2 The Motion of Simple Molecules in Liquids

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1 Introduction

In a dilute gas the molecules move freely with a spread of velocities given by the Maxwell–Boltzmann distribution. After they have moved for distances many times their diameters they collide with other molecules and are deflected into new rectilinear paths. Their mean motion over a long time is measured by the coefficient of diffusion, which can be expressed in terms of the angles of deflection of the colliding pairs.[1]

In liquids matters are not so simple since each molecule is in perpetual interaction with its neighbours; there are no mean-free-paths and no binary collisions. Molecules can also rotate in an irregular manner about one or more axes under the influence of the torques exerted by their neighbours or by an external field. The molecular motions can be studied on a macroscopic scale by measuring, for example, rates of diffusion or dielectric relaxation, but the relation of these crude macroscopic averages to what is happening at a molecular level is a difficult task. The purpose of this review is to describe the progress that has been made in this field in the past ten years.

Sections 2 and 3 introduce the statistical language used to describe molecular motion, the language of correlation functions and their spectra, or Fourier transforms. Perhaps the greatest advance of the past ten years has been the systematic use of this language to describe ever-increasing regions of chemical physics: statistical mechanics, the scattering of light, X-rays and neutrons, i.r., Raman and n.m.r. spectroscopy are subjects which have gained in precision and unity from these developments. Section 4 describes the measurement and computer simulation of the correlation functions of a monatomic liquid. Sections 5—7 extend the discussion to simple molecular liquids with emphasis on the study of orientational correlation functions by far-i.r. spectroscopy and light scattering. We give no derivations or proofs, only statements and references.

2 The Velocity Auto-correlation Function

A *distribution function* is an answer to a question of the following form: if there is a molecule with a specified position, orientation, velocity *etc.* at a certain time $t = 0$, what is the probability that there will be a molecule (the same or different) at a position distant by r, with an orientation changed by ϕ, with a velocity increased by v

[1] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, 'Molecular Theory of Gases and Liquids', Wiley, New York, 1954.

etc., at a time t? Such a function can be very complicated but often we are not interested in all these variables. Thus the equilibrium or thermodynamic properties are described by a time-averaged distribution function, or, what is equivalent, by an average taken over an ensemble of systems at a fixed time $t = 0$. They are functions of r and ϕ alone or, in a monatomic fluid, of r alone.[2] The dynamic and transport properties in which we are here interested can be described only if we know the time evolution of these functions, but then we can often ignore one of the other variables, *e.g.* r or ϕ.

The term *correlation function* (which we abbreviate c.f.) is used to describe a distribution function which has been normalized so as to approach zero for large values of the argument r and/or t (as is appropriate). It describes the degree of correlation between two events; such correlation is zero at large times or distances in an isotropic fluid. The most familiar distribution function is probably the radial function $g(r)$, which describes the equilibrium probability of there being two molecules at a separation r, and which can be measured from the X-ray diffraction pattern. At large separations this approaches unity (see below, Section 3), and the corresponding c.f. is therefore $g(r) - 1$, which is usually called $h(r)$, the total correlation function. We consider below (Section 3) the generalization of $h(r)$ to include time-dependence but start first with a more simple one-molecule c.f., the velocity auto-correlation function.

If a molecule has a velocity $v(0)$ at $t = 0$, and a velocity $v(t)$ at time t then a suitable measure of the degree of correlation of these velocities is the scalar product $v(0) \cdot v(t)$. After a sufficiently long time, *e.g.* 10^{-10} s, the magnitude and direction of $v(t)$ will bear no relation to that of $v(0)$ and so the scalar product goes to zero. The velocity auto-correlation function is defined as the average of this product over all molecules in a system at equilibrium, and is denoted $\langle v(0) \cdot v(t) \rangle$. It is convenient to use the symbol $\psi(t)$ for the normalized function $\langle v(0) \cdot v(t) \rangle / \langle v(0)^2 \rangle$. The importance of this function is its close relation to the coefficient of diffusion, but before discussing this it is useful to examine the behaviour of correlation functions in general, and this one in particular, as functions of time.

Consider first an almost collision-free gas in which a molecule has the same velocity at t as it has at $t = 0$. Hence the c.f. $\psi(t)$ is a constant, namely unity, since

$$\langle v(0) \cdot v(t) \rangle = \langle v(0)^2 \rangle = 3kT/m \tag{1}$$

where m is the mass of the molecule. A second idealized case is the perfect Einstein solid in which a molecule vibrates about a site at a constant angular frequency ω_E; here the c.f. is an oscillatory function proportional to $\cos(\omega_E t)$. A liquid behaves in an intermediate fashion as is shown in Figure 1, which is based on a computer simulation discussed in Section 4. The c.f. is constant or gas-like at short times (typically $t < 10^{-13}$ s), it oscillates weakly, and goes to zero at long times. The first negative region is easily explained as the rebound as a molecule reverses its velocity on colliding with a neighbour after travelling on average for the mean molecular separation.

[2] (*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 University Press, 1974; (*c*) A. F. M. Barton, 'The Dynamic Liquid State', Longmans, London, 1974.
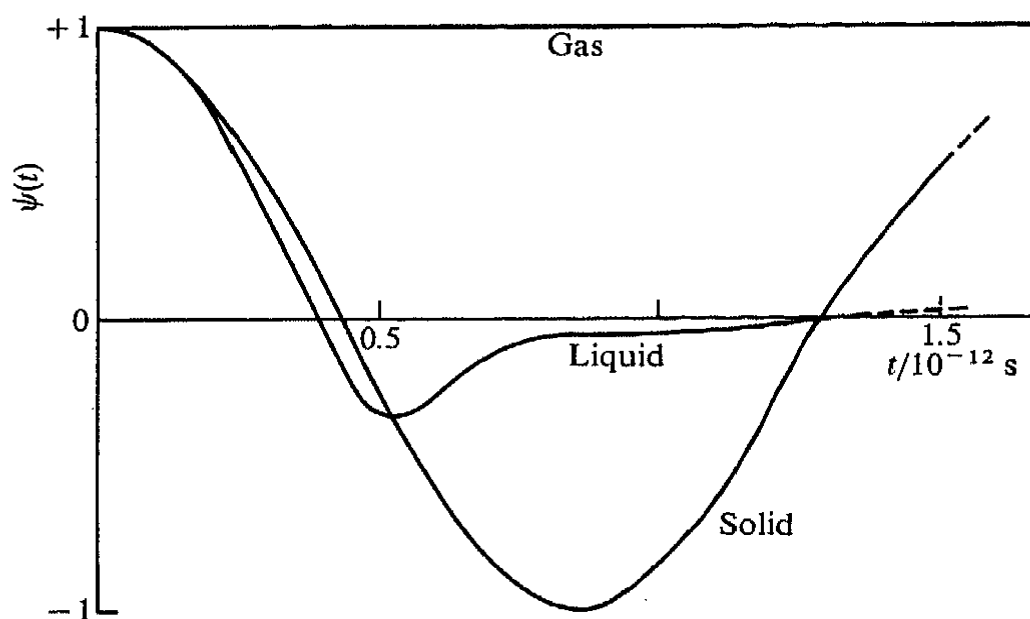
Figure 1 *The normalized velocity auto-correlation function for a collision-free gas, for an Einstein solid and for a liquid. The last is based on results obtained by computer simulation discussed in Section 4*

Each c.f. has a Fourier transform, and if the variable of the c.f. is time, as here, then that of the transform is frequency. We define the transform of $\psi(t)$ by

$$\tilde{\psi}(\omega) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \psi(t)e^{-i\omega t} \, dt \tag{2}$$

and, conversely, we have also the important relation

$$\psi(t) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} \tilde{\psi}(\omega)e^{i\omega t} \, d\omega \tag{3}$$

The function $\tilde{\psi}(\omega)$ is called the spectrum of $\psi(t)$ since it can be regarded as the 'sampling' of $\psi(t)$ by a signal of frequency ω. It is often easier to measure the spectra than the functions themselves. Equations (2) and (3) show that we can pass freely from c.f. to its spectrum, and *vice versa*, providing we know one of them for all values of its argument. In practice this is a considerable restriction.

The spectra of the three cases considered above can be found at once. If $\psi(t)$ is unity, then $\tilde{\psi}(\omega)$ is zero unless $\omega = 0$, and is infinite if $\omega = 0$. That is,

$$\tilde{\psi}(\omega) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_{-\infty}^{\infty} e^{-i\omega t} \, dt = (2\pi)^{\frac{1}{2}} \, \delta(\omega) \tag{4}$$

where $\delta(\omega)$ is Dirac's delta function. This is zero everywhere except where its argument is zero, where it is infinite, and it is normalized to unity,

$$\int_{-\infty}^{\infty} f(x)\delta(x - x^*) \, dx = f(x^*) \qquad \int_{-\infty}^{\infty} \delta(x) \, dx = 1 \tag{5}$$
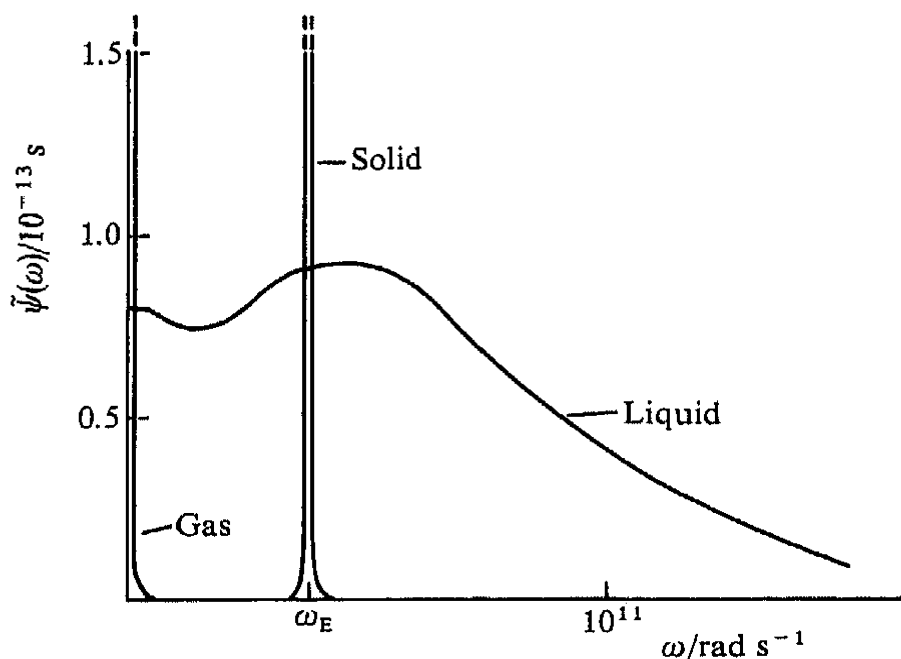
Figure 2   *The Fourier transforms of the correlation functions of Figure 1. Those for gas and solid are delta-functions, whilst that for the liquid has two broad components, a diffusive mode centred on $\omega = 0$, and an oscillatory mode at frequencies comparable with ω_E of the solid*

Thus the spectrum of a collision-free gas is a sharp line at zero-frequency; it will be seen below that the diffusion coefficient is then infinite. For an Einstein solid the c.f. is obtained by integrating the product of $e^{-i\omega t}$ and $\cos(\omega_E t)$, and this integral is zero unless $\omega = \omega_E$, so that the spectrum is now a sharp line at the Einstein frequency, or $\psi(\omega)$ is proportional to $\delta(\omega - \omega_E)$. For a liquid we have again both features in the spectrum. The integration of the curve in Figure 1 produces a spectrum with two peaks, characteristic of diffusional and oscillatory motion, but both are now very broad (Figure 2).

Thus the c.f. and its spectrum enable us to describe succinctly the essential features of translational motion in a liquid more accurately than was possible with the 'models' of the liquid state that used to be so popular; in which diffusion, for example, might be treated as an activated jump from one site to another. However, if we are to use these correlation functions we must be able to observe them or their spectra, to relate them on the one hand to macroscopic properties such as diffusion coefficients, and on the other to intermolecular forces by the methods of statistical mechanics. In the rest of this section we say something of the second of these problems, and touch on the fringes of the third. The first, the measurement of correlation functions, we cover in Section 4.

The connection between correlation functions and macroscopic properties is a consequence of two broad and related generalizations which lie at the root of our present understanding of transport properties. These are linear response theory and a theorem linking dissipative processes and the regression of fluctuations. Neither is new, for specialized versions of both were used for many years by Einstein, Onsager, and others, but the realization of their power and generality is much more recent; it

stems from the work of Callen, Green, Kubo, and others[3-6] during the years 1955—1965. Linear response theory describes the behaviour of two weakly coupled systems, as for example, when a beam of light or neutrons interacts with, and is scattered by a liquid, or when a beam of sound is absorbed and dispersed. Because the coupling is weak it follows that the response of the liquid can be calculated from a knowledge of its behaviour in the absence of the stimulus. This behaviour is described in terms of correlation functions of the appropriate dynamical variables (velocities, energies, *etc.*) in which the averages denoted by angle brackets are, it is important to note, averages over a system at equilibrium. By suitable ingenuity (sometimes called 'indirect Kubo methods') the stimulus can be chosen so that the response can include diffusional or viscous motion, or transport of thermal energy,[3,4] and so we are able to relate these transport, or non-thermodynamic, properties to averages over systems at equilibrium.

The theorem on fluctuations stems from a hypothesis due to Onsager which lies behind his reciprocal relations between coupled transport processes. Every system at equilibrium exhibits small departures from the average values of unconstrained dynamical properties (*e.g.* fluctuations of energy in a system at fixed temperature). These fluctuations regress with time and Onsager's result is that the average rate of their regression is governed by the usual macroscopic transport coefficients (*e.g.* thermal conductivity for thermal energy).[7] Again, we have this direct relation between a transport or dissipation process and a purely equilibrium phenomenon, *viz.* fluctuations.

These theorems lead to simple relations between the transport properties and the correlation functions, relations which can now be derived in at least six different ways of different assumptions and rigour,[3] and about whose truth there can now be no doubt. The first relation, due originally to Einstein, is the one most directly connected with the subject of this review for it shows that the coefficient of diffusion is the time-average of the velocity c.f.

$$D = \int_0^\infty \langle v(0) \cdot v(t) \rangle \, dt \tag{6}$$

or, from equation (3)

$$D = \frac{3kT}{2m}(2\pi)^{\frac{1}{2}} \tilde{\psi}(0) \tag{7}$$

It is characteristic of hydrodynamic properties such as diffusion and viscosity, that they are related to the zero-frequency intercept (Figure 2) of $\tilde{\psi}$ and similar functions. In fact the spectrum of a time-dependent c.f. can be regarded as a frequency-

The second problem, the relation of a c.f. to the underlying molecular behaviour, is more difficult and largely unsolved. One useful route which has been much followed recently is to express the c.f. in terms of so-called *memory functions*, which are believed to have more simple structures. This idea has a lot in common with the reduction of the total (static) correlation function $h(r)$ by expressing it in terms of the apparently more simple direct correlation function $c(r)$ of Ornstein and Zernike.[9,10] This reduction, which was re-introduced into modern statistical mechanics by Rushbrooke and Scoins,[11] has proved to be particularly fruitful, for it is easier to make intelligent approximations for $c(r)$ than for $h(r)$; for example, the Percus–Yevick approximation which lies behind much recent work on the static structure of liquids.[2,10] The introduction of memory functions into the time-dependent correlation functions is leading to equally fruitful approximations.

This approach is best described by discussing first the problem of Brownian motion, or the diffusion of a particle of essentially infinite mass m. Its motion may be described by Langevin's equation[6]

$$m\dot{v}(t) = -mcv + K(t) \qquad (8)$$

which separates the total force into two parts, a frictional retardation proportional to the velocity (c is a constant), and a randomly fluctuating force $K(t)$ which arises from the impacts of the molecules of the liquid in which the particle is suspended. The two forces are not unrelated for interaction with the molecules of the liquid is also the cause of the frictional retardation. This relation between the random and the systematic components is a very general phenomenon and when put into precise form becomes the mathematical expression of the fluctuation-dissipation theorem.[4]

Since the molecules hitting the Brownian particle are light, and their impacts frequent and (almost) independent, it is usual to assume that $K(t)$ is a Gaussian process with a correlation time negligibly short compared with the time steps of the Brownian motion. That is

$$\langle K(0) \cdot K(t) \rangle \propto \delta(t) \qquad (9)$$

It follows[3,4,6] that the velocity c.f. of the Brownian particle is an exponential in the magnitude of the time:

$$\langle v(0) \cdot v(t) \rangle = \langle v^2 \rangle \exp(-c|t|) \qquad (10)$$

and

$$D = kT/mc \qquad (11)$$

where c is the constant in equation (8). Such exponential decay is a valid solution for a massive particle but it will not do if the particle is itself one of the molecules of the liquid. The results in Figure 1 show that $\psi(t)$ is more complicated than (10), and, moreover, it is an even function of time whose derivative vanishes at $t = 0$, for at infinitessimally short times $v(t)$ must be the same as $v(0)$. Langevin's equation has

[9] L. S. Ornstein and F. Zernike, *Proc. Acad. Sci. Amsterdam*, 1914, **17**, 793, reprinted in 'Equilibrium Theory of Classical Fluids', ed. H. L. Frisch and J. L. Lebovitz, Benjamin, New York, 1964.
[10] A. Münster, 'Statistical Thermodynamics', Springer-Verlag, Berlin, 1969, Vol. 1, Chap. 10.
[11] G. S. Rushbrooke and H. I. Scoins, *Proc. Roy. Soc.*, 1953, **A216**, 203.

therefore been generalized for the discussion of molecular motion by the replacement of the constant c by what is, in effect, a frequency-dependent coefficient of friction. We write

$$m\dot{v}(t) = -m \int_0^t v(t-t')M_0(t')\,dt' + K(t) \tag{12}$$

where $M_0(t)$ is a memory function which describes the past history of the friction, which is itself a correlation function, and which therefore has, in turn, a memory function which describes its own evolution.[6] That is, there exists a function $M_1(t)$ defined by

$$\dot{M}_0(t) = -\int_0^t M_0(t-t')M_1(t')\,dt' \tag{13}$$

This argument can be extended indefinitely to $M_2(t)$, $M_3(t)$ etc. If we take the correlation of (12), (13), etc. with $v(0)$, use the fact that this velocity is not correlated with $K(t)$,

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

and take Laplace transforms* of each expression, then Mori showed that we obtain the transform $\tilde{\psi}(p)$ of the original c.f. $\psi(t)$ as a continued fraction.[6]

This approach is useful only if the memory functions are more simple than the original c.f. The first $M_0(t)$ will show a peak at $t = 0$, representing the quasi-Brownian or inertial motion of the molecule, and a tail at longer times representing the damped oscillatory motion. (The memory function of an oscillator of frequency ω_E is a constant, ω_E^2.) One might hope that, if not the first, then one of the low-order memory functions could be adequately approximated by a $\delta(t)$, thus truncating the continued fraction of Mori. In Section 4 we discuss the computer simulation of the velocity c.f. and in Section 5 extend the discussion to the rotational velocity c.f. and its memory functions, but first introduce, in the next section, a more general two-particle c.f.

3 The Density–Density Correlation Function

The velocity c.f. of the last section describes the motion of one molecule. It is equally important to be able to discuss the motions of pairs for two reasons; first, the intermolecular forces in a liquid are, to a first approximation, the sum of the interactions of the molecules in pairs only, and so we must know the static c.f. for pairs even to obtain the thermodynamic properties of internal energy, pressure etc., and, secondly, because the observed scattering of electromagnetic radiation by matter is a coherent interference of the scattering from two different centres.

Let the limiting† density on a molecular scale at point $r = 0$ and at $t = 0$ be denoted

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* A Laplace transform differs from a Fourier transform by the replacement of the oscillating function $\exp(-i\omega t)$ by the monotonically decaying function $\exp(-pt)$, so that $\tilde{\psi}(p)$ can be regarded as the result of sampling $\psi(t)$ by a probe with a relaxation time of p^{-1}. The integration in a Laplace transform is over all $t > 0$.

† The limit is the ratio $(\delta N/\delta V)$ of the number of molecules δN with centres in a volume δV containing the point $r = 0$, as δV goes to zero.

$n(0, 0)$, and that at r and t by $n(r, t)$. We define a density–density distribution function $g^*(r, t)$ by

$$g^*(r, t) = n^{-1}\langle n(0, 0)\, n(r, t)\rangle \tag{15}$$

where n is the mean number density, or N/V. If we average over an ensemble at a fixed time, say $t = 0$, then we obtain the static or, as it is commonly called, the radial distribution[1,2] $g(r)$

$$ng(r) = n^{-1}\langle n(0)\, n(r)\rangle \qquad (r \neq 0) \tag{16}$$

We have, however, specified that there is a molecule at $r = 0$, and so we have there a density described by the delta-function $\delta(r)$, and we have shown in (16) that the probability that there is a second molecule at r is proportional to $ng(r)$. Hence

$$g^*(r, 0) = \delta(r) + ng(r) \tag{17}$$

The two terms are called the *self* and the *distinct* parts of g^*. As time passes the first broadens out into a curve as the molecule originally at $r = 0$ diffuses away, and this curve finally collapses to a line $g^*_{\text{self}} = 0$. The second term also loses its structures with time and goes finally to the constant value $g(r) = 1$, (Figure 3). We therefore form the c.f. corresponding to g^* by subtracting this long-time limit and the result $G(r, t)$ is called the van Hove c.f.[12]

$$G(r, t) = g^*(r, t) - n \tag{18}$$

The Fourier transform of this c.f. over the three dimensions of space and one of time is $S(k, \omega)$, the *structure factor*,

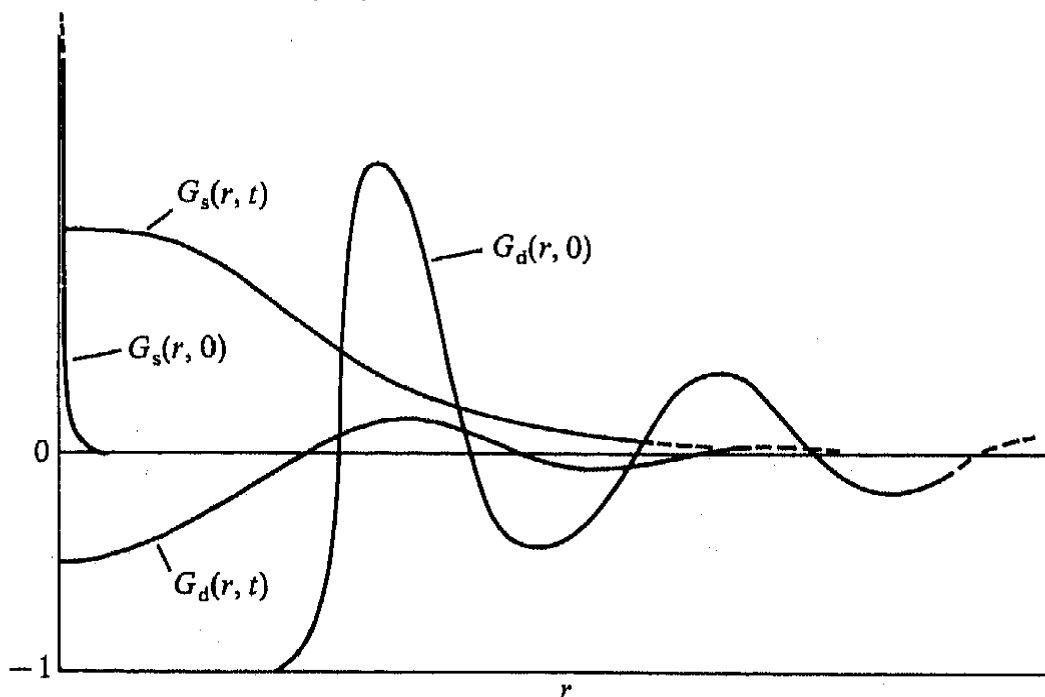$$S(k, \omega) = \frac{1}{(2\pi)^2} \int_V \int_{-\infty}^{\infty} G(r, t)\exp[i(r \cdot k - \omega t)]\, dr\, dt \tag{19}$$

Figure 3 *The self and distinct parts of van Hove's correlation function $G(r, t)$. At zero time the self part is a delta-function at $r = 0$ and the distinct is the (static) pair c.f. $h(r) = g(r) - 1$. At infinite time both parts go to zero*

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

It is the structure factor which is measured by the radiation (electromagnetic or neutron) scattered by the liquid. An incoming wave of length λ is characterized by a vector k_0 which has the direction of the wave and a magnitude of $2\pi/\lambda$. The wave scattered with vector k_1 has an intensity which is proportional to $S(k, \omega)$, where $k = k_0 - k_1$ and ω is the change of angular frequency. Alternatively, we can say that this wave has suffered a change of momentum of $\hbar k$ and of energy $\hbar\omega$.

Neutrons scattered from a monoenergetic (or monochromatic) beam can be analysed for change of angle and speed, and so $S(k, \omega)$ can be measured as a function of both variables, at least over limited ranges. The scattering can be either incoherent (from one centre) or coherent (from a pair of centres), according to the nature of the nucleus. Different isotopes of one atom behave differently in this respect. The former arises from the self-part of the c.f. and the latter from the distinct, and so, in particularly favourable cases, both parts of the transforms of G can be studied experimentally. Thermal neutrons have a wavelength of *ca.* 1 Å and so k^{-1} is comparable with the intermolecular spacing, and the coherently scattered beam yields useful information on $G_{distinct}(r, t)$ on taking the inverse transform.[5,13]

If the analysis by speed (or energy) is omitted then what is obtained is an integral of $S(k, \omega)$ over all ω, which is therefore a function of k only, $S(k)$. Information on the time dependence of the c.f. has now been lost, and the transform of $S(k)$ yields only the static distribution function $g(r)$. With a beam of X-rays all the scattering is coherent, analysis by energy is virtually impossible and so only $S(k)$ and $g(r)$ can be observed. Neutron scattering has therefore told us about the dynamics of liquids in a way which was not possible with X-rays.

Visible light is scattered coherently with negligible change of momentum, and the spectrum observed is therefore $S(0, \omega)$. 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 $S(k \approx 0)$ is related to the compressibility[1,2,10]

$$(2\pi)^3 S(k \approx 0) = n \int_0^\infty [g(r) - 1]\, dt = kT\left(\frac{\partial n}{\partial P}\right)_T - 1 \tag{20}$$

Such scattering is small in a normal liquid but intense near the critical point where $(\partial n/\partial P)_T$ is infinite.

The spectrum of the scattered light is more useful for it has three distinct peaks,[14] a Rayleigh line at $\omega = 0$ and two Brillouin lines at $\omega = \pm Ws_w$, where W is the speed of sound in the liquid and s_w the wavenumber of the particular sound wave responsible for the scattering. The Rayleigh line arises from density (or more properly, refractive index) fluctuations arising from fluctuations of local entropy at fixed pressure. Such fluctuations do not propagate through the fluid and so the Rayleigh line is centred on $\omega = 0$. It may also contain a weak and very broad depolarized component, discussed in Section 6. The Brillouin lines arise from fluctuations of density due to fluctuations of pressure at fixed entropy. Such fluctuations propagate as sound waves which are

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

[14] D. McIntyre and J. V. Sengers, in ref. 2(*a*); H. L. Strauss, in 'Chemical Applications of Lasers', ed. C. B. Moore, Academic Press, New York, 1974.

present in all liquids at equilibrium, and which diffract the 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.

The Rayleigh and Brillouin lines provide a wealth of information, even for a monatomic liquid. The total intensity yields the compressibility (20), the ratio of intensities yield C_p/C_v, 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^{10} Hz, that is, above the range accessible by mechanically generated sound waves.[15]

4 The Simulation and Measurement of Correlation Functions in Monatomic Liquids

The study of the dynamics of liquids by computer simulation started with the work of Alder and Wainwright[16] in 1959, who solved Newton's equations of motion for 32 hard spheres moving in a cubical box. It has progressed rapidly, hand-in-hand with the advances in computer speed and capacity, but even now it is clearly impossible to handle systems of 10^{23} molecules; the present practicable limit is about 10^3, or perhaps up to 10^4 for particularly simple systems. In a sample of liquid of this size many molecules would be near a wall and so not representative of those in a bulk liquid. This problem is solved by surrounding the cubical sample on all sides by replicas of itself so that even molecules at a side or edge interact only with molecules in a similar environment.[17] In these conditions even a sample of 1000 molecules is amply large enough to study the dynamics and thermodynamics of a liquid, since correlation functions decay virtually to zero over lengths of the order of 10 molecular diameters, except for liquids near their critical points.

Before we can solve the equations of motion we must choose an intermolecular potential, and the most popular for simulating the liquefied inert gases has been the Lennard-Jones (12, 6) potential,[1] which is a reasonable compromise between simplicity and realism. Geometrically more complicated potentials are now being used to simulate diatomic molecules;[18] one of the most complicated that has so far been used is that chosen by Rahman and Stillinger[19] for a simulation of water.

The first, and still perhaps the most informative simulation of the properties of a monatomic liquid was Rahman's study[20] of 864 Lennard-Jones (12, 6) particles confined to a cubic cell of side $10.2\,\sigma$ at a reduced temperature of $kT/\varepsilon = 0.786$, where σ and ε are the collision diameter and depth of the Lennard-Jones potential. The density and temperature were chosen to simulate argon at $1.374\,\mathrm{g\,cm^{-3}}$ and 94.4 K. The velocity c.f. and its transform are shown in Figures 1 and 2. From the area under the curve in Figure 1 or, equivalently, from the intercept at zero frequency in Figure 2 we get a diffusion coefficient of $2.43 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$, which is the

[15] D. Sette in ref. 2(*a*).

[16] B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 1959, **31**, 459.

[17] B. J. Alder and W. G. Hoover, and W. W. Wood, in ref. 2(*a*).

[18] J. Barojas, D. Levesque, and B. Quentrec, *Phys. Rev.*, 1973, **A7**, 1092; P. S. Y. Cheung and J. G. Powles, *Mol. Phys.*, 1975, **30**, 921.

[19] A. Rahman and F. H. Stillinger, *J. Chem. Phys.*, 1971, **55**, 3336.

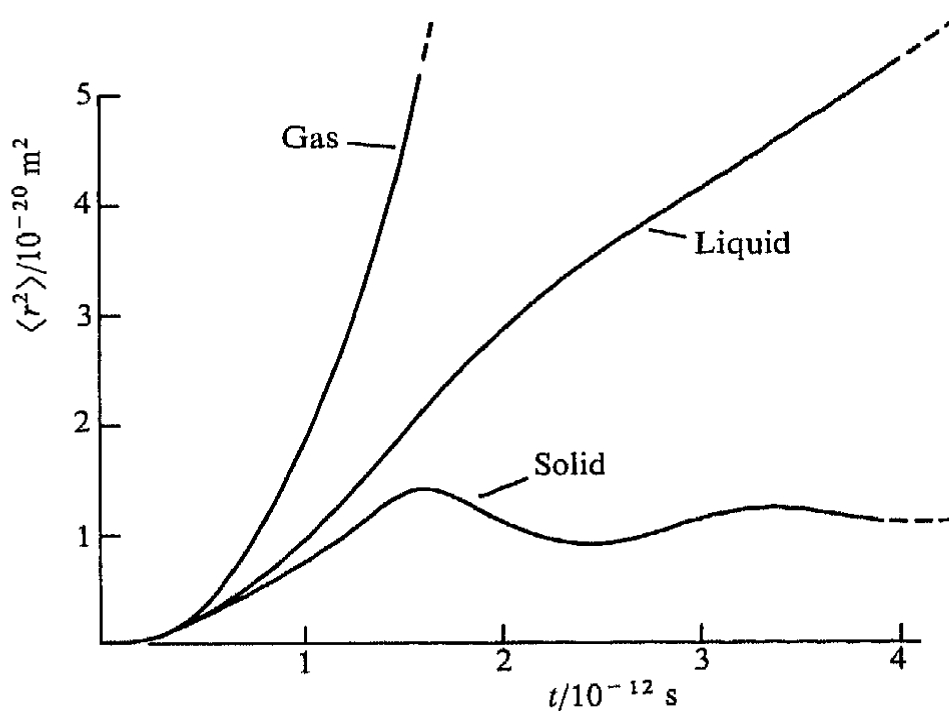[20] A. Rahman, *Phys. Rev.*, 1964, **136**, A405.

Figure 4 *The mean-square displacement as a function of time (schematic)*

same as that of liquid argon[21] at a temperature of 90 K. However, the full curves give much more detailed information on the molecular motion than the value of the macroscopic or hydrodynamic coefficient of diffusion, and, in particular, show the inadequacy of the unmodified Langevin equation.

It is instructive to calculate the mean-square displacement, $\langle r^2 \rangle$, of any one molecule as a function of time (Figure 4). This was computed directly by Rahman, or, in principle, could have been obtained from the self-term of van Hove's c.f.

$$\langle r^2(t) \rangle = \int_0^\infty r^2 G_s(r, t)\, dr \tag{21}$$

At short time $\langle r^2 \rangle$ grows quadratically with time; that is, the motion of the molecule is unretarded, as in a perfect gas. For a crystal, in which the average is taken, from a fixed zero time, over the unrelated phases of the oscillators, $\langle r^2 \rangle$ settles down to a constant value. For a liquid the initially unretarded motion quickly passes into a linear dependence of $\langle r^2 \rangle$ on time, which corresponds to a constant rate of diffusion. For 'argon' this linear or hydrodynamic regime is reached after *ca.* 2.5×10^{-12} s, a time in which a molecule has moved, on average, through a distance of about σ. The hydrodynamic regime is thus reached surprisingly quickly.

At high temperatures, or at densities substantially lower than those of a typical liquid, the negative region of the velocity c.f. disappears, and there is a monotonic fall with this increasing time. In this region the dissection of the c.f. into memory functions has proved useful.[22] Much recent interest has centred about this decay to zero at long times of this positive c.f. in a fluid of moderate density. The decay is slow

[21] J. Naghizadeh and S. A. Rice, *J. Chem. Phys.*, 1962, **36**, 2710.
[22] D. Levesque and L. Verlet, *Phys. Rev.*, 1970, **A2**, , 2514.

(*i.e.*, not exponential) and the consensus of opinion[23] is that at long times it goes as $t^{-\frac{3}{2}}$. Such a slow decay gives rise to an anomalously large coefficient of diffusion at these densities. The cause of the tail is probably to be found in a weak vortex pattern which a moving molecule apparently generates. If a molecule is moving along, say, the x-axis at a particular time then its very motion will tend to establish a pattern of motion in the neighbouring molecules which resembles a vortex ring with cylindrical symmetry about the x-axis. The motion of the molecules in this ring gives an impetus to the first molecule along the x-axis, thus tending to prolong its motion in that direction.[23] Such long tails in the c.f., and the complicated molecular motions which give rise to them, are clearly going to make it difficult to develop a statistical theory of transport for fluids of densities between those of the dense liquid and the dilute gas. That is, no early truncation of the memory function expansion is likely to do justice to the complexity of the motions.

The measurement of correlation functions for a real liquid is more difficult than their computer simulation. In Section 3 we saw that their spectra can be obtained from scattering experiments but these rarely cover a sufficiently complete range of k or ω for their successful Fourier inversion. If we want to study the one-molecule correlation functions then we must use incoherent neutron scattering, and so are restricted to substances containing atoms at least one of whose isotopes has a large incoherent cross-section. The best is the proton, with an incoherent cross-section of 79.7 barn and a coherent of 1.8 barn, and after that the best is apparently sodium for which both areas are 1.7 barn. For argon (incoherent 0.4 barn and coherent 0.5 barn) Dasannacharya and Rao[24] have obtained $G_s(r, t)$ at 85 K, but only with an accuracy of *ca.* 15%. From this result we could go to the diffusion coefficient by calculating $\langle r^2 \rangle$ from equation (21), and then obtaining D from the limiting slope of Figure 4, or we can use the fact that if G_s at time t has a Gaussian shape (as they aver) then its width $w(t)$ is related to the velocity c.f. by [5,13,25]

$$w(t) = \tfrac{2}{3} \int_0^t \langle v(0) \cdot v(t) \rangle (t - t') \, dt' \tag{22}$$

For liquid sodium the results are more extensive although, judging by the agreement between different workers,[8,13] not necessarily more accurate. Figure 5 shows a spectrum of the velocity c.f., which resembles that for a liquid of Lennard-Jones molecules (Figure 2) more closely than either resemble the Lorentzian form predicted by a simple Langevin equation. The coefficient of diffusion calculated from the intercept of the spectrum at zero frequency is *ca.* 2.8×10^{-9} m^2 s^{-1}, which is in only rough agreement with the experimental value[26] of 4.3×10^{-9} m^2 s^{-1}.

[23] B. J. Alder and T. E. Wainright, *Phys. Rev.*, 1970, **A1**, 18; T. E. Wainright, B. J. Alder, and D. M. Gass, *Phys. Rev.*, 1971, **A4**, 233; R. Zwanzig, in 'Statistical Mechanics – New Concepts, New Problems, New Applications', ed. S. A. Rice, K. F. Freed, and J. C. Light, University of Chicago Press, Chicago, 1972, p. 241; Papers by B. J. Alder and J. M. Deutch, and the discussion on them, in 'Transport Phenomena – 1973', ed. J. Kestin, American Institute of Physics, 1973.

[24] B. A. Dasannacharya and K. R. Rao, *Phys. Rev.*, 1965, **137**, A417.

[25] B. J. Berne and G. D. Harp, *Adv. Chem. Phys.*, 1970, **17**, 63; B. J. Berne, in 'Physical Chemistry, an Advanced Treatise', ed. D. Henderson, Academic Press, New York, 1971, Vol. 8B; B. J. Berne and D. Forster, *Ann. Rev. Phys. Chem.*, 1971, **22**, 563; R. T. Bailey, in 'Molecular Spectroscopy', ed. R. F. Barrow, D. A. Long, and D. J. Millen, (Specialist Periodical Reports). The Chemical Society, London, 1974, Vol. 2, p. 173.

[26] P. A. Egelstaff, 'Introduction to the Liquid State', Academic Press, London, 1967, p. 4.
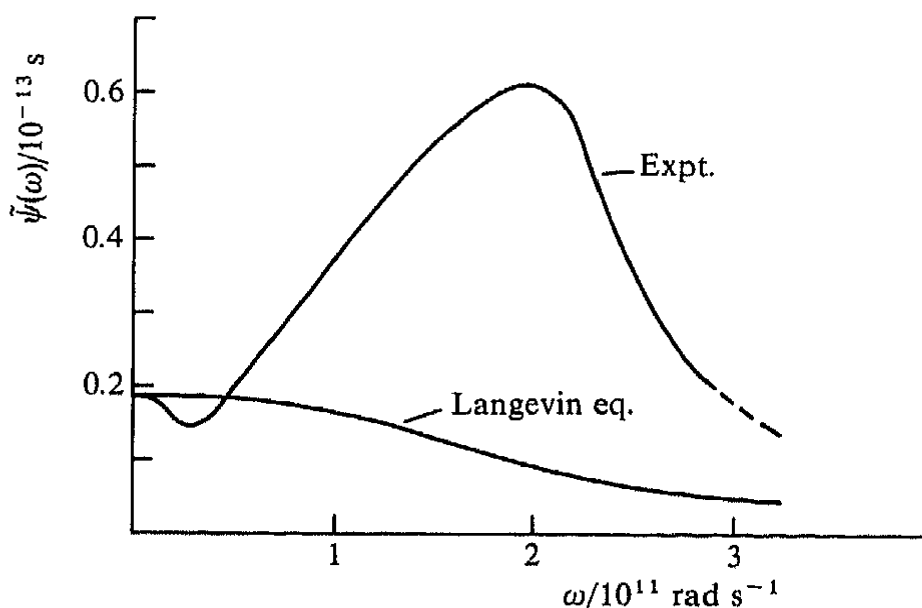
Figure 5 *The experimental Fourier transform of the velocity c.f. for liquid sodium[8] compared with the form of this function predicted by Langevin's equation*

5 Absorption in Molecular Liquids

In this Section and the next two we describe how we can study the rotary motion of molecules by means of the bandshapes of their spectra, which are linked to orientational auto-correlation functions. Let u be a unit vector along a convenient axis of the molecule (usually along the permanent dipole moment, if any), and J the angular velocity vector, which is perpendicular to u in a diatomic molecule. We shall use the following correlation functions; the first in this section, the second in Section 6 and the third in Section 7.

$$^{(IR)}\psi(t) = \langle u(0) \cdot u(t) \rangle$$

$$^{(R)}\psi(t) = \tfrac{1}{2}\langle 3[u(0) \cdot u(t)]^2 - 1 \rangle \tag{23}$$

$$^{(J)}\psi(t) = \langle J(0) \cdot J(t) \rangle / \langle J^2(0) \rangle$$

Here (IR) stands for infra-red, and (R) for Rayleigh rather than Raman since we shall be considering scattered light that is symmetrically disposed about the exciting line and not about a line displaced from it.

The Fourier transform of $^{(IR)}\psi(t)$ is related to the dielectric absorption[27,28] that arises from the attempt of dipolar molecules to respond to a small perturbing electric field, which may oscillate over a wide range of frequencies. Energy is absorbed because they cannot follow the applied field F instantaneously. More than fifty years ago Debye discussed this phenomenon in terms of a rotational Langevin equation, in which the torque on a dipole μ at an angle θ to the field F is opposed by a frequency-independent microscopic coefficient of friction ζ which arises from the force-fields of neighbouring molecules.

$$\mu \times F = -\zeta \dot{\theta} \tag{24}$$

[27] N. E. Hill, A. G. Price, W. E. Vaughan, and M. Davies, 'Dielectric Properties and Molecular Behaviour', Van Nostrand Reinhold, London, 1969.

[28] S. Kielich, in 'Dielectric and Related Molecular Processes', ed. Mansel Davies, (Specialist Periodical Reports), The Chemical Society, London, 1973, Vol. 1, p. 192.

The Langevin equation per unit moment of inertia is then (*cf.* equation 8)

$$\ddot{\theta}(t) = -\zeta\dot{\theta}(t) + \Gamma(t) \tag{25}$$

where $\Gamma(t)$ is the random torque imposed on a molecule by the motion of its neighbours. If $\phi(t)$ is the angle between $u(0)$ and $u(t)$ then[25,29]

$$\langle u(0) \cdot u(t) \rangle = \langle \cos \phi(t) \rangle \tag{26}$$

These equations describe adequately the rotational dynamics, and so the absorption, up to field frequencies of *ca.* 10^{12} Hz. As we move into the far-i.r. region[30] of 10^{13} Hz (*i.e.,* for molecular motion at times of 10^{-13} s) then the same limitations apply to these equations as applied before to the translational Langevin equation. An obvious weakness appears if the absorption is expressed in terms of $\alpha(\omega)$, the absorption coefficient per unit path length. Integration[29] of equation (25) gives an absorption coefficient $\alpha(\omega)$ proportional to $\omega^2(1+\omega^2)^{-1}$, which means that at high frequencies $\alpha(\omega)$ has a plateau, and spectral transparency is not regained.

The trouble lies, as before, in the neglect of molecular inertia, and so the assumption that the random torque $\Gamma(t)$ has an infinitely small correlation time. Only then is ζ independent of time. Equation (25) is the truncation of the rotational equivalent of Mori's continued fraction[6] (Section 2) so that the memory function is a peak at $t = 0$;

$$^{(IR)}M(t) = D\delta(t) \tag{27}$$

where D is a rotational diffusion coefficient equal to $kT\zeta/I$. If $\Gamma(t)$ is to be non-Gaussian,[25] and if ζ is to be a function of time, then we must generalize Langevin's equation, in the same way as we went from equation (8) to equation (12);

$$^{(IR)}\dot{\psi}(t) = -\int_0^t {}^{(IR)}\psi(t-t')^{(IR)}M_0(t')\,\mathrm{d}t' + \Gamma(t) \tag{28}$$

This equation has been used recently to describe the far-i.r. absorption of furan and chloroform.[31] The memory function $^{(IR)}M_0(t)$ which replaces the delta-function of the simple Langevin equation is the c.f. of the random torque

$$^{(IR)}M_0(t) = \langle \Gamma(0) \cdot \Gamma(t) \rangle \tag{29}$$

Since $^{(IR)}M_0(t)$ is itself a c.f. it has its own memory function $^{(IR)}M_1(t)$ defined by the analogue of equation (13), and we can again extend the series indefinitely. Mori's continued fraction for the Laplace transform starts

$$^{(IR)}\tilde{\psi}(p) = \frac{^{(IR)}\tilde{\psi}(0)}{p + {}^{(IR)}\tilde{M}_0(p)} = \frac{^{(IR)}\tilde{\psi}(0)}{p + {}^{(IR)}\tilde{M}_0(0)/(p + r^{(IR)}\tilde{M}_1(p))} = etc. \tag{30}$$

Table 1 summarizes how this series can be used as a framework into which to fit some of the widely used models for molecular rotation. The rotational, like the transla-

[29] G. Wyllie, in ref. 28, p. 21; G. Williams, *Chem. Rev.*, 1972, **72**, 55.
[30] C. Brot, in 'Dielectric and Related Molecular Processes', ed. Mansel Davies, (Specialist Periodical Reports), The Chemical Society, London, 1975, Vol. 2, p. 1.
[31] B. Quentrec and P. Bezot, *Mol. Phys.*, 1974, **27**, 879.

tional velocity c.f., is necessarily an even function of time,[32] and has a Taylor expansion

$$\langle u(0) \cdot u(t) \rangle = 1 - \frac{t^2}{2!} \langle \dot{u}^2(0) \rangle + \frac{t^4}{4!} \langle \ddot{u}^2(0) \rangle - \cdots \tag{31}$$

The mean angular velocity $\langle \dot{u}^2(0) \rangle$ of a linear molecule is $2kT/I$. The mean square acceleration $\langle \ddot{u}^2(0) \rangle$ comprises two terms; a radial or centripetal acceleration due to the fact that the vector u is of fixed length, and a tangential acceleration. The first is independent of the molecular interactions and is $8(kT/I)^2$, and the second is $\langle \mathcal{O}^2(V) \rangle / I$ where $\mathcal{O}(V)$ is the torque that the environment exerts on the molecule *via* the intermolecular potential V. The substitution of these expressions into equation (31) gives the equation of motion of an ensemble of interacting molecules. The equation shows the value of the c.f. representation in isolating the short-time behaviour from that at long times. The former can be followed analytically but the latter can be obtained only by invoking statistical arguments which usually lead to an exponential tail in the c.f.

Gordon[32] and others[25] have calculated the first few terms of the expansions of $^{(IR)}\psi(t)$, $^{(R)}\psi(t)$, and $^{(J)}\psi(t)$; each contains the torque, a functional of the intermolecular potential V, $\langle \mathcal{O}(V) \rangle$, or its time derivative. The true c.f. is even in time and Table 1 shows the degree to which particular models satisfy this condition. Gordon's M and J diffusion models are zeroth-order truncations of Mori's series and so have a term in t^3, and all higher odd terms. In these models the torque is not defined at the moment of impact (*i.e.*, it becomes instantaneously infinite) and so although transparency is regained in the far-i.r. (as ω^{-2}), it is regained more slowly than is found experimentally[33] for many dipolar liquids, and for those solid phases in which translational freedom is lost but rotational is retained. More recently[31,35] the truncation at $M_1(t)$ shown in the last section of Table 1 has been used to ensure evenness to t^4. The torque $\langle \mathcal{O}(V) \rangle$ is now well-defined at all times although its derivative $\langle \dot{\mathcal{O}}(V) \rangle$, which is part of the term in t^6, is not. This is because the truncation at $M_1(t)$ implies that the angular acceleration is randomized in direction at each impact, so that its derivative has an infinite singularity. The absorption spectrum $\alpha(\omega)$ is the Fourier transform of $^{(IR)}\psi(t)$ and behaves asymptotically as ω^{-4} at high frequency. It reduces[31] to a Debye curve when $\omega^4 \ll \omega^2$, as is shown in Figure 6 where it is compared with experimental results[33] for liquids and rotationally-free solids. Further comparisons with experiment can be found in the papers of Quentrec and Bezot[31] and Evans and Evans.[35]

It is remarkable that, although the agreement of $\alpha(\omega)$ with the experimental results is good over several decades of frequency, the overall memory function, $^{(IR)}M(t)$, is even only to t^2. This function is another equilibrium property and so should be even in time. One possible remedy would be to truncate Mori's series at

[32] R. G. Gordon, *J. Chem. Phys.*, 1966, **44**, 1830; *Adv. Magn. Resonance*, 1968, **3**, 1; R. E. D. McClung, *J. Chem. Phys.*, 1972, **57**, 5478.

[33] I. W. Larkin, *J.C.S. Faraday Symposia*, 1972, **6**, 112; R. Haffmanns and I. W. Larkin, *J.C.S. Faraday II*, 1972, **68**, 1729; M. Evans, M. Davies, and I. W. Larkin, *ibid.*, 1973, **69**, 1011; I. W. Larkin, *ibid.*, 1973, **69**, 1278; I. W. Larkin and M. Evans, *ibid.*, 1974, **70**, 477; I. W. Larkin, *ibid.*, 1974, **70**, 1457; M. Evans, *ibid.*, 1975, **71**, 2051.

[34] F. Bliot, C. Abbar, and E. Constant, *Mol. Phys.*, 1972, **24**, 241; F. Bliot and E. Constant, *Chem. Phys. Letters*, 1973, **18**, 253; 1974, **29**, 618.

[35] G. J. Evans and M. Evans, *J.C.S. Faraday II*, 1976, **72**, in press.

Table 1 *Some dynamical models in Mori's formalism*

Model and references	$^{(IR)}M_n(t)$	$^{(IR)}M_n(p)$	Description and comment	$^{(IR)}\psi(t)$
Debye 25, 27—30	$^{(IR)}M_0(t) = D\delta(t)$	$^{(IR)}M_0(p) = D$	Molecular inertia neglected; infinitesimal angular displacement in infinitely short time. Used to describe dielectric absorption at low frequencies but leads to a 'Debye plateau' in the far-i.r.	$\exp(-t/\tau_m)$ where τ_m is the Debye relaxation time. Not an even function of t
Gordon M-diffusion 30, 32, 33	$^{(IR)}M_0(t) = {}^{(IR)}M_0(0)e^{-\gamma_0 t}$	$^{(IR)}M_0(p) = \dfrac{{}^{(IR)}M_0(0)}{p+\gamma_0}$	Instantaneous elastic collisions perturb the rotation at random times. Angular velocity vector is randomized in direction; torque is infinite at impact. A slow return to transparency in the far-i.r.	This has a Taylor expansion $1 - at^2 + \mathrm{O}(t^4)$ and so starts as an even function of t
Gordon J-diffusion 32, 34	$^{(IR)}M_0(t) = M_{FR}(t)e^{-\gamma_J|t|}$ where $M_{FR}(t)$ is the memory function of a free rotator		As for M-diffusion except that angular velocity is randomized in both direction and magnitude. An 'inertia-corrected' Debye model	A complicated function whose Taylor expansion has a term in t^3
25, 31, 35	$^{(IR)}M_1(t) = {}^{(IR)}M_1(0)e^{-\gamma_1 t}$		Torque is always finite. Describes both low-frequency and far-i.r. absorption more satisfactorily than previous models. The past history of molecular movements and interactions influences future behaviour, i.e. a non-Markovian model	Taylor expansion is even to t^4 but contains a term in t^5. Exponential at long times, oscillatory at short – a reflection of molecular libration, and the origin of the far-i.r. Poley absorption

higher and higher order, but this introduces an inacceptably large number of averages $^{(IR)}M_2(0), \ldots, {}^{(IR)}M_n(0)$, which cannot be obtained analytically and which would therefore remain as phenomenological coefficients. A limitation of Mori's approach is that it does not give a natural picture of the long-time or hydrodynamic tail of the c.f. of angular velocity $^{(J)}\psi(t)$, as emphasized in many papers at a conference in Paris.[36] The long-time behaviour of $^{(J)}\psi(t)$ appears to go as $t^{-\frac{3}{2}}$, as for the translational case discussed in Section 4. Such a limit is expected also for $^{(IR)}\psi(t)$, at least for spherical tops, but this tail would distort the spectrum only on the low-frequency side of the Debye absorption.

It is natural to expect i.r. absorption associated with the rotation of a dipolar molecule in a liquid, but not so obvious that non-dipolar molecules also absorb in the far-i.r. and high microwave region.[37] This arises from the small, temporary, dipole induced in a normally non-polar molecule by the fluctuating fields of moving neighbours. The reciprocal of the half-width of the absorption band is of the order of the lifetime of the induced dipole, which is generally *ca.* 0.2×10^{-12} s. The associated c.f. is one of orientation coupled with interaction, and it falls to zero much more rapidly than its purely orientational dipolar counterpart $^{(IR)}\psi(t)$.

Mori's approximation injects a unity into the description of both permanent and induced dipolar absorption, as can be seen by the ease with which the truncation at M_1, which was successful in reproducing the permanent dipole absorption (Figure 6), also reproduces the induced dipole absorption in a range of liquids from nitrogen to benzene (Figures 7 and 8). For these liquids both $M_0(0)$ and $M_1(0)$ are multimolecular in origin since an isolated molecule would not absorb. Both averages are related to $\langle \mathcal{O}^2(V) \rangle$, although not in a simple way, and so can be used as rough probes for the change with pressure and temperature of the mean-square torque.[38]

6 Depolarized Rayleigh Scattering—a Study of $^{(R)}\psi(t)$

We saw in Section 3 that light scattered from a monatomic liquid had two components, a Rayleigh line of the same frequency as the incoming light, and, surrounding it on either side, a pair of Brillouin lines shifted by an amount proportional to the speed of sound in the liquid. In a molecular liquid there is usually also a weak, very broad depolarized band, centred on the incident frequency which leads to the so-called Rayleigh wings. It is now generally agreed that this band arises from the re-orientation of single molecules, an interpretation which differs from that of collective (shear-wave) modes which prevailed[39] before the c.f. formalism was introduced about ten years ago. However, both mechanisms may be involved in the long-time tails on the c.f. $^{(R)}\psi(t)$ which molecular dynamic studies have shown to be present. As with the corresponding tails in the translational velocity c.f. (Section 4), these probably arise from a coupling of the motion, in this case orientational, of a single molecule with the hydrodynamic transverse velocity gradients.[40]

[36] 'Molecular Motions in Liquids', ed. J. Lascombe, Reidel, Dordrecht, 1974.
[37] M. Davies, *Ann. Reports,* 1970, **67**, 65; M. Davies, G. W. F. Pardoe, J. Chamberlain, and H. A. Gebbie, *Trans. Faraday Soc.,* 1970, **66**, 273; G. W. F. Pardoe, *ibid.,* p. 2699; G. J. Davies, J. Chamberlain, and M. Davies, *J.C.S. Faraday II,* 1973, **69**, 1223; G. J. Davies and J. Chamberlain, *ibid.,* 1973, **69**, 1739; G. J. Davies and M. Evans, *ibid.,* 1975, **71**, 1275.
[38] G. J. Davies and M. Evans, *J.C.S. Faraday II,* 1976, **72**, in press.
[39] I. L. Fabelinskii, 'Molecular Scattering of Light', Plenum Press, New York, 1968.
[40] J.-L. Greffe, J. Goulon, J. Brondeau, and J.-L. Rivail, in ref. 36, p. 151.
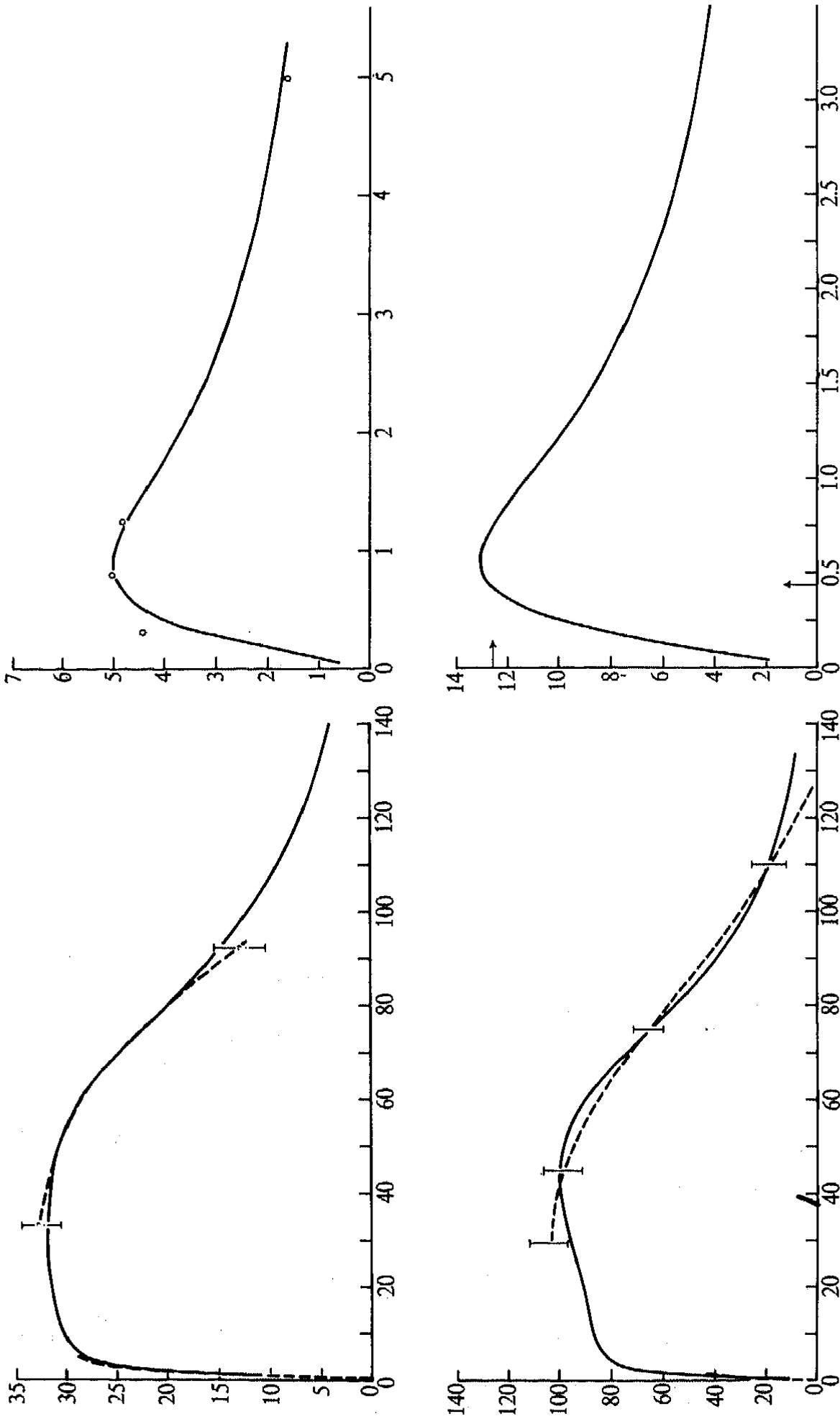
Figure 6 *The absorption (top left) and dielectric loss (top right) of t-butyl chloride in the rotator solid phase at 238 K. The abscissae are wavenumbers (cm^{-1}) and the ordinates are α in neper cm^{-1} and ε". The dashed lines are the experimental absorption[33] and the points the experimental measurements of dielectric loss in the microwave region.[33] The full lines are calculated from the truncation in the last line of Table 1. The lower figures are similar results for the absorption and loss in liquid Me$_2$CClNO$_2$ at 296 K. The arrows in the lower right-hand figure mark the position and intensity of the peak in the dielectric loss*
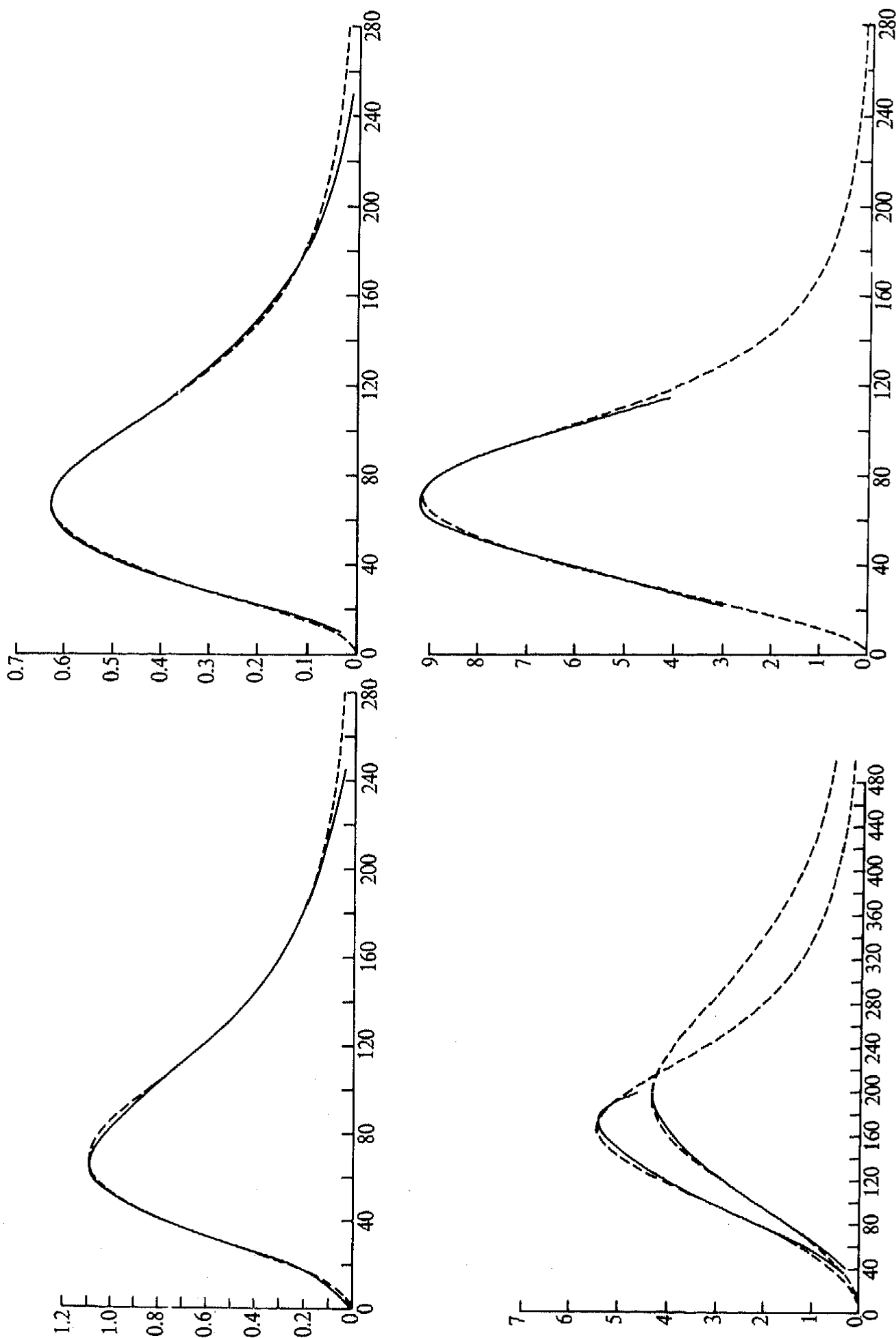
Figure 7 *The absorption*[38] *α in neper cm*$^{-1}$ *for non-dipolar substances as a function of wavenumber in cm*$^{-1}$. *Liquid N$_2$ at 76.4 K (top left), liquid CO$_2$ at 273 K (top right), liquid CH$_4$ at 98 K (bottom left, the broader band), solid CH$_4$ at 77 K (bottom left, the narrower band), and liquid (CN)$_2$ at 301 K (bottom right). The experimental results are shown by the full curves and the theoretical calculations, from the truncation in the last line of Table 1, by the dashed curves.*
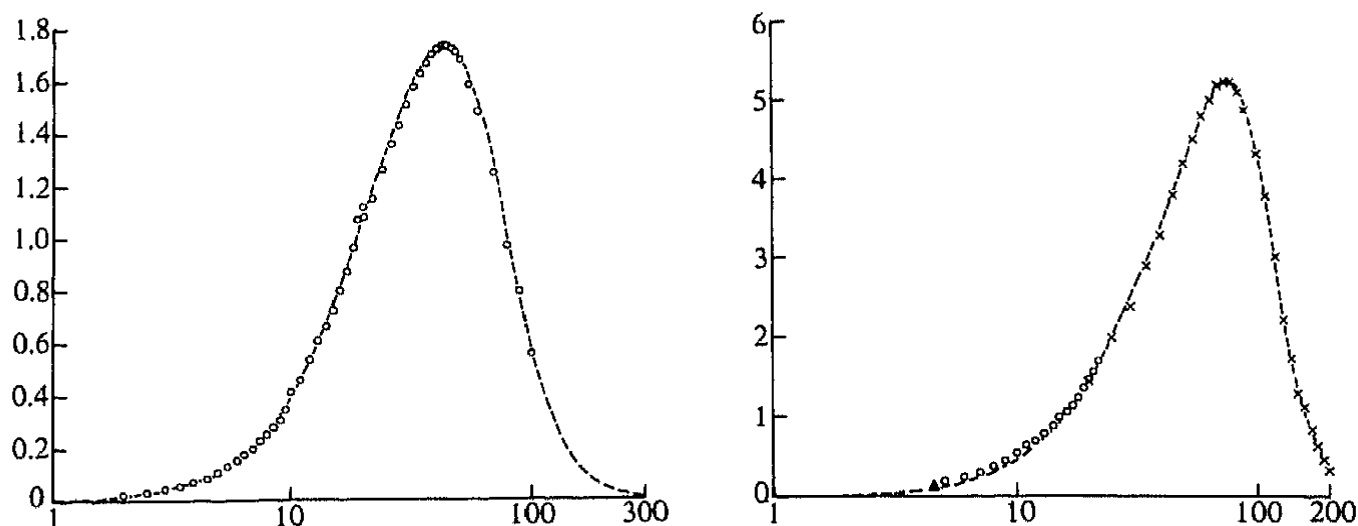
Figure 8 *The absorptions*[38] α *in* neper cm^{-1} *as a function of wavenumber in* cm^{-1} *for the non-dipolar liquids* CCl_4 *(left) and* C_6H_6 *(right)*

If the incoming light is travelling in the x-direction, if it is polarized in the z-direction (vertically), and is observed in the y-direction, polarized in the x-direction (horizontally) then the scattered spectrum is $I_{VH}(\omega)$, and it arises from a dipole induced in the x-direction by a field along the z-direction. Such a dipole is proportional to the xz-element of the electric polarizability of the scattering volume. For a system with isotropically polarizable molecules (*e.g.* CCl_4), this element is zero. Gordon[32] showed in 1966 that this depolarized component is the Fourier transform of the average motion of the polarizability tensor and so, for self-correlation in a linear or symmetric top molecule, of the c.f. $^{(R)}\psi(t)$. The depolarized light scattered from liquids with anisotropic polarizability arises from local fluctuations of the orientation from the random isotropic average. If it is assumed that the movement of neighbouring molecules is uncorrelated then the scattered intensity at frequency ω from the exciting line is

$$I_{VH}(\omega) \propto (\alpha_\| - \alpha_\perp)^2 \int_{-\infty}^{\infty} {}^{(R)}\psi(t)e^{-i\omega t}\,dt \tag{32}$$

This expression is similar to the quantal equation[32] for the rotational absorption in the microwave and far-i.r. bands;

$$A(\omega) \propto \frac{\alpha(\omega)}{\omega[1-\exp(-\hbar\omega/kT)]} \propto \mu^2 \int_{-\infty}^{\infty} {}^{(IR)}\psi(t)e^{-i\omega t}\,dt \tag{33}$$

$I_{VH}(\omega)$ and $A(\omega)$ have quantitatively the same features. The low-frequency Lorentzian[41] of the scattered light corresponds to the low-frequency Debye relaxation in dipolar absorption. This Lorentzian is imposed on a broader background which extends to *ca.* 100—150 cm^{-1} corresponding to the far-i.r. Poley absorption.[27,30] Beyond this the intensity falls exponentially with frequency.

The Lorentzian behaviour at low frequencies implies that the long-time behaviour of both $^{(IR)}\psi(t)$ and $^{(R)}\psi(t)$ is exponential with relaxation times of τ_M and τ_R respectively, the reciprocals of the half-widths of the Lorentzians. Details of the

[41] D. A. Pinnow, S. J. Candau, and T. A. Litovitz, *J. Chem. Phys.*, 1968, **39**, 347; H. Dardy, V. Volterra, and T. A. Litovitz, *J.C.S. Faraday Symposia*, 1972, **6**, 71; *J. Chem. Phys.*, 1973, **59**, 4491.

molecular motion are reflected in the deviations from the exponentials at short times, and give rise to an added background or shoulder in the scattered light, and to the Poley absorption in the i.r.

A simple comparison of τ_M with τ_R tells us something of the mechanism of re-orientation; for example whether it is by large rotational jumps or not.[42] Thus if motion about an axis can be described by a model of rotational diffusion with individual time steps of a short time τ, then Hubbard's equation[43] links τ, τ_M, and τ_R

$$\tau = I/6kT\tau_R = I/2kT\tau_M \tag{34}$$

If the Rayleigh scattering is observed as a function of temperature[41] then, in principle, the different contributions to the scattering can be assigned different energies of activation which can be compared with those obtained from viscosity and dielectric measurements. For the substituted benzenes[41] good agreement with experiment can be obtained by attributing the spectrum of linearly anisotropic molecules to a single mechanism of re-orientation. However, the far wing of the Rayleigh scattering contains also information about intermolecular properties since a weak exponential scattering is observed here even with molecules with scalar polarizabilities[44] such as CCl_4. Bucaro and Litovitz[45] used a simple binary-collision approach to model this scattering for spherically polarizable molecules. However, the spectra of anisotropic liquids show the same quasi-exponential tail and also a shoulder around $50\text{---}90\,\text{cm}^{-1}$ which cannot be accounted for by this simple, distortional, binary mechanism.

After subtracting the collision-induced component of $^{(R)}\psi(t)$, Dardy et al.[41] found that a molecule such as benzene behaves much as a free-rotator at short times. There is an average rotation of ca. $15°$ between collisions. The long-time behaviour of $^{(R)}\psi(t)$ is found to be exponential, reflecting the ultimate diffusional behaviour. It can be shown[30,46] that the short-time behaviour of a c.f. is revealed in greater detail by an analysis of its second derivative; for example, $^{(R)}\ddot{\psi}(t)$ is related to the correlation of angular momenta and angular orientation. This c.f. shows[42,46] that there is not a complete loss of memory during collisions in molecules like benzene and so the simple diffusion model which lies behind the Hubbard equation is inadequate.

The Rayleigh scattering has been observed also as a function of pressure[47] and from these measurements the change with density of $^{(R)}\psi(t)$ and $^{(R)}\ddot{\psi}(t)$ can be obtained. The mechanism of re-orientation appears to involve rotation which is randomly affected by collisions but it is a process which is not described accurately by the J-diffusion model. The c.f. $^{(R)}\ddot{\psi}(t)$ has a negative region and oscillates [as is well documented[33,37] for $^{(IR)}\ddot{\psi}(t)$], thus showing that there is not a complete randomization of the angular velocity at each collision. There is also evidence that memory of

[42] F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, 1972, **56**, 413.

[43] P. S. Hubbard, *Phys. Rev.*, 1963, **131**, 1155.

[44] J. P. McTague and G. Birnbaum, *Phys. Rev. Letters*, 1968, **21**, 661; W. S. Gornall, H. E. Howard-Lock, and S. P. Stoicheff, *Phys. Rev.*, 1970, **A1**, 1288.

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

[46] T. Keyes and D. Kivelson, *J. Chem. Phys.*, 1972, **56**, 1057; *ibid.*, 1972, **57**, 4599; A. G. St. Pierre and W. A. Steele, *J. Chem. Phys.*, 1975, **62**, 2286.

[47] J. F. Dill, T. A. Litovitz, and J. A. Bucaro, *J. Chem. Phys.*, 1975, **62**, 3839; P. van Konynenburg and W. A. Steele, *ibid.*, p. 2301; M. Perrot, J. Devaure, and J. Lascombe, *Mol. Phys.*, 1975, **30**, 97.

one impact is carried through to the next, and beyond. The oscillations in $^{(R)}\ddot{\psi}(t)$ are most pronounced in strongly anisotropic molecules such as benzene, and suggest that such strong anisotropic forces lead towards molecular libration.[33] This mechanical anisotropy is accentuated at high molecular densities. The J-diffusion model is qualitatively adequate only for the simplest molecules, such as N_2 and CO.

From the Mori series for depolarized Rayleigh scattering we see that the truncation

$$^{(R)}M_0(t) = D_R \, \delta(t) \tag{35}$$

is equivalent to the Debye model of dielectric absorption, and leads to the Lorentzian,

$$I_{VH}(\omega) \propto (\alpha_{\parallel} - \alpha_{\perp})^2 D_R (D_R + \omega^2)^{-1} \tag{36}$$

which is adequate only at long times. The shoulder[42,47] found at higher frequencies in moderately and highly anisotropic liquids can neither be described by a Lorentzian nor fitted by the distortional mechanism of Bucaro and Litovitz.[45]

The truncation

$$^{(R)}M_0(t) = {}^{(R)}M_0(0) \exp(-\gamma_0 t) \tag{37}$$

yields, on Fourier transformation of the corresponding $^{(R)}\psi(t)$, the scattering function of the M-diffusion model, which is proportional to ω^{-4} at high frequencies and reduces to a Lorentzian when $\omega^4 \ll \omega^2$. The equilibrium average $^{(R)}M_0(0)$ is still, for this model, a property of a single molecule (no torque involved); for a linear molecule it is $3kT/I$.

The limitations of the M- and J-diffusion models in their treatment of torque (Section 5), and the false assumption of complete randomization of angular velocity at each collision have been revealed by the measurements at high pressure. Thus the J-diffusion model is adequate for the Rayleigh scattering in liquid CO_2 up to 100 bar, but fails at higher pressures when the index n of the frequency dependence (ω^{-n}) changes to higher n at intermediate and high frequencies. This sharper asymptotic fall-off with ω suggests that the truncation

$$^{(R)}M_1(t) = {}^{(R)}M_1(0) \exp(-\gamma_1 t) \tag{38}$$

might lead to a suitable function for $I_{VH}(\omega)$. A finite torque is now implied in $^{(R)}M_1(0)$; for a linear molecule

$$^{(R)}M_1(0) = \frac{\langle \mathcal{O}^2(V) \rangle}{24kTI} - \frac{5}{3}\left(\frac{kT}{I}\right) \tag{39}$$

The function $I_{VH}(\omega)$ is again Lorentzian at low frequencies but now has a peak[25] around 50 cm^{-1}, near the shoulder found by Dardy *et al.*[41] in anisotropic liquids.

The complete spectrum of depolarized scattered light can be written as the sum of three terms;

$$I(\omega) = I_{VH}(\omega) + I_{COL}(\omega) + I_{VH\text{-}COL}(\omega) \tag{40}$$

where $I_{COL}(\omega)$ is the collisional part of the intensity observable in molecules with isotropic polarizability such as CCl_4. The theoretical expressions from which the sign and magnitude of the cross-term can be calculated are only crude, but its neglect[42]

does not seem to affect the consistency of the subsequent analysis of the results. In anisotropic molecules $I_{VH}(\omega)$ accounts for almost all the intensity and $I_{COL}(\omega)$ is restricted to the wings. Bucaro and Litovitz[45] predict

$$I_{COL}(\omega) \propto \omega^{12/7} \exp(-\omega/\omega_0) \qquad (\omega > \omega_0) \tag{41}$$

where ω_0 is calculated from a chosen intermolecular potential, usually of the Lennard-Jones form. $I_{COL}(\omega)$ is a Lorentzian if $\omega < \omega_0$. The equivalent expression in the far-i.r.[41] is

$$\alpha_{COL}(\omega) \propto \omega^{26/7} \exp(-\omega/\omega_0) \qquad (\omega > \omega_0) \tag{42}$$

but this fits the results much less satisfactorily[48] than the anisotropic term shown in Figures 7 and 8.

Bucaro and Litovitz[49] emphasize the similarity between $I_{COL}(\omega)$ and the population-corrected dielectric loss factor in non-polar liquids, *viz.*

$$\varepsilon''(\omega)\left[1 - \exp\left(\frac{\hbar\omega}{kT}\right)\right]^{-1}$$

They have shown that both are fairly well described by semi-empirical equations such as (41) and (42). Both have separate high- and low-frequency portions, whereas the generalized Langevin theory of Kubo, Mori, and others stresses that these peaks in the i.r. (or shoulders in the Rayleigh spectrum) are to be treated as part of the lower frequency orientational processes – a unifying formalism for both dipolar (aniso-tropic) and non-dipolar (isotropic) molecules. It would therefore seem to be fruitful to treat $I_{COL}(\omega)$ by invoking Mori's truncation at first-order, with both $^{(R)}M_1(0)$ and $^{(R)}M_0(0)$ as torque dependent parameters.

7 N.M.R. Spin–Rotation Relaxation—a Study of $^{(J)}\psi(t)$

The relaxation of nuclear spins is determined by their coupling with the translational and rotational motions of the molecule. For a nucleus of spin $\frac{1}{2}$, the spin–rotation interaction of a linear molecule has a Hamiltonian of the form $-c\mathbf{I} \cdot \mathbf{J}$, where $\mathbf{I}$ is the angular momentum of the nucleus, $\mathbf{J}$ is that of the molecule, and c is the spin–rotation coupling constant.[25,32] When this is the only part of the total energy which leads to relaxation of the spins then the spin–relaxation time T_1 is

$$\frac{1}{T_1} = \frac{c^2}{3\hbar^2} \int_{-\infty}^{\infty} \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle e^{-i\omega_0 t} \, dt \tag{42}$$

where $^{(J)}\psi(t)$ is the third c.f. defined in equation (23), and ω_0 is the Larmor precession frequency. In a typical liquid ω_0^{-1} is of the order of 10^{-6} s, and this is so much longer than the time for the angular momentum c.f. to decay to zero (say, 10^{-11} s) that the exponential term in (42) can be put equal to unity.

For a linear molecule the expansion[25] of $^{(J)}\psi(t)$ in powers of t^2 resembles those of the ratios $^{(IR)}\ddot{\psi}(t)/^{(IR)}\ddot{\psi}(0)$ and $^{(R)}\ddot{\psi}(t)/^{(R)}\ddot{\psi}(0)$. Gerschel, Darmon, and Brot[50] showed that the (IR) ratio oscillated at short times, and measurements of light scattering from

[48] M. Evans, *J.C.S. Faraday II*, 1975, **71**, 71.

[49] J. A. Bucaro and T. A. Litovitz, *J. Chem. Phys.*, 1971, **55**, 3585; T. A. Litovitz, in ref. 36, p. 613.

[50] A. Gerschel, I. Darmon, and C. Brot, *Mol. Phys.*, 1972, **23**, 317.

liquids at high pressures[47] have shown that the (R) ratio does also. There has been little if anything reported from n.m.r. studies of the full time dependence of $^{(J)}\psi(t)$, but Berne and Harp[25] have made computer calculations which show that it is negative for an interval of time if the pair potential is anisotropic. It remains positive and changes little over an interval of 10^{-12} s if the pair potential is of the Lennard-Jones form.

If there is no molecular interaction then $\langle O^2(V) \rangle$ is zero, the c.f. $^{(J)}\psi(t)$ is unity, and its memory function $^{(J)}M(t)$ is zero. Hence $^{(J)}M(t)$ can be looked upon as a molecular memory of the interactions. In contrast, $^{(IR)}M(t)$ and $^{(R)}M(t)$ are non-zero decaying functions even in the absence of torque since there is always a distribution of frequencies of rotation. If $^{(J)}\psi(t)$ is, at any time, negative, then $^{(J)}M(t)$ must be non-zero; that is, a molecule retains some memory of its interactions. Berne and Harp[25] find that in simulated CO $^{(J)}M(t)$ goes almost to zero within 0.3×10^{-12} s, and that there is then a much slower decay, with a final positive tail. The time of 0.63×10^{-12} s is roughly that taken by a molecule to move from the centre of its 'cage' and meet one of its neighbours at the 'wall'.

An example of an n.m.r. study of spin–rotation relaxation is the work of Rigny and Virlet[51] on the relaxation of the fluorine nuclei in UF_6, WF_6, and MoF_6, all of which are liquid at temperatures little above room temperature. They are unusual in that, contrary to the behaviour of most liquids,[52] the spin–rotation interaction is the dominant mechanism of relaxation even at temperatures well below the critical. The molecules retain their angular momentum for a long (correlation) time, but the rotation is not free since they can move only about 1 radian at 343 K before their angular momentum changes.

These conclusions are revealed by using the generalized Langevin equation which now takes the form

$$\dot{J}(t) = -\int_0^t {}^{(J)}\boldsymbol{M}(t-t')\boldsymbol{J}(t')\,dt' + \boldsymbol{\Gamma}_J(t) \tag{43}$$

where $\Gamma_J(t)$ is the random torque and M the memory function. The associated spectrum is then

$$\frac{{}^{(J)}\tilde{\psi}(i\omega)}{\langle J^2(0) \rangle} = \int_0^\infty \langle J(0) \cdot J(t) \rangle e^{-i\omega_0 t}\,dt \tag{44}$$

$$= {}^{(J)}\tilde{\psi}(0)[i\omega_0 + {}^{(J)}M(\omega_0)]^{-1}$$

where ω_0 is the Larmor frequency of spin precession. This is again sufficiently small to be neglected so the exponential term is unity. That is, $\Gamma_J(t)$ fluctuates so rapidly that its c.f., which is related to $^{(J)}M(\omega)$ by

$$^{(J)}M(\omega) = \frac{1}{\langle J^2(0) \rangle} \int_0^\infty \langle \Gamma_J(0) \cdot \Gamma_J(t) \rangle e^{-i\omega t}\,dt \tag{45}$$

is a delta function. The simple Langevin equation is thus regained with $^{(J)}M$ independent of frequency. Therefore

$$\frac{1}{T_1} \propto \int_0^\infty {}^{(J)}\psi(t)\,dt \propto \frac{{}^{(J)}\tilde{\psi}(0)}{{}^{(J)}M} = {}^{(J)}\tilde{\psi}(0)\tau_J \tag{46}$$

[51] P. Rigny and J. Virlet, *J. Chem. Phys.*, 1967, **47**, 4645.
[52] J. G. Powles, in 'Molecular Relaxation Processes', ed. M. Davies, Academic Press, New York, 1966.

where τ_J is the angular momentum correlation time, inversely proportional to T_1, the spin–rotation relaxation time. As the temperature is raised the torque fluctuates more rapidly, the 'friction' is reduced, and so T_1 decreases. It is found in practice that this decrease follows an Arrhenius law.[27]

For spherical tops such as CH_4, CF_4, SF_6, and the hexafluorides above, the contribution of spin–rotation interaction to the n.m.r. lineshape is comparable with, and greater than at high temperatures, that of spin–spin magnetic dipole interaction. The latter is the contribution to spin resonance relaxation from the interaction of a pair of identical nuclei in the same molecule of spin quantum s, and a separation defined by the vector u and the scalar distance b. The spin–spin relaxation time is

$$[T_2(\omega)]_{ss}^{-1} \approx \frac{2\gamma^4 \hbar^2 s(s+1)}{b^6} \int_0^\infty {}^{(R)}\psi(t)\,\mathrm{d}t \qquad (47)$$

where γ is the gyromagnetic ratio. This relaxation time provides therefore a method of measuring the area under the ${}^{(R)}\psi(t)$ curve, which is a correlation time and is to be compared with a diffusion coefficient in the translational case, equation (6). It does not, however, tell us anything about ${}^{(R)}\psi(t)$ itself as a function of time. Such n.m.r. results can be compared usefully[30] with those of dielectric measurements,[27,28] particularly at temperatures near the triple point where rotational diffusion might be a useful concept. At the boiling point and at higher temperatures the mechanism of reorientation is generally interpreted with the help of the spin–rotation component of T_1, thus taking advantage of the increased periods of rotation. The principal interest of such work is to study any anisotropy of motion; sometimes the rotation is almost free about one axis and diffusional about another perpendicular to it.[53]

The integral of ${}^{(R)}\psi(t)$ over all time defines a correlation time τ_R. In the limit of rotational diffusion this is related to τ_J by Hubbard's equation,[43]

$$\tau_R \tau_J = I/6kT \qquad (48)$$

and in the limit of a rarely perturbed free spherical-top rotation by

$$\tau_R = \tau_J/5 \qquad (49)$$

For the intermediate region McClung[32] has discussed the relation between τ_R and τ_J for spherical tops in terms of the M- and J-diffusion models. These approach the limits of equations (48) and (49) when τ_J is very small and very large. Sillescu has extended[54] the Debye model of Brownian motion and the random jump model[29] of rotation to take account of temporal fluctuations in their rates. Further developments in the use of n.m.r. in this field can be found in the comprehensive reports edited by Harris.[55]

We conclude by applying the formulation in terms of memory functions to spin resonance relaxation. From the equipartition of kinetic energy over two degrees of

[53] D. K. Green and J. G. Powles, *Proc. Phys. Soc.*, 1965, **85**, 87; T. T. Bopp, *J. Chem. Phys.*, 1967, **47**, 3621; D. E. Woessner, B. S. Snowden, and E. T. Strom, *Mol. Phys.*, 1968, **14**, 265; J. Jones and T. M. Di Gennaro, *J. Chem. Phys.*, 1969, **50**, 2392; A. A. Marryot, T. C. Farrar, and M. S. Malmberg, *ibid.*, 1971, **54**, 64.

[54] H. Sillescu, *J. Chem. Phys.*, 1971, **54**, 2110.

[55] 'Nuclear Magnetic Resonance', ed. R. K. Harris, (Specialist Periodical Reports), The Chemical Society, London, 1971–1975, Vols. 1–4.

rotational freedom we have

$$kT = \langle \mathbf{J}^2(0) \rangle / 2I \tag{50}$$

so that

$$\tau_J = \int_0^\infty {}^{(J)}\psi(t)\, \mathrm{d}t \tag{51}$$

When $^{(J)}M$ and $^{(R)}M$ are both delta functions we have

$$
\begin{aligned}
{}^{(J)}\psi(t) &= e^{-t/\tau_J} \\
{}^{(R)}\psi(t) &= e^{-t/\tau_R}
\end{aligned}
\tag{52}
$$

and τ_J and τ_R are linked by Hubbard's relation.

The mean field of force due to the neighbours tends to hold a given molecule in a fixed orientation for a variable time while superimposed on this time-smoothed field is a rapid fluctuation due to the actual molecular motions. This is approximated in Brownian theory by a random torque of simple character superimposed on a steady orientating field. If the constraining field is strong the molecule moves as a damped gyrostatic pendulum. If the constant is highly anisotropic the motion about one axis may approach free rotation. If the molecule is a spherical top its components of rotation behave independently. All these different modes are not describable by a simple exponential c.f. and the introduction of memory functions will probably lead to more satisfactory descriptions. Thus

$$^{(J)}M_0(t) = {}^{(J)}M_0(0) \exp(-t/\tau_J') \tag{53}$$

is likely to lead to a better account of the dependence of the correlation time τ_J on temperature. In the M-diffusion model the product $\tau_J\tau_R$ goes through a minimum, dependent on $\langle \mathcal{O}^2(V) \rangle$, which is more realistic than Hubbard's relation, equation (48). With the truncation

$$^{(J)}M_1(t) = {}^{(J)}M_1(0) \exp(-t/\tau_J'') \tag{54}$$

we have that $(T_1^{-1})_{SR}$ depends both on $\langle \mathcal{O}^2(V) \rangle$ and its time-derivative, so that the product $\tau_J\tau_R$ might behave ever more realistically. These applications have, however, still to be explored.