *vanishes*, and in general for most molecules having a C_n axis and a few mirror planes. Therefore the single-particle reorientational autocorrelation functions for a Brownian particle are insensitive probes of the coupling of translational and rotational motions. Thus the far i.r. spectrum (Poley absorption) of dense fluids is usefully dominated by orientational effects in the Brownian regions. The topic was also treated by Berne in the Faraday Symposium:[82c] he has extended the use of hydrodynamic models of molecular translation to the rotational case, where the discrepancy between theory and measurement is much larger. One conclusion is that transport coefficients, for example, may not be calculable with the presently available molecular dynamics algorithms.

Beer and Pecora found,[82c] from depolarized Rayleigh spectroscopy, that the collective (multi-particle) reorientation times of the three xylenes in concentrated solution or in the pure liquid have very different viscosity dependences, while the single molecule times (auto-correlation) have the same dependences. It is concluded that dipolar forces are not the dominant influence in determining the orientational correlations in these liquids. Stuckart, Montrose and Litovitz,[82c] compared induced light scattering and i.r. absorption in fluids such as Ne, Ar, Kr, Xe, CH_4 and CF_4. The spectra were analysed with a two-component induction mechanism for the light scattering (a long-range dipole-induced dipole and a short-range mechanism) and a single short-range interaction for the far i.r. It was concluded that at liquid densities the high-frequency parts of both spectra arise from isolated binary collisions. It is argued that the short-range interaction mechanisms in the molecular and atomic liquids are the same if interactions are considered as occurring between the individual atoms of neighbouring molecules.

Frenkel and van der Elsken[82c, 105] have approached the difficult problem of induced absorption in dense fluids, where at a certain stage one needs to know the correlation function of a dynamical variable in terms of its dependence on the separation between two particles. Assuming this dynamical variable to be pairwise additive, it is possible to relate the time-dependent four-point density correlation function $f(r_1, r_2, r_3, r_4; t)$ to the process under consideration. It is possible to compute the correlation functions, $g_1(t)$, of the different parts of the perturbing potential, which of course depends on the dynamics of the surrounding molecules.

[105] D. Frenkel and J. van der Elsken, *Chem. Phys. Letters*, 1976, **40**, 14.

7 Summary

The following points present themselves from a consideration of the present state of relaxation studies.

(1) There is an obvious and pressing need to co-ordinate research into the relaxation properties of a few representative fluids by simultaneous use of all the techniques available (*e.g.* Rayleigh/Raman scattering, near and far i.r. spectroscopy, slow neutron scattering, spin–spin, spin–rotation, and quadrupole n.m.r. relaxation, dynamic Kerr effect, and the newer methods such as depolarization of fluorescence which are just being developed). The study should be over a wide range of temperature, if possible at a constant number density, and *vice versa*. Any analytical theory which adequately represented such data would be of substantial significance.

(2) There are drawbacks and difficulties to each separate technique, both theoretical and experimental in origin, which ought not to be underemphasized. In particular the roles of vibrational relaxation, collision-induced absorption, and the dynamic internal field in electro-optical effects need careful consideration.

(3) The original *M* and *J* diffusion models are over-used. They are useful and relatively easy to apply to experimental results, but they were never intended as anything more than simplistic models with the least number of arbitrary parameters. This formalism in a refined version will continue to be used but, it is to be hoped, not at the expense of other, more general theories.

(4) Experimentalists should try to determine whether the Mori hydrodynamic formalism is really capable of reproducing their data as suggested in point (1). There is a school of thought[106] which relegates the Mori continued fraction to the status of a mere Taylor expansion, and emphasizes the non-rigorous nature of an impressionist formalism. Scaife[106] has revealed some internal inconsistencies in Kubo's own derivation of his second fluctuation–dissipation theorem. However, the derivation of Berne *et al.*[7] seems to be sound.

(5) Molecular dynamics is potentially a powerful technique given the correct potentials. It is capable, with generous allocation of computer time, of yielding much of the desired insight into the fluid state.

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[106] Conference on Brownian Motion, Institute for Advanced Studies, Dublin, Ireland, August, 1976.