Time-correlation Functions and Molecular Motion

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1 Introduction

The time-independent thermodynamic properties of molecular liquids and solids and their rationalization in terms of time-independent statistical mechanics receive considerable attention in undergraduate courses in chemistry and physics. The dynamical properties of such systems involve translational, vibrational, and reorientational modes of molecular motion and whereas the vibrational motions, which give rise to infrared, Raman, and neutron-scattering spectra, are well covered in undergraduate courses, considerably less attention is given to translational and reorientational modes of motion. Many of the important physical properties of liquids and solids relate to the latter modes of motion, and in recent years there has been a considerable interest in their study using many experimental techniques. Table 1 lists a selection of the techniques, and will be discussed below. In parallel with experimental studies, a sound theoretical framework has emerged, based on time-correlation functions, which allows translational and reorientational motions to be described formally and in physical terms. In addition there have been simulations, by computer, of the dynamics of assemblies of molecules which yield various time-correlation functions and which may be used for comparison with experimental data and with simple models for motion. We shall see that molecular motions play an essential part in the interpretation of data from relaxation studies, absorption spectroscopy, and certain scattering experiments. Such experiments cover in total the frequency range 10^{-4}—10^{12} Hz. Clearly an appreciation of the nature of molecular motions, their time-scale, and their variation with temperature and applied pressure, in liquids and solids, as revealed by different techniques, should be an essential part of courses concerned with molecular behaviour. However, there are several difficulties which must be overcome before this can be fully achieved. One major difficulty is that a description of translational and reorientational motions is best given through the medium of time-correlation functions and chemists are, on the whole, unfamiliar with such quantities. Excellent accounts of time-correlation functions are available, but most are at research level, with the attendant mathematical sophistication, or do not give sufficient information to serve as an introduction. One aim of the present review is to give an account of time-correlation functions amply illustrated with examples of their deduction for simple models which have practical importance. In addition, it is shown how time-correlation functions may be related to experimental quantities taking as examples (i) the linear response of a dielectric medium and (ii) quasi-elastic scattering from moving point-scatterers. The remainder of the review gives examples of time-correlation functions which have been obtained experimentally using several of the techniques listed in Table 1.

Table 1

Experimental	*Time/frequency range*	*Measured quantity*	*Molecular probe*	*Time-correlation function*	*Refs.*
Tracer diffusion	Seconds to years	Translational diffusion coefficient, D_t	Tagged molecule	$D_t = (\frac{1}{3}) \int_0^\infty \langle v(0).v(t) \rangle \, dt$ $= \lim_{t \to \infty} \{\langle [r(t) - r(0)]^2 \rangle / 6t\}$	1—3
Dielectric relaxation	10^{-4}—10^{11} Hz	Permittivity $\epsilon(t)$ and $\epsilon(\omega)$	(i) Dipole moment	$\langle P_1[u(t)] \rangle$; $\langle \mu_i(0) \, . \, \mu_j(t) \rangle$, D_r	2—18
			(ii) Ions, ion pairs, vacancies	$\langle P_1[u(t)] \rangle$ and mixed correlation functions	
Kerr-effect relaxation	10^{-4}—10^{7} Hz and 10^{-11}—4×10^{-11} s	Electric-field induced optical birefringence	Dipole moments, permanent and induced, optical anisotropy	$\langle P_1[u(t)] \rangle$, $\langle P_2[u(t)] \rangle$	19—24, 112
Mechanical relaxation	10^{-4}—10^{8} Hz	Mechanical storage and loss moduli and compliances	Elastic dipole (in crystals)		6, 14—16, 25
Depolarization of fluorescence	10^{-6}—10^{-9} s	Time-dependence of fluorescence	Transition dipole	$\langle P_2[u(t)] \rangle$	2, 26—30
Nuclear magnetic resonance	10^{3}—10^{8} Hz	Relaxation times T_1, T_{1_ρ}, T_2	Nuclear magnetic moment	Average correlation times	2, 31—34

Quasi-elastic light scattering	10^2—10^{11} Hz	Scattering functions (i) $F_s(\boldsymbol{k},t)$ (ii) $S(\boldsymbol{k},\omega)$	Particle scattering cross-sections, fluctuations in thermodynamic variables, polarizability ellipsoid	(i) Correlation functions for translational and rotational motions of macromolecules, dynamics of fluctuations in pure liquids (ii) Correlation functions for reorientation	2, 35—41
Neutron scattering	10^8—10^{12} Hz	$S(\boldsymbol{k},\omega)$	Scattering cross-section	Correlation functions for translational and rotational motions, correlation times	2, 42—46
Infrared spectroscopy	3 × 10^{10}—10^{14} Hz	(i) Far infrared, $n(\omega)$, $\alpha(\omega)$, $\epsilon(\omega)$	(i) Permanent and induced dipole moments and multi-moments.	$\langle P_1[u(t)]\rangle, \dfrac{\mathrm{d}^2}{\mathrm{d}t^2}\langle P_1[u(t)]\rangle$	2, 47—56
		(ii) Near infra-red $\alpha(\omega)$, vibration–rotation spectra	(ii) Vibration–rotation transition moments	$\langle P_1[u(t)]\rangle, \dfrac{\mathrm{d}^2}{\mathrm{d}t^2}\langle P_1[u(t)]\rangle$	
Raman spectroscopy	10^{18}—10^{14} Hz	$\alpha(\omega)$, vibration–rotation spectra	vibration–rotation transition moments	$\langle P_2[u(t)]\rangle, \dfrac{\mathrm{d}^2}{\mathrm{d}t^2}\langle P_2[u(t)]\rangle$	47, 50

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2 Time-correlation Functions

A. General Considerations.—There are several accounts dealing with time-correlation functions as they arise for different modes of motion and for different experimental techniques (see Table 1 and refs. therein). Of the available accounts, those of Zwanzig,[3] Gordon,[47] Berne,[2] and Berne and co-workers[57,58] are particularly instructive owing to their wide scope.

In this section we consider the definitions of the autocorrelation function $C(t)$ for a dynamical variable A of a system whose macroscopic thermodynamic properties are independent of time. A might be the velocity $\boldsymbol{v}$, position $\boldsymbol{r}$, or dipole moment $\boldsymbol{\mu}$, suitably defined, for a molecule in an assembly of molecules. $C(t)$ may be defined as the ensemble-averaged quantity

$$\begin{aligned} C(t) &= \iint A(p,q;\,\tau)\,A(p,q;\,t+\tau)f(p,q)\,\mathrm{d}p\mathrm{d}q \\ &= \langle A(\tau)\,A(t+\tau)\rangle \equiv \langle A(0)\,A(t)\rangle \end{aligned} \tag{1}$$

$A(t+\tau)$ is the value of A at time $(t+\tau)$ given that the value was $A(\tau)$ at time τ. For a stationary system the product $\langle A(\tau)A(t+\tau)\rangle$ is dependent on the interval t but not on the arbitrary time τ. $f(p,q)$ is the equilibrium phase-space distribution function; $f(p,q)\mathrm{d}p\mathrm{d}q$ is the probability that a molecule has conjugate momenta and co-ordinates in the ranges p to $(p + \mathrm{d}p)$ and q to $(q + \mathrm{d}q)$ respectively. A depends upon p and q explicitly and, because these quantities vary with time for a given molecule, A will vary with time for that molecule.

$C(0) = \iint A^2(p,q;\,\tau)f(p,q)\mathrm{d}p\mathrm{d}q = \langle A^2(\tau)\rangle$ is the mean-square value of A which is calculable, in principle, from time-independent statistical mechanics. The deduction of $C(t)$ is made as follows: Figure 1 shows $A(p,q)$, in phase-space, along a trajectory arising from the thermal motions of the system. We first obtain $A(\tau)\,.\,A(t+\tau)$ averaged over all trajectories which may occur for the interval t, and weight this averaged quantity by the probability $f(p,q)\mathrm{d}p\mathrm{d}q$ of having the initial (p,q) condition for the molecule. The process is repeated from all allowed (p,q) starting conditions and $C(t)$ is obtained using equation (1).

$C(t)$ may also be defined as a time-averaged quantity:[2]

$$C(t) = \lim_{T\to\infty}\left(\frac{1}{T}\right)\int_0^T A(\tau)\,A(t+\tau)\,\mathrm{d}\tau \tag{2}$$

This may be visualized as follows: the dynamical variable follows a trajectory in phase-space as time progresses (Figure 1) and we may form $A(\tau)A(t+\tau)$ starting at the arbitrary time τ. But there is an equal probability that we should take such a product for the interval t at any time τ through the complete trajectory in order to obtain an averaged quantity for an interval of time t. Equation (2) becomes in the limit $T \to \infty$ this average quantity. For a stationary system the

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[57] B. J. Berne and G. D. Harp, *Adv. Chem. Phys.*, 1970, **17**, 63.
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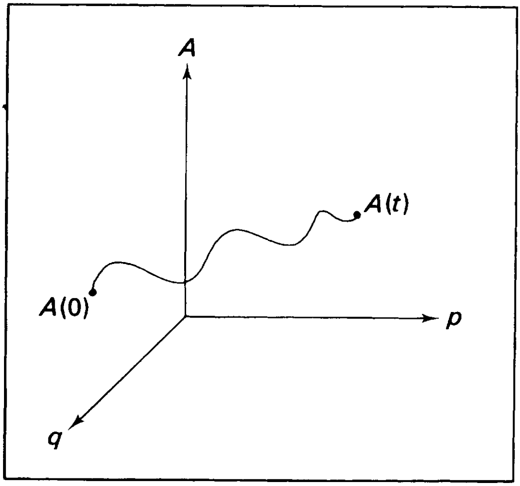

Figure 1 *Schematic illustration of a phase-space trajectory for the dynamical variable A*

ensemble-averaged quantity, equation (1) and the time-averaged quantity, equation (2), are equal, this being known as the ergodic hypothesis.[2,41]

For a comprehensive account of the properties of molecular time-correlation functions, both classical and quantum mechanical, the reader is referred to Berne.[2] The present account considers only classical functions and we note that these have several special mathematical properties[2] amongst which are the following:

(*a*) classical time-correlation functions are even in time, $C(t) = \langle A(0)A(t)\rangle = \langle A(0)A(-t)\rangle$. Thus a series expansion of $C(t)$ contains only terms in even powers of t. Several models for molecular motion give correlation functions whose series expansions involve terms in odd powers of t, and these are not strictly acceptable correlation functions (*e.g.* for an exponential function of time).

(*b*) $C(t)$ satisfies the inequality $-1 \leqslant [C(t)/C(0)] \leqslant 1$. Thus $C(t)$ may become negative with increased t, as is the case for the classical rotator in three dimensions (see Section 2D below). For many models for motion $C(t) \to 0$ as $t \to \infty$, and for such cases we may define a correlation time τ_c for the process as

$$\tau_c = \int_0^{\infty} \left[\frac{C(t)}{C(0)}\right] \mathrm{d}t \qquad (3)$$

For the special case of an exponential correlation function $C(t) = C(0)\exp[-(t/\tau')]$, then $\tau_c = \tau'$. For a distribution of correlation (or 'relaxation') times, where

$$C(t) = C(0) \int p(\tau') \{\exp[-(t/\tau')]\} \,\mathrm{d}\tau'$$

then from equation (3)

$$\tau_c = \langle\tau'\rangle = \int p(\tau')\,\tau'\,\mathrm{d}\tau'$$

For certain models of motion, $C(t) \to$ constant as $t \to \infty$, such a result being obtained for site models of non-equivalent sites and for the rotational diffusion of a symmetric top (see *e.g.* ref. 41).

$C(t)$ described above refers to the autocorrelation function of the dynamical variable A, *e.g.* the molecular time-autocorrelation functions $\langle \boldsymbol{v}_i(0)\cdot\boldsymbol{v}_i(t)\rangle$, $\langle \boldsymbol{r}_i(0)\cdot\boldsymbol{r}_i(t)\rangle$, and $\langle \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle$ for a reference molecule i. Cross-correlation functions between molecules, $\langle \boldsymbol{v}_i(0)\cdot\boldsymbol{v}_j(t)\rangle$, $i \neq j$ *etc.*, may be important in certain systems, for example (i) cross-correlations between group dipole moments along a polymer chain or (ii) cross-correlations between diffusing particles in a bulk liquid. Cross-correlation functions will be discussed as they arise, but for detailed accounts the reader is referred to Berne.[2] Berne and Pecora.[41] and Williams.[7,13]

In order to clarify the nature of $C(t)$, we consider simple models for molecular motion.

B. Translational Diffusion.—Consider the centre-of-mass motion of spherical particles (atoms, molecules) in the liquid state to be governed by a diffusion equation

$$\nabla_t^2\, G_s(\boldsymbol{R},t) = \frac{\partial^2 G_s}{\partial R^2}(\boldsymbol{R},t) + \frac{2}{R}\cdot\frac{\partial G_s}{\partial R}(\boldsymbol{R},t) = \frac{1}{D_t}\cdot\frac{\partial G_s}{\partial_t}(\boldsymbol{R},t) \tag{4}$$

where ∇_t^2 is the radial part of the Laplacian operator, and is familiar from quantum mechanics; D_t is the translational diffusion coefficient and $G_s(\boldsymbol{R},t)\,\mathrm{d}^3R$ is the probability that the particle is in the volume element d^3R about $\boldsymbol{R}$ at time t, given it was at the origin at $t = 0$. It is readily verified by substitution in equation (4) that $G_s(\boldsymbol{R},t)$ is given by

$$G_s(\boldsymbol{R},t) = \frac{1}{[4\pi D_t t]^{3/2}}\exp\left[\frac{-R^2}{4D_t t}\right] \tag{5a}$$

$$G_s(\boldsymbol{R},0) = \delta(\boldsymbol{R}) \tag{5b}$$

where equation (5b) expresses the condition that the particle is at the origin at $t = 0$. $G_s(\boldsymbol{R},t)$ is called the Van Hove self space-time correlation function.[59] This correlation function is used in quasi-elastic light scattering.[2,37,40,41] The time-dependence of the intensity of light scattered from N independently moving spherical point-scatterers may be related to an 'intermediate' self-scattering function $F_s(\boldsymbol{k},t)$ where[2]

$$F_s(\boldsymbol{k},t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \exp\{-i\boldsymbol{k}.[\boldsymbol{r}_j(\tau) - \boldsymbol{r}_j(t+\tau)]\}\right\rangle \tag{6}$$

where $\boldsymbol{r}_j(t+\tau)$ is the position of the jth scatterer at $(t+\tau)$ given that its position was $\boldsymbol{r}_j(\tau)$ at time τ. The sum is taken over all N scatterers in the scattering

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[59] L. Van Hove, *Phys. Rev.*, 1954, **95**, 249.

volume. $\boldsymbol{k}$ is the scattering vector[40,41] of magnitude $|\boldsymbol{k}| = (4\pi n/\lambda_0)\sin(\theta/2)$ where n, λ_0, and θ are refractive index, free-space wavelength, and scattering angle respectively. Equation (6) expresses a time-average over the arbitrary time τ. Assuming the system to be ergodic, and if all scatterers are equivalent, allowing the sum to be omitted, equation (6) may be written as the phase-space average (ensemble-average)

$$F_s(\boldsymbol{k},t) = \int G_s(\boldsymbol{R},t)\,[\exp(i\boldsymbol{k}.\boldsymbol{R})]\,d^3R \tag{7}$$

from equations (5) and (7)

$$F_s(\boldsymbol{k},t) = \exp(-D_t k^2 t) \tag{8}$$

Thus for the simple case of independent spherical point-scatterers undergoing translational diffusion, the time-correlation function $F_s(\boldsymbol{k},t)$ is exponential in time and D_t may be determined from the k-dependence of its correlation time $(D_t k^2)^{-1}$. $F_s(\boldsymbol{k},t)$ may be determined experimentally in the time domain using photon-correlation spectroscopy.[35-41] Scattering measurements may also be conducted in the frequency domain where the spectrum $I(\boldsymbol{k},\omega)$ is measured as a function of frequency (ω) for given values of $\boldsymbol{k}$. For the simple case of scattering which led to equation (8), $I(\boldsymbol{k},\omega)$ is related to $F_s(\boldsymbol{k},t)$ according to the Fourier transformation[60,61]

$$I(\boldsymbol{k},\omega) = NA_s^2\,\frac{1}{2\pi}\int_{-\infty}^{\infty} F_s(\boldsymbol{k},t)\exp[i(\omega-\omega_0)t]\,dt \tag{9}$$

where A_s is the scattering-amplitude factor and ω_0 is the angular frequency of the incident radiation. From equations (8) and (9)

$$I(\boldsymbol{k},\omega) = \frac{NA_s^2}{\pi}\left[\frac{D_t k^2}{(D_t k^2)^2 + (\omega-\omega_0)^2}\right] \tag{10}$$

This spectrum is Lorentzian-shaped with half-width $\Delta\omega_k = 2D_t k^2$; thus D_t may be obtained from the k-dependence of $\Delta\omega_k$. Thus simple translational diffusion gives rise to the time-correlation functions* $G_s(\boldsymbol{R},t)$ and $F_s(\boldsymbol{k},t)$ involving D_t and the latter quantity may be obtained experimentally either directly from $F_s(\boldsymbol{k},t)$ or from $I(\boldsymbol{k},\omega)$.

Before leaving the case of translational diffusion, we note that $G(\boldsymbol{R},t)$ and $F_s(\boldsymbol{k},t)$ as given by equations (5) and (8) are not even in time and are thus not strictly acceptable as correlation functions. This is a consequence of the fact that equation (4) does not take into account the masses of the diffusing particles. We note that the Einstein relation $\langle\Delta R^2(t)\rangle = 6D_t t$ is inappropriate at the shortest times for the same reason. Proper inclusion of particle mass will lead to

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*The general definition of $G_s(\boldsymbol{R},t)$ takes the form of a time-correlation function:

$$G_s(\boldsymbol{R},t) = \langle\delta(\boldsymbol{R} - [\boldsymbol{r}_j(t) - \boldsymbol{r}_j(0)])\rangle$$

(see *e.g.* ref. 41, p. 58).

[60] G. Arfken, 'Mathematical Methods for Physicists', Academic Press, New York, 1966.

[61] R. Bracewell, 'The Fourier Transformation and its Applications', McGraw Hill, New York, 1965.

time-correlation functions whose series expansions contain only even powers of t, but the formulation and solution of the equations of motion will be complicated. Berne[2] has outlined an approach, based on information theory, which leads to equation (5), and hence (8), in the long-time region, but includes the finite masses of the particles so that $G_s(\boldsymbol{R},t)$ is better behaved at short times. $G_s(\boldsymbol{R},t)$ is deduced subject to the constraints that $G_s(\boldsymbol{R},t)$ be normalized, $G_s(\boldsymbol{R},0) = \delta(\boldsymbol{R})$, and that $\langle \Delta R^2(t)\rangle$ be known, and he obtains[2]

$$G_s(\boldsymbol{R},t) = \left[\frac{3}{2\pi\langle \Delta R^2(t)\rangle}\right]^{3/2} \cdot \exp\left[\frac{-3R^2}{2\langle \Delta R^2(t)\rangle}\right] \tag{11}$$

$$F_s(\boldsymbol{k},t) = \exp\left[\frac{-k^2\langle \Delta R^2(t)\rangle}{6}\right] \tag{12}$$

Equation (11) is the well-known Gaussian approximation[2] for $G_s(\boldsymbol{R},t)$. $\langle \Delta R^2(t)\rangle$ is given quite generally by[2]

$$\langle \Delta R^2(t)\rangle = 2\int_0^t \langle \boldsymbol{v}(0).\boldsymbol{v}(\tau)\rangle\,(t-\tau)\,\mathrm{d}\tau \tag{13}$$

If $\langle \boldsymbol{v}(0)\cdot\boldsymbol{v}(t)\rangle$ is specified, $\langle \Delta R^2(t)\rangle$, $F_s(\boldsymbol{k},t)$, and $G_s(\boldsymbol{R},t)$ follow from equations (11)—(13). Berne[2] specified $\langle \boldsymbol{v}(0).\boldsymbol{v}(t)\rangle = \langle v^2(0)\rangle\exp(-\gamma|t|)$, where γ is a 'friction-coefficient'. Insertion into equation (13) gives for $t > 0$

$$\langle \Delta R^2(t)\rangle = 2\langle v^2(0)\rangle\left[\left(\frac{t}{\gamma}\right) - \frac{1}{\gamma^2}\,[1-\exp(-\gamma t)]\right] \tag{14}$$

Thus

$$\langle \Delta R^2(t)\rangle = \langle v^2(0)\rangle.t^2;\ t \ll \gamma^{-1} \tag{15a}$$

$$\langle \Delta R^2(t)\rangle = 2\langle v^2(0)\rangle t/\gamma \equiv 6D_t t;\ t \gg \gamma^{-1} \tag{15b}$$

Equation (15b) corresponds to translational diffusion, equation (5a), while equation (15a) corresponds to the case of free-particle motion with $\langle v^2(0)\rangle = 3kT/M$. Clearly equation (14) taken with equations (11) and (12) leads to an improvement over equations (5) and (6) and will be applicable to the translational motions of, say, spherical polymer molecules (*e.g.* high molecular weight polystyrene) in a continuum of small solvent molecules. However, equation (14) fails to account for the motions of small molecules—as evidenced by computer simulations[2]—since $\langle \boldsymbol{v}(0)\cdot\boldsymbol{v}(t)\rangle$ there does not follow the simple exponential relation in time.

C. Rotational Diffusion.—The rotational diffusion of a unit vector may be considered[2,41,62] as a random motion of a point on the surface of a sphere of unit radius. If* $f(\Omega,t)\mathrm{d}\Omega$ is the probability that the unit vector points into the solid angle $\mathrm{d}\Omega$ around Ω at time t, *given* that its direction was uniquely along the $+z$ direction at $t = 0$, then the diffusion equation may be written in polar-co-ordinate form as

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*$f(\Omega,t)$ as defined here should be written in the notation of the conditional probability function $f(\Omega,t|0,0)$, but here and in the following sections we write $f(\Omega,t)$ for the sake of brevity.

[62] B. J. Berne, P. Pechukas, and G. D. Harp, *J. Chem. Phys.*, 1968, **49**, 3125.

$$\nabla_r^2 f(\Omega,t) = \frac{1}{\sin^2\theta}\left[(\sin\theta)\frac{\partial}{\partial\theta}\left((\sin\theta)\frac{\partial f}{\partial\theta}(\Omega,t)\right) + \frac{\partial^2}{\partial\phi^2}f(\Omega,t)\right]$$
$$= \frac{1}{D_r}\cdot\frac{\partial f}{\partial t}(\Omega,t) \qquad (16)$$

where D_r is the rotational diffusion coefficient.

If we assume that the motion always occurs in a manner such that $f(\Omega,t)$ is symmetric with respect to the (arbitrary) z-axis, as may be the case for an isotropic liquid, then $f(\Omega,t)$ depends on θ and t but not on ϕ. For this special case equation (16) may be rewritten in terms of the variable $u = \cos\theta$:

$$(1 - u^2)\frac{\partial^2 f}{\partial u^2} - 2u\frac{\partial f}{\partial u} = \frac{1}{D_r}\frac{\partial f}{\partial t} \qquad (17)$$

Equation (17) is conveniently solved[19] by expanding $f(\Omega,t)$ in terms of Legendre polynomials.[60]

$$f(\Omega,t) = \sum_{m=0}^{\infty} P_m(u)a_m(t) \qquad (18)$$

Substituting equation (18) into equation (17) gives

$$\sum_{m=0}^{\infty} a_m(t)[(1 - u^2)\frac{\mathrm{d}^2}{\mathrm{d}u^2}P_m(u) - 2u\frac{\mathrm{d}}{\mathrm{d}u}P_m(u)] = \sum_{m=0}^{\infty}\frac{P_m(u)}{D_r}\cdot\frac{\mathrm{d}a_m(t)}{\mathrm{d}t} \qquad (19)$$

But the term in square brackets on the l.h.s. is $-m(m + 1)P_m(u)$ (see *e.g.* ref. 60, p. 424), so equation (19) becomes

$$-\sum_{m=0}^{\infty} a_m(t)\,[m(m + 1)\,P_m(u)] = \frac{1}{D_r}\cdot\sum_{m=0}^{\infty} P_m(u)\frac{\mathrm{d}}{\mathrm{d}t}a_m(t) \qquad (20)$$

Equating coefficients of $P_m(u)$ yields a set of uncoupled equations each of the form

$$\frac{\mathrm{d}}{\mathrm{d}t}a_m(t) = -\,m(m + 1)\,D_r a_m(t) \qquad (21)$$

Hence

$$a_m(t) = a_m(0)\exp[-\,m(m + 1)\,D_r t] \qquad (22)$$

$$f(\Omega,t) = \sum_{m=0}^{\infty} P_m(u)\,a_m(0)\exp[-m(m + 1)\,D_r t] \qquad (23)$$

The probability of obtaining the vector in the range u to $u + \mathrm{d}u$ is

$$\not{f}(u,t)\,\mathrm{d}u = \int_0^{2\pi} f(\Omega,t)\,\mathrm{d}u\,\mathrm{d}\phi = 2\pi f(\Omega,t)\,\mathrm{d}u\,\cdot$$

At $t = 0$ the vector is uniquely along the $+z$-axis, so $\not{f}(u,0) = \delta(u - 1)$, but this delta function may be expanded as $\sum_{m=0}^{\infty}\frac{1}{2}(2m + 1)P_m(u)$, and comparing this with

$2\pi f(\Omega,0) = 2\pi \sum_{m=0}^{\infty} P_m(u)a_m(0)$ gives $a_m(0) = (2m + 1)/(4\pi)$. Equation (23) may be written as

$$f(\Omega,t) = \frac{1}{4\pi} \cdot \sum_{m=0}^{\infty} (2m + 1) P_m(u) \exp[- m(m + 1) D_r t] \tag{24}$$

The orientational time-correlation functions $\langle P_n[\cos\theta(t)]\rangle \equiv \langle P_n[u(t)]\rangle$ are defined by the relation

$$\langle P_n[u(t)]\rangle = \int_{-1}^{1} \int_{0}^{2\pi} f(\Omega,t) P_n(u) \, du \, d\phi \tag{25}$$

The orthogonality and normalization conditions for Legendre polynomials are expressed by

$$\int_{-1}^{1} P_n(u) P_m(u) \, du = 0, n \neq m; \quad \int_{-1}^{1} P_n{}^2(u) \, du = 2/(2n + 1) \tag{26a, b}$$

Hence, from equations (24) and (25),

$$\langle P_n[u(t)]\rangle = \exp[- n(n + 1) D_r t] \tag{27}$$

Equations (24) and (27) are the results for rotational diffusion governed by equation (16). $f(\Omega,t)$ involves products of space functions, $P_m(u)$, and time functions, $\exp[-m(m + 1)D_r t]$ and, since both functions decrease rapidly with increasing m, $f(\Omega,t)$ is dominated by the first few terms in the series. The correlation functions, equation (27), are just individual decay functions in equation (24), and being exponential in time $\langle P_n[u(t)]\rangle$ decays with increasing rapidity with increasing n. The pattern for the evaluation of $C(t)$ for translational and rotational diffusion is (i) solve the equations of motion for the conditional space–time distribution functions $G(\boldsymbol{R},t)$ and $f(\Omega,t)$ and (ii) deduce the phase-space averages $C(t)$ using equations (7) and (25). Averaging over a momentum distribution is not involved since equations (4) and (16) involve co-ordinates but not momenta. This means that the mass or inertia of the molecule has not been explicitly considered, with the result that the translator or rotator moves at its terminal linear or angular velocity, but with constantly changing direction.

Equations (24) and (27) may only be applied in the 'long-time' region for large molecules moving in a continuum of small (solvent) molecules—in common with equations (5) and (8) for translational diffusion. There is ample evidence from experiment[5,7,47,49–56,63] and from computer simulations[2,57,58,64–69] that orientational correlation functions for small molecules

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[64] B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 1959, **31**, 459.
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in the liquid state do not conform to equations (24) and (27), but resemble the free-rotator correlation functions at short times (see Section 2D below). It is appropriate at this point to indicate difficulties which arise when a time-correlation function which is not even in time [*e.g.* equation (27)] is applied to experimental results. This may be illustrated by the example of the dielectric relaxation and far-infrared absorption of a dipolar medium. For the special case of a low-permittivity medium, say a dilute solution of dipolar molecules in a non-polar medium, the permittivity $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ is related to $\langle P_1[u(t)]\rangle$ according to[5,7-12]

$$\begin{aligned}\frac{\epsilon(\omega)-\epsilon_\infty}{\epsilon_0-\epsilon_\infty} &= \int_0^\infty\left[-\frac{d}{dt}\langle P_1[u(t)]\rangle\right][\exp -i\omega t]\,dt\\ &= 1 - i\omega\int_0^\infty \langle P_1[u(t)]\rangle\,[\exp -i\omega t]\,dt\end{aligned} \tag{28}$$

where ϵ_0 and ϵ_∞ are the limiting low- and high-frequency permittivities respectively. For the case of a rotational diffusion, equation (28) becomes, with the aid of equation (27), the well-known single relaxation time equation

$$\frac{\epsilon(\omega)-\epsilon_\infty}{\epsilon_0-\epsilon_\infty} = \frac{1}{1+i\omega(2D_r)^{-1}} \tag{29}$$

The plot of $\epsilon''(\omega)$ against $\log\omega$ gives a bell-shaped curve having its maximum at $\omega_m = 2D_r$. Although such an equation may be used to represent dielectric relaxation data for a variety of liquids and solids[4-6] considerable difficulties arise at very high microwave frequencies and in the far-infrared range where the attenuation factor $\alpha(\omega) = \omega\epsilon''(\omega)/(nc)$ is measured. It is a property of one-sided Fourier transforms[61] that for a function of time $g(t)$,

$$\mathscr{F}\left[\frac{dg(t)}{dt}\right] = i\omega\mathscr{F}[g(t)] - g(0)_{+0} \tag{30}$$

for $g(t) = [d\langle P_1[u(t)]\rangle/dt]$, equations (28) and (30) give for $\epsilon''(\omega)$

$$\frac{\omega\epsilon''(\omega)}{\epsilon_0-\epsilon_\infty} = -\left\{\int_0^\infty\left[\frac{d^2}{dt^2}\langle P_1[u(t)]\rangle\right]\cos\omega t\,dt + \left[\frac{d}{dt}\langle P_1[u(t)]\rangle\right]_{t=0}\right\} \tag{31}$$

For rotational diffusion, equation (27), equation (31) becomes

$$\frac{\omega\epsilon''(\omega)}{\epsilon_0-\epsilon_\infty} = \frac{\omega^2\tau_1}{1+\omega^2\tau_1{}^2} \tag{32}$$

where $\tau_1 = (2D_r)^{-1}$. Equation (32) for $\omega\tau_1 \gg 1$ gives $\omega\epsilon''(\omega) = (\epsilon_0 - \epsilon_\infty)/\tau_1$, *i.e.* the rotational diffusion model gives $\alpha(\omega)$ = constant at frequencies higher than the relaxation region, a wholly unrealistic and physically unacceptable result. The reason is clear: the correlation function is badly behaved at short times owing to the omission of inertia in its derivation. For $\langle P_1[u(t)]\rangle$ even in time, which will be obtained when inertial effects are correctly included, $\langle P_1[u(t)]\rangle$ has zero slope at $t = 0$ so equation (31) becomes

$$\frac{\omega\epsilon''(\omega)}{\epsilon_0-\epsilon_\infty} = \int_0^\infty\left[\frac{d^2}{dt^2}\langle P_1[u(t)]\rangle\right]\cos\omega t\,dt \tag{33}$$

which on inversion gives

$$\frac{d^2}{dt^2}\langle P_1[u(t)]\rangle = \frac{2}{\pi}\int_0^\infty \left[\frac{\omega\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty}\right]\cos\omega t \mathrm{d}\omega \tag{34}$$

while inversion of equation (28) gives

$$\langle P_1[u(t)]\rangle = \frac{2}{\pi}\int_0^\infty \left[\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty}\right]\cos\omega t \frac{\mathrm{d}\omega}{\omega} \tag{35}$$

Thus $\langle P_1[u(t)]\rangle$ is obtained from a cosine transform of $\epsilon''(\omega)$ *vs.* logω data while $\langle \ddot{P}_1[u(t)]\rangle$ is obtained as a cosine transform of $\omega\epsilon''(\omega)[\propto \alpha(\omega)]$ *vs.* ω data.

D. Classical Free Rotation.—Correlation functions involve distributions over co-ordinates and momenta and in Sections B and C above we have seen simple examples where correlation is lost through change of molecular co-ordinates in time. In order to illustrate loss of correlation involving momentum distributions, we consider the simple model[2] of free rotation, in a plane, of a rod of moment of inertia I, whose rotational velocity ω_r is governed by a Boltzmann distribution function $f(\omega_r) = [I/(2\pi kT)]^{\frac{1}{2}} \exp[-I\omega_r^2/(2kT)]$. If x is a unit vector along the axis of the rod, then for a given angular velocity ω_r, $x(0).x(t) = \cos\omega_r t$. This scalar product obviously does not decay in time. The average quantity $\langle x(0).x(t)\rangle$, *i.e.* averaged over $f(\omega_r)$, does decay as a result of the superposition of cosine functions:

$$\langle x(0).x(t)\rangle = \int_{-\infty}^{\infty} f(\omega_r)\cos\omega_r t \, \mathrm{d}\omega_r = \exp(-kTt^2/I) \tag{36}$$

For free rotation in three dimensions, $\langle x(0).x(t)\rangle \equiv \langle P_1[u(t)]\rangle$ and is given by[2,7,9,55,70]

$$\langle P_1[u(t)]\rangle = \sum_{m=0}^{\infty}(-1)^m (kTt^2/I)^m \frac{1}{1.3.5\ldots(2m-1)} \tag{37}$$

These correlation functions are both even in time and involve the molecular factor I but do not involve intermolecular factors. Collisions are involved in establishing and maintaining the Boltzmann distribution of ω_r but if the time-scale between collisions is far longer than that required for molecular rotation, collisions, and hence intermolecular interactions, are not involved in the decay of $\langle x(0)\cdot x(t)\rangle$. The effect of collisions on time-correlation functions for three-dimensional rotators, leading for example to the J and M diffusion models of Gordon, have been extensively discussed[2,8,9,47,52,54] and this is a topic which continues to receive considerable attention since it embraces all the problems of the fast rotational motions of small molecules in the liquid and gaseous states. Note that $\langle x(0).x(t)\rangle$, equation (36), is always positive for the plane rotator but goes negative for the three-dimensional rotator, equation (37). For the latter case such behaviour is rationalized by saying that the rotating vector tends, after a certain time, to point on average in the opposite direction to that which it had at $t = 0$.

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E. Barrier Systems.—The classical motions of molecules, ions, or vacancies between equilibrium sites in a crystalline solid may give rise to dielectric and mechanical relaxation processes.[4–7,11,12,14–17,71–77] Cole[11] has shown how time-correlation functions for dielectric relaxation may be deduced for site-models. Williams and Cook[12] have extended this work and have included Group Theory as an aid to the solution of the basic rate equations for complicated barrier systems. These orientational time-correlation functions are exponential, or weighted sums of exponential, functions of time since the inertia of the molecule is not taken into account in the rate equations.*

Consider first the simple case of a two-site model, Figure 2, where a dipole may occupy two orientations, π apart, separated by a barrier E, and moves between sites with a transition probability k. The *a priori* occupational probabilities $p_1(t), p_2(t)$ for sites 1 and 2 are governed by the rate equations

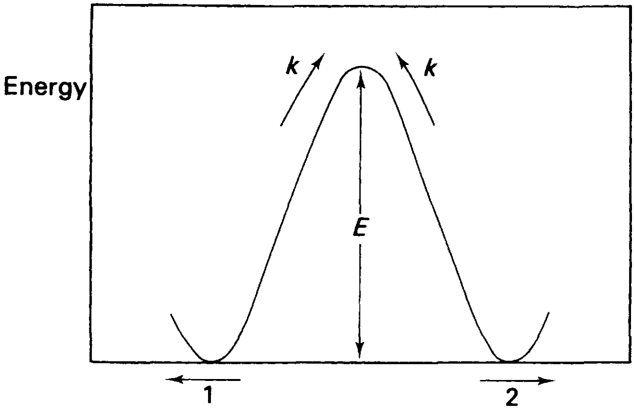

Figure 2 *Energy diagram for dipole reorientation between two equivalent sites π apart*

$$\frac{\mathrm{d}p_1(t)}{\mathrm{d}t} = -kp_1(t) + kp_2(t); \quad \frac{\mathrm{d}p_2}{\mathrm{d}t}(t) = kp_1(t) - kp_2(t) \qquad (38\text{a, b})$$

Whilst such equations may be solved by several methods,[12,14–16,72–75] that[12] involving matrices[78] and Group Theory[79,80] is particularly useful for all site

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*Brot[9] has considered the short-time behaviour for molecular motion in a barrier system.

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models possessing a degree of symmetry. Equation (38) may be written in matrix form as

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{p}(t) = \boldsymbol{T}\boldsymbol{p}(t) \tag{39}$$

whose general solution is[78]

$$\boldsymbol{p}(t) = [\exp \boldsymbol{T}t]\boldsymbol{p}(0) = \boldsymbol{S}[\exp \boldsymbol{D}t]\boldsymbol{S}^{-1}\boldsymbol{p}(0) \tag{40}$$

where $\boldsymbol{p}(t) = \{p_1(t), p_2(t)\}$ and is the column vector of the $p_i(t)$, and $\boldsymbol{T} = \begin{bmatrix} -k & k \\ k & -k \end{bmatrix}$. $\boldsymbol{S}$ is the matrix that performs the transformation $\boldsymbol{S}^{-1}\boldsymbol{T}\boldsymbol{S} = \boldsymbol{D}$, where $\boldsymbol{D}$ is a diagonal matrix. If $\boldsymbol{S}$ and $\boldsymbol{D}$ can be found, $\boldsymbol{p}(t)$ follows from equation (40) with the aid of the relation[78] $\exp\{\mathrm{diag}\,\lambda_m t\} = \{\mathrm{diag}\,(\exp\lambda_m t)\}$. Here the λ_m are the elements of $\boldsymbol{D}$. Although the solution to equation (40) is simple for the two-site model, we introduce Group Theory at this stage since its use in more complicated site-models is well illustrated by the two-site model. An orthogonal matrix $\boldsymbol{Q}$ is deduced using the symmetry of the sites[12] and we perform the transformation $\boldsymbol{Q}^{-1}\boldsymbol{T}\boldsymbol{Q} = \boldsymbol{W}$. $\boldsymbol{W}$ is a matrix which is blocked out along its main diagonal. Its constituent smaller matrices may be taken individually and their eigenvalues and eigenvectors determined. This leads to a matrix $\boldsymbol{U}$ where $\boldsymbol{U}^{-1}\boldsymbol{W}\boldsymbol{U} = \boldsymbol{D}$. Hence

$$\boldsymbol{p}(t) = \boldsymbol{Q}\boldsymbol{U}[\exp \boldsymbol{D}t]\,\boldsymbol{U}^{-1}\,\boldsymbol{Q}^{-1}\,\boldsymbol{p}(0) \tag{41}$$

In suitable cases[12] $\boldsymbol{Q} = \boldsymbol{S}$, and this occurs provided that no class appears more than once in the reducible representation generated using the sites as the basis set. For the two-site model the C_2 character table gives $\Gamma = A + B$, and forming $\boldsymbol{Q}$ from A and B irreducible representations and hence $\boldsymbol{W}$ we find $\boldsymbol{Q}^{-1}\boldsymbol{T}\boldsymbol{Q} = \boldsymbol{D}$ and $\boldsymbol{U} = \boldsymbol{E}$. Here $\boldsymbol{E}$ is the identity matrix, and $\boldsymbol{Q} = \boldsymbol{S}$. Hence

$$\boldsymbol{S} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}; \quad \boldsymbol{D} = \begin{bmatrix} 0 & 0 \\ 0 & -2k \end{bmatrix} \tag{42a, b}$$

$$\boldsymbol{p}(t) = \begin{bmatrix} p_1(t) \\ p_2(t) \end{bmatrix} = \tfrac{1}{2}\begin{bmatrix} 1 + \psi_2(t), & 1 - \psi_2(t) \\ 1 - \psi_2(t), & 1 + \psi_2(t) \end{bmatrix}\begin{bmatrix} p_1(0) \\ p_2(0) \end{bmatrix} \tag{43}$$

where $\psi_2(t) = \exp(-2kt)$.

$\langle \boldsymbol{\mu}(0).\boldsymbol{\mu}(t)\rangle$, which is the non-normalized dipole vector-time-correlation function $= \mu^2\langle \boldsymbol{x}(0).\boldsymbol{x}(t)\rangle$, is obtained[11,12] as the average of the decay functions $\xi_1(t)$ and $\xi_2(t)$ for dipoles starting in sites 1 and 2 respectively at $t = 0$.

$$\langle \boldsymbol{\mu}(0).\boldsymbol{\mu}(t)\rangle = \mu^2 \sum_{i=1}^{2} {}^0p_i\,\xi_i(t);\; \xi_i(t) = \sum_{i=1}^{2} p_{ji}(t)\,\boldsymbol{\mu}_i\,.\,\boldsymbol{\mu}_j \tag{44a, b}$$

${}^0p_i$ is the equilibrium occupation probability of site i; the sum is taken over all sites. $p_{ji}(t)$ is the conditional probability that the dipole is in site j at t given it was in site i at $t = 0$. $p_{j1}(t)$ follows from equation (43) with $p_1(0) = 1, p_2(0) = 0$ with similar considerations for $p_{j2}(t)$. Now $\boldsymbol{\mu}_1.\boldsymbol{\mu}_1 = \boldsymbol{\mu}_2.\boldsymbol{\mu}_2 = -\boldsymbol{\mu}_1.\boldsymbol{\mu}_2$, so

$$\langle \boldsymbol{\mu}(0)\,.\,\boldsymbol{\mu}(t)\rangle = \mu^2\exp(-2kt) \tag{45}$$

and the correlation function is exponential in time with a relaxation time $(2k)^{-1}$. For more complicated barrier systems several relaxation times may arise and also $\langle \boldsymbol{\mu}(0).\boldsymbol{\mu}(t)\rangle$ will not generally decay to zero for sites that are non-equivalent in energy. As examples we consider[12] (i) a six-site model having C_6 symmetry, (ii) a six-site model having D_{4h} symmetry, and (iii) a three-site model having C_{2v} symmetry. Table 2 indicates these models and gives the essential matrices.

(i) All sites are equal in energy and the transition probabilities k_{i-j} are all equal to k. Of the five decay functions,[12] $\psi_j(t)$, only three are distinguishable and $\psi_2(t) = \exp(-4kt)$, $\psi_3(t) = \psi_4(t) = \exp(-kt)$, $\psi_5(t) = \psi_6(t) = \exp(-3kt)$. For this case all the $\xi_i(t)$ are equal since the loss of correlation in time starting from a given site is the same as that from any of the six equivalent sites. Also ${}^0p_i = \frac{1}{6}$ for $i = 1$—6; thus

$$\langle \boldsymbol{\mu}(0).\boldsymbol{\mu}(t)\rangle = \mu^2\xi_1(t) = \mu^2 \sum p_{j1}(t)\, \boldsymbol{\mu}_1.\boldsymbol{\mu}_j$$

where

$$p_{j1}(t) = \tfrac{1}{6}\begin{bmatrix} 1 + \psi_2(t) + 2\psi_3(t) + 2\psi_5(t) \\ 1 - \psi_2(t) + \psi_3(t) - \psi_5(t) \\ 1 + \psi_2(t) - \psi_3(t) - \psi_5(t) \\ 1 - \psi_2(t) - 2\psi_3(t) + 2\psi_5(t) \\ 1 + \psi_2(t) - \psi_3(t) - \psi_5(t) \\ 1 - \psi_2(t) + \psi_3(t) - \psi_5(t) \end{bmatrix} \tag{46}$$

Hence $\langle \boldsymbol{\mu}(0).\boldsymbol{\mu}(t)\rangle = \mu^2\exp(-kt)$. Thus of the three relaxation modes $\psi_2(t)$, $\psi_3(t)$, and $\psi_5(t)$ only $\psi_3(t)$ is active in the dielectric experiment. Similar considerations show that $\langle 3\cos^2\theta(t) - 1\rangle/2$, which corresponds to Kerr-effect relaxation, is characterized by $\psi_5(t)$. This emphasizes that different experimental techniques may probe different aspects of the motion where the motion is completely described by the basic rate equations. It is therefore necessary, in general, to compare the time-correlation functions obtained from several related experiments[15,16] in order to establish the mechanism of relaxation.

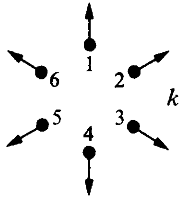
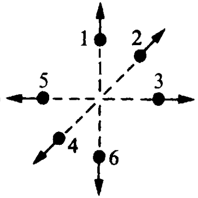
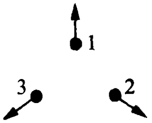
(ii) Sites 1 and 6 are equal in energy; sites 2—5 are equivalent but different in energy from sites 1 and 6. There are four distinguishable decay functions,[12] $\psi_2(t) = \exp[-2(2k_1 + k_2)t]$, $\psi_3(t) = \exp[-2(k_2 + 2k_3)t]$, $\psi_4(t) = \exp[-4k_1t)$, and $\psi_5(t) = \psi_6(t) = \exp[-2(k_2 + k_3)t]$. Since $\xi_1(t) = \xi_6(t)$, $\xi_2(t) = \xi_3(t) = \xi_4(t) = \xi_5(t)$, and ${}^0p_1 = {}^0p_6 = [2(1 + 2\eta)]^{-1}$, ${}^0p_2 = {}^0p_3 = {}^0p_4 = {}^0p_5 = \eta[2(1 + 2\eta)]^{-1}$, where $\eta = (k_1/k_2)$, it follows that

$$\langle \boldsymbol{\mu}(0)\,.\,\boldsymbol{\mu}(t)\rangle = \mu^2\frac{[\xi_1(t) + 2\eta\xi_2(t)]}{(1 + 2\eta)} = \mu^2\frac{[\psi_4(t) + 2\eta\,\psi_5(t)]}{(1 + 2\eta)} \tag{47}$$

In this case two of the four relaxation modes are active in a dielectric experiment. Note that all of $\langle\mu^2\rangle = \sum\limits_i {}^0p_i\,\mu_i^2$ is relaxed for models (i) and (ii), *i.e* $\langle \boldsymbol{\mu}(0).\boldsymbol{\mu}(t)\rangle$ decays to zero.

(iii) Sites 2 and 3 are equivalent but are different in energy from site 1. Use of the C_{2v} character table gives $\boldsymbol{Q}$ and hence $\boldsymbol{W}$, where $\boldsymbol{W}$ contains one 1×1 and one 2×2 matrix. The latter matrix has one eigenvalue which is zero; thus use of Group Theory easily leads to $\boldsymbol{D}$ and $\boldsymbol{U}$ where

Table 2

		T	**S**	**D**
(i)		$\begin{bmatrix} -2 & 1 & 0 & 0 & 0 & 1 \\ 1 & -2 & 1 & 0 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 & 0 \\ 0 & 0 & 1 & -2 & 1 & 0 \\ 0 & 0 & 0 & 1 & -2 & 1 \\ 1 & 0 & 0 & 0 & 1 & -2 \end{bmatrix}$	$\begin{array}{cccccc} a & a & 2b & 0 & 2b & 0 \\ a & -a & b & y & -b & -y \\ a & a & -b & y & -b & y \\ a & -a & -2b & 0 & 2b & 0 \\ a & a & -b & -y & -b & -y \\ a & -a & b & -y & -b & y \\ A & B & \multicolumn{2}{c}{\underbrace{\qquad\qquad}_{E_1}} & \multicolumn{2}{c}{\underbrace{\qquad\qquad}_{E_2}} \end{array}$ $6a^2 = 1;\quad 12b^2 = 1;\quad 4y^2 = 1$	diag $[(0, -4k, -k, -k, -3k, -3k)]$
		T	**Q**	**D**
(ii)		$\begin{bmatrix} -4k_1 & k_2 & k_2 & k_2 & k_2 & 0 \\ k_1 & -p & k_3 & 0 & k_3 & k_1 \\ k_1 & k_3 & -p & k_3 & 0 & k_1 \\ k_1 & 0 & k_3 & -p & k_3 & k_1 \\ k_1 & k_3 & 0 & k_3 & -p & k_1 \\ 0 & k_2 & k_2 & k_2 & k_2 & -4k_1 \end{bmatrix}$ $p = 2(k_2 + k_3)$	$\begin{array}{cccccc} a & 0 & 0 & a & 0 & 0 \\ 0 & b & b & 0 & a & 0 \\ 0 & b & -b & 0 & 0 & a \\ 0 & b & b & 0 & -a & 0 \\ 0 & b & -b & 0 & 0 & -a \\ a & 0 & 0 & -a & 0 & 0 \\ \multicolumn{2}{c}{\underbrace{\qquad\qquad}} & & & \multicolumn{2}{c}{\underbrace{\qquad\qquad}} \\ A_{1g} & B_{1g} & A_{2u} & E_u & & \end{array}$ $2a^2 = 1;\ 4b^2 = 1$	diag$[(0, -2(k_2 + 2k_1), -2(k_2 + 2k_3), -4k_1, -2(k_2 + k_3), -2(k_2 + k_3))]$
(iii)		$\begin{bmatrix} -2k_1 & k_2 & k_2 \\ k_1 & -(k_2 + k_3) & k_3 \\ k_1 & k_3 & -(k_2 + k_3) \end{bmatrix}$	$\begin{array}{ccc} 1 & 0 & 0 \\ 0 & b & b \\ 0 & b & -b \\ A_1 & \multicolumn{2}{c}{\underbrace{\qquad\qquad}_{B_2}} \end{array}$ $2b^2 = 1$	diag$[(0, -(k_2 + 2k_1), -(k_2 + 2k_3))]$

$$\boldsymbol{U} = \begin{bmatrix} \alpha & \gamma & 0 \\ \alpha y/\beta & -\gamma/(2\beta) & 0 \\ 0 & 0 & 1 \end{bmatrix} ; \ \alpha^2(1 + 2y^2) = 1, \tfrac{3}{2}\gamma^2 = 1, \ \beta^2 = \tfrac{1}{2} \tag{48}$$

$y = (k_1/k_2)$. $\boldsymbol{p}(t)$ and $\langle \boldsymbol{\mu}(0) . \boldsymbol{\mu}(t) \rangle$ follow from equations (41) and (44). Hence[11,12]

$$\langle \boldsymbol{\mu}(0).\boldsymbol{\mu}(t) \rangle = \frac{\mu^2}{(1 + 2y)^2} [(1 + 2y\cos\theta_{12})^2 + 2y(1 - \cos\theta_{12})^2 \, \psi_2(t) + 2y(1 + 2y)(1 - \cos^2\theta_{12}) \, \psi_3(t)] \tag{49}$$

where θ_{12} is the angle between the dipole direction in sites 1 and 2, $\psi_2(t) = \exp[-(2k_1 + k_2)t]$, and $\psi_3(t) = \exp[-(k_2 + 2k_3)t]$. The correlation function does not decay to zero but to $\mu^2(1 + 2y\cos\theta_{12})^2/(1 + 2y)^2$. This is just $[\langle \boldsymbol{\mu} \rangle]^2$ where $\langle \boldsymbol{\mu} \rangle$ is the mean dipole moment; $\langle \boldsymbol{\mu} \rangle = \sum_{i=1}^{3} {}^0p_i \, \boldsymbol{\mu}_i$ for the three-site model. Since site 1 has a different energy from that of the equivalent sites 2 and 3, $\langle \boldsymbol{\mu} \rangle$ lies along the dipole direction for site 1. This is an example where correlation is not completely lost with increasing time. For a polycrystalline material the random distribution of the co-ordinates of barrier systems ensures that $\langle \boldsymbol{\mu} \rangle$ will average to zero for a bulk material. For such a case dielectric relaxation determines an effective dipole moment $\mu_{\text{eff}} = [\langle \mu^2 \rangle - \langle \boldsymbol{\mu} \rangle^2)]^{\frac{1}{2}}$ and a relaxation governed by $\psi_2(t)$ and $\psi_3(t)$. Such barrier models are used[4,5,12,14–17,71–77] for relaxation in rotator-phase organic crystals and doped inorganic crystals.

F. Many-body Systems.—The simple models considered above illustrate how time-correlation functions are deduced *via* time-dependent distribution functions. Although such models may approximately represent the long-time behaviour of various systems, they fail at short times ($t < 10^{-10}$ s), particularly for systems comprising small molecules. In general, the equilibrium and dynamic behaviour of an ensemble of molecules may only be correctly deduced by taking into account the attraction–repulsion interactions of all its molecules. Formally the problem involves the solution of the Liouville equation of motion for a given system[2,3,41] or, alternatively, the N equations of motion,[2] one for each molecule! Such problems are essentially intractable analytically, so as an alternative the dynamics of large ensembles ($N \sim 10^2$) of interacting particles have been solved numerically with the aid of a computer,[2,57,58,64–68] a method which is commonly termed 'molecular dynamics'. Such simulations yield the equilibrium information (*e.g.* radial distribution functions) and the various time-correlation functions. These have been carried out for argon,[65] diatomic molecules,[2,57,58,66,67] and liquid water[68] and will be discussed below. In principle it should be possible to fit different experimental time-correlations obtained for a given system using a simulation based on a parameterized form of the intermolecular potential, hence deducing its parameters. There is little doubt that this is the most thorough approach available for interpreting the observed equilibrium and dynamic properties of liquids and solids. The technique of molecular dynamics is limited to $t < 10^{-10}$ s for small-molecule systems, whereas motions occur in many systems on a far longer time-scale. Such slower motions cannot be simulated since one includes a very large number of molecules and the time required for the computations becomes prohibitive (see ref. 2, p. 621).

Another representation of motions in liquids and solids involves the memory functions of time-correlation functions $C(t)$. This has been reviewed by Berne and co-workers.[2,57,58] It may be shown quite generally that $C(t)$ obeys the equation

$$\frac{\partial C(t)}{\partial t} = -\int_0^t K_0(\tau)C(t-\tau)\,\mathrm{d}\tau \tag{50}$$

where $K_0(\tau)$ is the memory function of $C(t)$, and is a real even function of time. The r.h.s. of equation (50) is a convolution of K_0 with C. With the aid of the convolution theorem[61] and equation (30), Fourier transformation of equation (50) gives

$$C(\omega) = \mathscr{F}[C(t)] = \frac{C(0)}{\mathrm{i}\omega + \mathscr{F}[K_0(t)]} \tag{51}$$

The memory function $K_0(t)$ is one of a family* of memory functions $K_n(t)$ which obey the set of coupled equations[2]

$$\frac{\partial K_{n-1}(t)}{\partial t} = -\int_0^t K_n(\tau)\,K_{n-1}(t-\tau)\,\mathrm{d}\tau \tag{52}$$

From equation (52) we have

$$\mathscr{F}[K_{n-1}(t)] = \frac{K_{n-1}(0)}{\mathrm{i}\omega + \mathscr{F}[K_n(t)]} \tag{53}$$

Repeated use of equation (53), for different values of n, in equation (51) yields the continued-fraction representation of time-correlation functions:

$$\mathscr{F}[C(t)] = \cfrac{C(0)}{\mathrm{i}\omega + \cfrac{K_0(0)}{\mathrm{i}\omega + \cfrac{K_1(0)}{\mathrm{i}\omega + \,\ldots\ldots\ldots\, \cfrac{K_{n-1}(0)}{\mathrm{i}\omega + \mathscr{F}[K_n(t)]}}}} \tag{54}$$

If the nth order memory function has a white spectrum so that $\mathscr{F}[K_n(t)] = \rho_n$ where ρ_n is a constant, then the series in equation (54) is truncated. This may be used as a starting assumption from which $C(t)$ and $\mathscr{F}[C(t)]$ may be obtained. Alternatively the series may be truncated using an assumed form for a particular $K_n(t)$. Berne[2,57,58] and more recently Evans and Davies[54] have discussed the use of empirical forms for certain memory functions. Evans and co-workers (*e.g.* refs. 52—54 and refs. therein) have fitted far-i.r. absorptions $\alpha(\omega)$ for a variety of liquids, liquid crystals, and rotator-phase solids by assuming $K_1(t) = K_1(0)\exp(-\gamma_1 t)$, $t > 0$, which from equation (54) gives

$$\mathscr{F}[C(t)] = \frac{K_1(0) - \omega^2 - \mathrm{i}\omega\gamma_1}{\gamma_1 K_1(0) + \mathrm{i}\omega^3 - \omega^2\gamma_1 - \mathrm{i}\omega[K_1(0) + K_0(0)]} \tag{55}$$

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*Note: For motion governed by the modified Langevin equation (see ref. 2, p. 609), $K_0(t) = \langle \boldsymbol{F}(0)\cdot\boldsymbol{F}(t)\rangle$, the correlation function of the random force $\boldsymbol{F}$.

Now $\alpha(\omega)$ is related to $\mathscr{F}[C(t)]$ *via* equations (28) and (33) so $\alpha(\omega)$ may be expressed analytically[52–54] in terms of three quantities, $K_0(0)$, $K_1(0)$, and γ_1, where $K_0(0)$ is just $(2kT/I)$ for a diatomic molecule. In general these may be regarded as parameters to be determined by fitting $\alpha(\omega)$ by a least mean squares procedure. Knowing $K_0(0)$, $K_1(0)$, and γ_1 both $C(t)$ and $\epsilon''(\omega)$ may be determined since they are analytically related to these quantities.[52–54] We note that $C(t)$ thus obtained is even up to $0(t^4)$ and is a single exponential form at long times with relaxation time

$$\tau_1 = \left[\frac{[K_0(0) + K_1(0)]^2 - 2K_0(0)\,\gamma_1{}^2}{K_0{}^2(0)\,\gamma_1{}^2}\right]^{\frac{1}{2}} \tag{56}$$

Thus the fitting of far-i.r. data with parameters $\{K_0(0), K_1(0), \gamma_1\}$ gives a prediction of the lower-frequency dielectric relaxation behaviour of a given system. $K_0(0)$ is a molecular property (*e.g.* $2kT/I$ for a diatomic molecule) while $K_1(0) = K_0(0) + \langle 0(V)^2\rangle$, where the latter quantity is the intermolecular mean-square torque. The continued-fraction approach, as used by Evans and co-workers, represents a valuable method for characterizing, in a quantitative manner, far-i.r. data for liquids and solids and appears to be highly successful in practice.

G. Interrelations between Time-correlation Functions and Orientational Distribution Functions.—For the special case where the reorientation of a unit vector occurs with axial symmetry, on average, with respect to an arbitrarily chosen initial direction but does not necessarily follow the rotational diffusion equation, equations (24) and (27) may be generalized to read

$$f(\Omega,t) = \frac{1}{4\pi}\sum_{m=0}^{\infty}(2m + 1)\,P_m(u)\,\psi_m(t) \tag{57}$$

$$\langle P_n[u(t)]\rangle = \psi_n(t) \tag{58}$$

$\psi_0(t) = 1$; $\psi_m(t)$, $m \neq 1$ are normalized decay functions, $0 \leqslant |\psi_m(t)| \leqslant 1$. Equation (57) expresses the dynamics of orientation but experimental measurements which determine individual $\langle P_n[u(t)]\rangle$ or their mixtures give only a part of $f(\Omega,t)$. Given this situation, it is essential that experiments should be made which determine at least $\psi_1(t)$ and $\psi_2(t)$ for a given system. A comparison of these in terms of assumed models for motion should rule out certain mechanisms and favour others. Alternatively if a computer simulation is possible $\psi_1(t)$ and $\psi_2(t)$ should be evaluated for assumed forms of intermolecular potential and agreement sought with the experimental data. In practice few experimental determinations of both $\psi_1(t)$ and $\psi_2(t)$ have been made, but examples are: (i) low-frequency motions in certain supercooled liquids using[23,81,82] dielectric

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[81] M. S. Beevers, J. Crossley, D. C. Garrington, and G. Williams, *J.C.S. Faraday II*, 1977, 73, 458.

[82] M. S. Beevers, J. Crossley, D. C. Garrington, and G. Williams, *Faraday Symposia Chem. Soc.*, 1976, No. 11.

relaxation [$\psi_1(t)$] and Kerr-effect relaxation [$\psi_2(t)$] and (ii) high-frequency motions in simple molecular liquids as obtained using[50] i.r. [$\psi_1(t)$] and Raman [$\psi_2(t)$] vibration–rotation spectra. At the present time most papers on molecular motion give results for a single experimental technique and interpretations are made with assumed models for motion involving adjustable parameters. It is hoped that this rather unsatisfactory situation will be remedied in future as a result of comparisons being made between the dynamics data (correlation function, correlation times) obtained using different techniques.

We enquire whether there are inter-relations between the $\psi_n(t)$ of equations (57) and (58). Berne and co-workers[2,57,62] have deduced approximate inter-relations which may apply independently of the detailed mechanism for motion. Using information theory and given that $f(\Omega,t)$ is normalized and positive and that $\psi_1(t)$ be known, they obtain

$$f(\Omega,t) = \frac{\exp[\beta(t)\cos\theta]}{4\pi\, B_{\frac{1}{2}}[\beta(t)]} \tag{59}$$

$$\psi_n(t) = \frac{B_{n+\frac{1}{2}}[\beta(t)]}{B_{\frac{1}{2}}[\beta(t)]} \tag{60}$$

where $\beta(t)$ is a Lagrange undetermined multiplier and is evaluated at each value of t from equation (60) with $n = 1$. $B_{n+\frac{1}{2}}(\beta) = [\pi/2\beta]^{\frac{1}{2}}\, I_{n+\frac{1}{2}}(\beta)$, where $I_{n+\frac{1}{2}}(\beta)$ is a modified spherical Bessel function of the first kind. The functions $B_{n+\frac{1}{2}}(\beta)$ are given by Berne[2] for different values of n. Thus if $\psi_1(t)$ and hence $\beta(t)$ is known experimentally, $\psi_2(t)$, $\psi_3(t)$, *etc.* are obtained from equation (60). Berne and co-workers[2,62] found that this method was successful for the test cases of 'molecular dynamics' simulations of $\psi_1(t)$ and $\psi_2(t)$ for diatomic molecules and this led them to write[62] 'nature seems to prefer smooth distributions'. The approach is especially useful for the 'fast' motions in systems of small molecules since it provides a link between the results of different experimental techniques. If, however, molecules move in a discontinuous manner, *e.g.* jumps through large angles of arbitrary size as occur in site-model situations or for molecules moving slowly in the supercooled or highly viscous liquid state,[23,81–85] then the information-theory approach may not apply. Williams and co-workers[23] have considered the 'fluctuation-relaxation' model (known in n.m.r. work as the 'strong-collision' model) for which the molecule moves 'instantly' and randomizes completely when it suffers a fluctuation in its environment. This leads to $\psi_n(t)$ being equal for all n ($n > 1$) at $\zeta(t)$, where $\zeta(t)$ is a characteristic time function for the fluctuations. This contrasts with the information-theory approach where $\psi_{n+1}(t)$ decays faster than $\psi_n(t)$. Williams and co-workers[23] found $\psi_1(t) \simeq \psi_2(t)$ for several viscous liquids undergoing 'slow' ($t > 10^{-3}$ s) molecular motions, a result which is in accord with the 'fluctuation-relaxation' model but not with rotational diffusion [equation (27)] or with the predictions of information theory.

[83] G. Williams in ref. 9, p. 151.

[84] G. Williams and P. J. Hains, *Faraday Symposia Chem. Soc.*, 1972, No. 6, p. 14.

[85] M. F. Shears, G. Williams, A. J. Barlow, and J. Lamb, *J.C.S. Faraday II*, 1976, **70**, 1783.

Clarkson and Williams[86] used the information-theory method of Berne and co-workers to deduce $f(\Omega,t)$ from a knowledge of $\psi_1(t)$. Using equations (59) and (60), *i.e.* for $\psi_1(t)$, gives $\beta(t)$ from equation (60), and this value is inserted into equation (59) to yield $f(\Omega,t)$ at t. In addition they extended the analysis to the case where both $\psi_1(t)$ *and* $\psi_2(t)$ are known, and this introduces a further Lagrange undetermined multiplier, χ say. They applied the first approximation [equations (59) and (60)] and the second approximation (involving β and χ) to (i) classical rotational diffusion [equation (24)], (ii) computer simulations of motion in carbon monoxide by Berne and Harp,[2,57] and (iii) i.r. and Raman vibration–rotation data for $\psi_1(t)$ and $\psi_2(t)$ for methane.[87] They conclude that the first approximation yields quite satisfactory estimates of $f(\Omega,t)$ and there is no necessity in practice to use the extended analysis. Thus for suitable systems, and these include small molecules undergoing rapid reorientation ($t < 10^{-10}$ s), it is possible to obtain good estimates of $\psi_2(t)$, $\psi_3(t)$, *etc.* and $f(\Omega,t)$ from a knowledge of $\psi_1(t)$.

In the above we have considered the simple case of the reorientation of a vector, occurring with axial symmetry so that $f(\Omega,t)$ depends on θ and t. For the general case of the orientation of three chosen molecular axes it is necessary to express the generalized orientation function in terms of spherical harmonics $Y_{lm}(\theta,\phi)$ or Wigner rotation matrices $D^J{}_{M,K}(\alpha,\beta,\gamma)$, where α, β, and γ are Euler angles. The corresponding time-correlation functions are considerably more complicated than those considered in this article and the reader is referred to Berne,[2] Berne and Pecora,[41] and Steele[88] for further accounts.

3 Relationships between Time-correlation Functions and Experimentally Determined Quantities

A. Introduction.—The time-correlations considered above refer to the natural motions of a system in the absence of an applied field, but how may such motions be studied experimentally? Two approaches are particularly useful: (*a*) the response of the system to a weak perturbing field is measured in the time or frequency domains; or (*b*) the scattering behaviour of the system for monochromatic incident radiation is studied in the time or frequency domains. For (*a*) if the applied field is sufficiently weak the time factors of the response are those due to the natural motions of the system in the absence of the field. For (*b*) if the energy and momentum changes involved in the scattering process are negligible (quasi-elastic scattering) then the autocorrelation function for the amplitude of the scattered radiation or its power spectrum will simply correspond to a modulation of the frequency of the incident radiation caused by the natural motions of the scatterers. In order to see how relations between experimentally determined quantities and field-free time-correlation functions may arise we consider simple examples illustrating (*a*) and (*b*) above.

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[86] T. S. Clarkson and G. Williams, *J.C.S. Faraday II*, 1974, **70**, 1705.
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B. Quasi-elastic Light Scattering from Moving Point Scatterers.—Of the accounts of the dynamic scattering of monochromatic light (see *e.g.* refs. 2, 35—41, and 89) those of Cummins and co-workers[35] and Peticolas[37] are particularly valuable for the special case of a stationary system of point scatterers which undergo translational motions. Consider the situation (Figure 3) where a parallel beam of plane-polarized monochromatic radiation (light say) of angular frequency ω_0 and associated wave-vector $\boldsymbol{k}_x = [2\pi n/\lambda_0]\boldsymbol{u}_x$, where $\boldsymbol{u}_x$ is the unit vector in the propagation direction, is scattered from a volume of material containing N equivalent point scatterers (atoms, molecules). The beam is taken to be polarized parallel to the y-axis and the scattered radiation for a scattering angle θ is detected at the macroscopic distance R from the origin O of Figure 3. The scattering direction is denoted by the unit vector $\boldsymbol{u}_s$ and the wave-vector of this scattered radiation $\boldsymbol{k}_s = [2\pi n/\lambda_0]\boldsymbol{u}_s$, where $|\boldsymbol{k}_x| \simeq |\boldsymbol{k}_s|$ for quasi-elastic scattering. The incident radiation is in phase at plane I but the scattered radiation reaching the detector is composed of a superposition of waves of different phase since they have travelled different distances from plane I *via* the scatterers to the detector. If the scattering amplitude factor A is assumed to be independent of the orientation of the scatterers and of time then the amplitude $E_j(\boldsymbol{k},\tau)$ of the light scattered from a scatterer j, say, which is located at $r_j(\tau)$ from the origin at the arbitrary time τ is given by[37]

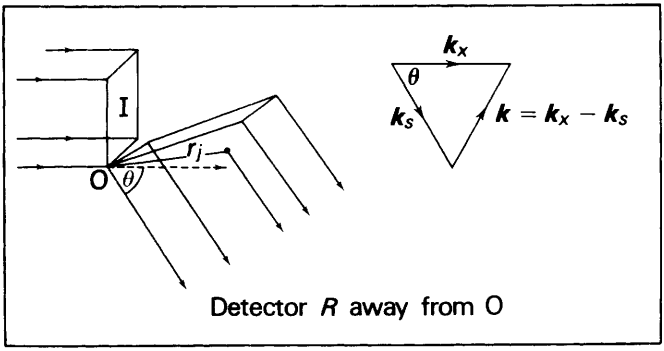

Figure 3 *Quasi-elastic light scattering from point scatterers indicating the relation between* $\boldsymbol{k}$, $\boldsymbol{k}_x$, *and* $\boldsymbol{k}_s$

$$E_j(\boldsymbol{k}_s,\tau) = A\exp\{-\mathrm{i}[\omega_0\tau - (2\pi/\lambda_0)\, D_j(\tau)]\} \qquad (61)$$

$D_j(\tau)$ is the distance travelled by the light from plane I to the jth particle and then to the detector. Geometrical considerations (*e.g.* see ref. 37) show that $D_j(\tau) = [R + r_j(\tau)\cdot(\boldsymbol{u}_x - \boldsymbol{u}_s)]$ so equation (61) may be written as

$$E_j(\boldsymbol{k},\tau) = A\exp\{-\mathrm{i}[\omega_0\tau - \boldsymbol{k}.\boldsymbol{r}_j(\tau) - \boldsymbol{k}_s\,.\,\boldsymbol{R}]\} \qquad (62)$$

where $\boldsymbol{k} = (\boldsymbol{k}_x - \boldsymbol{k}_s)$ and is the scattering vector. For quasi-elastic scattering $\boldsymbol{k}_x$,

[89] P. N. Pusey and M. F. Vaughan, in ref. 9, p. 48.

$\boldsymbol{k}_s$, and $\boldsymbol{k}$ form an isosceles triangle with $|\boldsymbol{k}| = 2|\boldsymbol{k}_x|\sin(\theta/2)$. The total scattering amplitude $E_s(\boldsymbol{k},\tau)$ is the sum of contributions from the N scatterers in the scattering volume:

$$E_s(\boldsymbol{k},\tau) = K\sum_{j=1}^{N} \exp\{-\,\mathrm{i}[\omega_0\tau - \boldsymbol{k}.\boldsymbol{r}_j(\tau) - \boldsymbol{k}_s.\boldsymbol{R}]\} \tag{63}$$

The average intensity of scattered light in the s-direction is

$$\langle I\rangle = \langle E_s^*(\boldsymbol{k},\tau)E_s(\boldsymbol{k},\tau)\rangle$$

where * indicates the complex conjugate and $\langle\ \rangle$ indicates a time-average (over all τ). If the scatterers are statistically independent, *i.e.* there is no correlation between the position or the motion between scatterers, then all cross-correlation terms in $\langle I\rangle$, *i.e.* $\langle\exp\{-\,\mathrm{i}\boldsymbol{k}.[\boldsymbol{r}_j(\tau) - \boldsymbol{r}_l(\tau)]\}\rangle$, $l \neq j$, are zero, giving $\langle I\rangle = NA^2$, the equilibrium result. The temporal behaviour of the scattered-light intensity is obtained from

$$\begin{aligned} G^{(1)}(\boldsymbol{k},t) &= \langle E_s^*(\boldsymbol{k},\tau)\, E_s[\boldsymbol{k},(t+\tau)]\rangle \\ &= A^2\Big\langle \sum_{j=1}^{N}\{\exp \mathrm{i}[\omega_0\tau - \boldsymbol{k}.\boldsymbol{r}_j(\tau)]\} \\ &\qquad \sum_{l=1}^{N}\{\exp -\mathrm{i}[\omega_0(t+\tau) - \boldsymbol{k}.\boldsymbol{r}_l(t+\tau)]\}\Big\rangle \\ &= NA^2[\exp(-\mathrm{i}\omega_0 t)]F(\boldsymbol{k},t) \end{aligned} \tag{64}$$

where $F(\boldsymbol{k},t)$ is a correlation function

$$F(\boldsymbol{k},t) = \frac{1}{N}\Big\langle \sum_{j=1}^{N}\{\exp[-\mathrm{i}\boldsymbol{k}.\boldsymbol{r}_j(\tau)]\}\sum_{l=1}^{N}\{\exp[+\,\mathrm{i}\boldsymbol{k}.\boldsymbol{r}_l(t+\tau)]\}\Big\rangle \tag{65}$$

$F(\boldsymbol{k},t)$ contains auto- ($j = l$) and cross- ($j \neq l$) correlation functions, and the autocorrelation terms have been introduced above in equation (6).

Experimentally $G^{(1)}(\boldsymbol{k},t)$ is not measured directly. In the time domain (photon-correlation spectroscopy[35–41,89]) the measured quantity is the normalized intensity correlation function for the scattered radiation, $g^{(2)}(\boldsymbol{k},t)$, which is defined as $g^{(2)}(\boldsymbol{k},t) = \langle E_s^*(\boldsymbol{k},\tau)E_s(\boldsymbol{k},\tau)E_s^*[\boldsymbol{k},(t+\tau)]E_s[\boldsymbol{k},(t+\tau)]\rangle/\langle I\rangle^2$. This is related to $g^{(1)}(\boldsymbol{k},t) = G^{(1)}(\boldsymbol{k},t)/\langle I\rangle$ according to the Siegert relation:[35–41,89]

$$g^{(2)}(\boldsymbol{k},t) = 1 + |g^{(1)}(\boldsymbol{k},t)|^2 \tag{66}$$

Thus the measurement of $g^{(2)}(\boldsymbol{k},t)$ gives $g^{(1)}(\boldsymbol{k},t)$ and hence $F(\boldsymbol{k},t)$. For the special case of statistically independent scatterers $F(\boldsymbol{k},t)$ becomes $F_s(\boldsymbol{k},t)$ of equation (6). In general the cross-correlation functions $\langle\exp\{-\,\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{r}_j(\tau) - \boldsymbol{r}_l(t+\tau)]\}\rangle$, $j \neq l$, will make a contribution to $F(\boldsymbol{k},t)$ and hence $G^{(1)}(\boldsymbol{k},t)$.

In the frequency domain the spectrum $I(k,\omega)$ of the scattered radiation is given by the Wiener–Khintchine relation[35–41,89]

$$I\,(k,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} |G^{(1)}(k,t)|\,\exp(\mathrm{i}\omega t)\mathrm{d}t \tag{67}$$

Use of equations (64) and (67) for statistically independent scatterers gives equation (9) above. In general from equations (64) and (67) we have

$$I(k,\omega) = \frac{NA^2}{2\pi}\int_{-\infty}^{\infty} \exp[+\mathrm{i}(\omega - \omega_0)t]F(k,t)\mathrm{d}t \tag{68}$$

Equations (64), (66), and (68) show how experimentally determined quantities $G^{(1)}(k,t)$ and $I(k,\omega)$ are related to a correlation function $F(k,t)$ which expresses the natural motions of the scatterers. In equations (64) and (68) the incident field factor involving ω_0 and the correlation function $F(k,t)$ appear as a product. In equation (64) this means that the motions of the scatterers lead to a modulation, through $F(k,t)$, of the single frequency ω_0. In the power spectrum equation (68), this leads to a k-dependent broadening of the scattered-line, centred on ω_0. Note that $F(k,t)$ is obtained from equation (64) in the time domain, while in the frequency domain it may be obtained from the Fourier inverse of equation (68). We considered the simple case of moving point scatterers to illustrate how experimentally determined quantities in scattering experiments may be related to certain time-correlation functions. There are many mechanisms for polarized and depolarized light-scattering from liquids and solids and many of these are considered in detail in the texts by Chu[40] and Pecora and Berne.[41] The development of the subject owes much to the work of Benedek, Cummins, Pecora, and Pike and the dynamic light-scattering techniques have been successfully applied to studies of the motions of small molecules,[35–41,63,90,91] of macromolecules,[35–41,89,92–95] of macromolecular gels,[96] and of structured solutions[97] and to very low-frequency motions in pure liquids.[98–102]

C. Dielectric Permittivity and Dipole Reorientation.—As an example of how experimentally determined quantities may relate to time-correlation functions for the case where a system is perturbed by a weak applied field, we consider the permittivity of a dipolar medium. The theory of dielectric relaxation is well documented[4–11,71] but is made complicated by local-field considerations. For detailed accounts the reader is referred to texts[4–6] and reviews,[7–9] and for

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assessments of the current situation to the papers of Deutch and co-workers.[103,104] Our derivations here follow closely those of Glarum[10] and Cole.[34] Consider a system of N equivalent dipolar molecules to which is applied a field $E^{\mathrm{M}}_z(t')$. The local field acting on the molecules is $E_z(t')$ say, and will be related to $E^{\mathrm{M}}_z(t')$. For the simple case of a medium of low permittivity, *i.e.* $\epsilon_0 \simeq \epsilon_\infty$, $E_z(t') \simeq E^{\mathrm{M}}_z(t')\,[(\epsilon_\infty + 2)/3]$.

The phase-space distribution function $f(p,q)$ for N equivalent dipolar molecules depends indirectly on time owing to the motions of the molecules and obeys the Liouville equation of motion,[2,34]

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \sum_{i}^{N} \left[\frac{\partial H}{\partial p_i}\cdot\frac{\partial f}{\partial q_i} - \frac{\partial H}{\partial q_i}\cdot\frac{\partial f}{\partial p_i}\right] \equiv \frac{\partial f}{\partial t} + \mathscr{L}f = 0 \qquad (69)$$

H is the Hamiltonian of the system, i refers to molecule i, and $\mathscr{L}$ is the Liouville operator: $\mathscr{L}f = \{f,H\} = -\{H,f\}$, where $\{\ \}$ indicates the Poisson bracket. If the uniform electric field $E_z(t)$ is applied to the specimen,

$$H(p,q;t) = H_0(p,q) - M_z(q)E_z(t) \qquad (70)$$

where $-M_z(q)E(t) = -\sum \boldsymbol{m}_i(q).\boldsymbol{E}_z(t)$ is the energy of interaction between the dipole moments and the field. We write $\mathscr{L} = \mathscr{L}_0 + \mathscr{L}_1$ and, noting that $M_z(q)$ is independent of momenta p_i,

$$\mathscr{L}_0 = \sum_{i}^{N} \left[\frac{\partial H_0}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H_0}{\partial q_i}\frac{\partial}{\partial p_i}\right] = -\ \{H_0,\cdot\} \qquad (71\text{a})$$

$$\mathscr{L}_1 = E_z(t)\sum_{i}^{N}\left[\frac{\partial M_z}{\partial q_i}\frac{\partial}{\partial p_i}\right] \qquad (71\text{b})$$

Writing $f = f_0 + f_1$, from equations (69)—(71) we have

$$\frac{\partial f_0}{\partial t} = -\ \mathscr{L}_0 f_0;\ \frac{\partial f_1}{\partial t} = -\ [\mathscr{L}_0 f_1 + \mathscr{L}_1 f_0] \qquad (72\text{a, b})$$

$\mathscr{L}_1 f_1$ is omitted in equation (72b) in order that $f_1 = O(E_z)$. This is the 'linear-response' condition that the change from f_0 to $(f_0 + f_1)$ is linear in the applied field E_z. The solution to equation (72a) is the field-free Boltzmann relation

$$f_0 = A\exp(-\beta H_0) \qquad (73)$$

where $\beta = (kT)^{-1}$ and A is a constant. Writing $f_1 = [\exp(-t\mathscr{L}_0)]y_1$, then differentiation and comparison with equation (72b) gives

$$\frac{\partial y_1}{\partial t} = -[\exp(t\mathscr{L}_0)]\mathscr{L}_1 f_0;\ y_1(t) = -\int_{-\infty}^{t}[\exp(t'\mathscr{L}_0)]\mathscr{L}_1 f_0\,\mathrm{d}t' \qquad (74\text{a, b})$$

Hence

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[103] U. M. Titulaer and J. M. Deutch, *J. Chem. Phys.*, 1974, **60**, 1502.
[104] D. E. Sullivan and J. M. Deutch, *J. Chem. Phys.*, 1975, **62**, 2130.

$$f_1(t) = -\int_{-\infty}^{t} \{\exp[-(t-t')\mathscr{L}_0]\}\,\mathscr{L}_1 f_0\,\mathrm{d}t' \tag{75}$$

The average moment in the field direction is

$$\begin{aligned}\langle M_z(t)\rangle &= \iint M_z(q)f(p,q;t)\,\mathrm{d}p\,\mathrm{d}q \\ &= -\iint \mathrm{d}p\,\mathrm{d}q \int_{-\infty}^{t} M_z(q)\{\exp[-(t-t')\mathscr{L}_0]\}\,\mathscr{L}_1 f_0\,\mathrm{d}t'\end{aligned} \tag{76}$$

From equations (71) and (73)

$$\mathscr{L}_1 f_0 = -\beta f_0 E_z(t)\sum_i \left[\frac{\partial M_z}{\partial q_i}\cdot\frac{\partial H_0}{\partial p_i}\right] = -\beta f_0 E_z(t)\dot{M}_z \tag{77}$$

since[2] $(\partial H_0/\partial p_i) = \dot{q}_i$, and where $\dot{M}_z = \mathrm{d}M_z(t)/\mathrm{d}t$. Equations (76) and (77) give

$$\langle M_z(t)\rangle = \beta\int_{-\infty}^{t}\mathrm{d}t'\,E_z(t')\iint M_z(q)\{\exp[-(t-t')\,\mathscr{L}_0]\}f_0\dot{M}_z(t)\,\mathrm{d}p\,\mathrm{d}q \tag{78}$$

Using the series expansion

$$\exp[-(t-t')\,\mathscr{L}_0] = \sum_n \frac{(-1)^n}{n!}(t-t')^n\,\mathscr{L}_0^{\,n} \tag{79}$$

each term in the series expansion of equation (78) may be integrated by parts giving

$$\iint M_z(q)\,\mathscr{L}_0^{\,n} f_0\dot{M}_z\,\mathrm{d}p\,\mathrm{d}q = (-1)^n\iint f_0\dot{M}_z(t')\,\mathscr{L}_0^{\,n}\,M_z(q)\,\mathrm{d}p\,\mathrm{d}q \tag{80}$$

since integrals of the form $\iint \mathscr{L}_0 f_0\,\mathrm{d}p\,\mathrm{d}q$ vanish. Equations (78) and (80) yield

$$\langle M_z(t)\rangle = \beta\int_{-\infty}^{t}\mathrm{d}t'\,E(t')\iint f_0\dot{M}_z[\exp(t-t')\,\mathscr{L}_0]\,M_z(q)\,\mathrm{d}p\,\mathrm{d}q \tag{81}$$

The operator $\exp(t-t')\mathscr{L}_0$ is a time-displacement operator, or propagator.[2,34,41] When it operates on A it transforms it from its value at time t' to the value it has at $(t-t')$ later, the change having resulted from the natural motions of the system. Equation (81) becomes

$$\langle M_z(t)\rangle = \beta\int_{-\infty}^{t}\mathrm{d}t'E(t')\iint f_0\,\dot{M}_z M_z(t-t')\,\mathrm{d}p\,\mathrm{d}q \tag{82}$$

We define a field-free correlation function $\Phi_z(t)$ as

$$\Phi_z(t) = \iint f_0 M_z(0)M_z(t)\,\mathrm{d}p\,\mathrm{d}q = \langle M_z(0)M_z(t)\rangle \tag{83}$$

Now

$$\dot{\Phi}_z(t) = \langle M_z(0)\dot{M}_z(t)\rangle = -\langle \dot{M}_z(0)_z M_z(t)\rangle\ ,$$

so equations (82) and (83) give the superposition integral

$$\langle M_z(t)\rangle = -\beta\int_{-\infty}^{t} E_z(t')\,\dot{\Phi}_z(t-t')\mathrm{d}t' \tag{84}$$

The total dipole moment correlation function $\Phi(t) = \langle M(0)\cdot M(t)\rangle/\langle M(0)\cdot M(0)\rangle$, where $M(t) = M_x(t)u_x + M_y(t)u_y + M_z(t)u_z$ and u_x, u_y, and u_z are the unit vectors associated with the x, y, and z directions. Now $\Phi(t) = 3\Phi_z(t)/\langle M(0)\cdot M(0)\rangle$, so equation (84) may be written as

$$\langle M_z(t)\rangle = -\frac{\langle M(0).M(0)\rangle}{3kT}\cdot\int_{-\infty}^{t} E_z(t')\dot{\Phi}(t-t')\mathrm{d}t' \tag{85}$$

This is our general result for the linear-response condition. Three forms of $E_z(t')$ are of interest.

(i) E_0 applied as a step at $t' = 0$:

$$\langle M_z(t)\rangle = \frac{\langle M(0).M(0)\rangle}{3kT} E_0[1 - \Phi(t)];\ t > 0 \tag{86a}$$

(ii) E_0 applied at $t = -\infty$ is removed as a step at $t' = 0$

$$\langle M_z(t)\rangle = \frac{\langle M(0).M(0)\rangle}{3kT} E_0\Phi(t);\ t > 0 \tag{86b}$$

(iii) Steady state: $E(t') = E_0\exp(\mathrm{i}\omega t')$; $-\infty < t < \infty$:

$$\langle M_z(t)\rangle = \frac{\langle M(0).M(0)\rangle}{3kT} E_0\exp(\mathrm{i}\omega t)\int_0^{\infty}\left[\frac{-\mathrm{d}\Phi(t')}{\mathrm{d}t}\right]\cdot\exp(-\mathrm{i}\omega t')\,\mathrm{d}t'$$

$$= \frac{\langle M(0)\,.\,M(0)\rangle}{3kT} E_0\exp(\mathrm{i}\omega t)\,[1 - \mathrm{i}\omega\int_0^{\infty}\Phi(t')\exp(-\mathrm{i}\omega t')\,\mathrm{d}t'] \tag{86c}$$

Since the electric polarization $P_z(t) = N\langle M_z(t)\rangle = (\epsilon - \epsilon_\infty)E_z\kappa\epsilon_v$, where ϵ_v is the permittivity of free space and κ is the internal field factor connecting the applied and local fields, we see that the time-dependent permittivity is proportional to $[1 - \Phi(t)]$ and $\Phi(t)$ for equations (86a and b) respectively. In the frequency domain from equation (86c) we write

$$\frac{\kappa(\omega)}{\kappa(0)}\cdot\frac{(\epsilon - \epsilon_\infty)}{(\epsilon_0 - \epsilon_\infty)} = \mathscr{F}\left[-\frac{\mathrm{d}}{\mathrm{d}t}\Phi(t)\right] \tag{87}$$

where $\mathscr{F}$ indicates the one-sided Fourier transform. For the simple case of a very dilute system of dipoles, $\epsilon_0 \simeq \epsilon_\infty$ and hence $\kappa(\omega) \simeq \kappa(0)$. Equation (87) becomes for this special case

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \mathscr{F}\left[-\frac{\mathrm{d}}{\mathrm{d}t}\Phi(t)\right] \tag{88}$$

For the case where $\Phi(t) = \exp[-(t/\tau)]$, equation (88) gives the familiar single-relaxation time expression [*cf.* equation (29)].

Equations (86) connect the transient experiments [equations (86a and b)] to the steady-state a.c. experiments [equation (86c)], one being related to the other by a Fourier transform of $\Phi(t)$.

Equations (85) and (86) are the important results of the linear response theory. The moment $\langle M_z(t)\rangle$ is proportional to the applied field and the proportionality factor, a susceptibility, is determined by the equilibrium quantity $\langle \boldsymbol{M}(0)\cdot\boldsymbol{M}(0)\rangle/(3kT)$ and a time-correlation function $\Phi(t)$, where $\Phi(t)$ is determined by the natural (field-free) motions of the system.

Note $\Phi(t)$ contains auto- and cross-correlation functions:

$$\Phi(t) = \frac{\langle[\sum_i^N \boldsymbol{\mu}_i(0)]\,.\,[\sum_i^N \boldsymbol{\mu}_i(t)]\rangle}{\langle[\sum_i^N \boldsymbol{\mu}_i(0)]\,.\,[\sum_i^N \boldsymbol{\mu}_i(0)]\rangle} = \frac{\sum_i^N \sum_j^N \langle\boldsymbol{\mu}_i(0)\,.\,\boldsymbol{\mu}_j(t)\rangle}{\sum_i^N \sum_j^N \langle\boldsymbol{\mu}_i(0)\,.\,\boldsymbol{\mu}_j(0)\rangle} \tag{89}$$

For the special case where cross-correlation functions $\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_j(t)\rangle$, $i \neq j$, are zero, then for equivalent molecules $\Phi(t) = \langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle/\langle\mu_i^2\rangle \equiv \langle P_1[u(t)]\rangle$, introduced and discussed above.

4 Experimental Determinations of Time-correlation Functions

A. Introduction.—Table 1 indicates the various time-correlation functions which are involved in the different experimental techniques, and the reader is referred to the key references given in the Table for detailed accounts. In this section we briefly consider certain of the techniques listed in the Table and give examples of results involving time-correlation functions. No attempt is made to give a comprehensive account since that is beyond the scope of this introductory review. However, comment is made, where appropriate, on the difficulties which may arise for the deduction of time-correlation functions from experimental data.

B. Dielectric Relaxation.—Much of the dielectrics literature[4–6] for liquids and solids gives $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ at a limited number of frequencies and such data are usually fitted by a single relaxation time expression or by a function involving a suitably chosen distribution of relaxation times, implying an orientational correlation function which is exponential or a weighted sum of exponentials in time. As examples where the experimental data have been transformed to give experimental orientational correlation functions we choose to refer to part of the work of Evans and co-workers[52–54,56,105] on the short-time, high-frequency motions of liquids, liquid crystals and rotator-phase solids, and to the work of Williams and co-workers[13,81–85] on the long-time, low-frequency motions of supercooled and other viscous molecular liquids and of solid amorphous polymers.

Evans and co-workers have deduced $\langle P_1[u(t)]\rangle$ or $\langle \ddot{P}_1[u(t)]\rangle$ for (i) 2-methyl-2-nitropropane, 2,2-dichloropropane, 2-chloro-2-nitropropane, and t-butyl chloride in their liquid and rotator-phase solid states,[52] (ii) water in non-polar organic solvents,[105] and (iii) 4-cyano-4-n-heptylbiphenyl in its nematic and isotropic states.[56] For these systems the far-i.r. absorption $\alpha(\omega)$ is fitted using the parameters $K_0(0)$, $K_1(0)$, and γ_1 of the memory-function approach outlined above (Section 2F), and hence $\langle P_1[u(t)]\rangle$ and/or $\langle \ddot{P}_1[u(t)]\rangle$ is determined. In all

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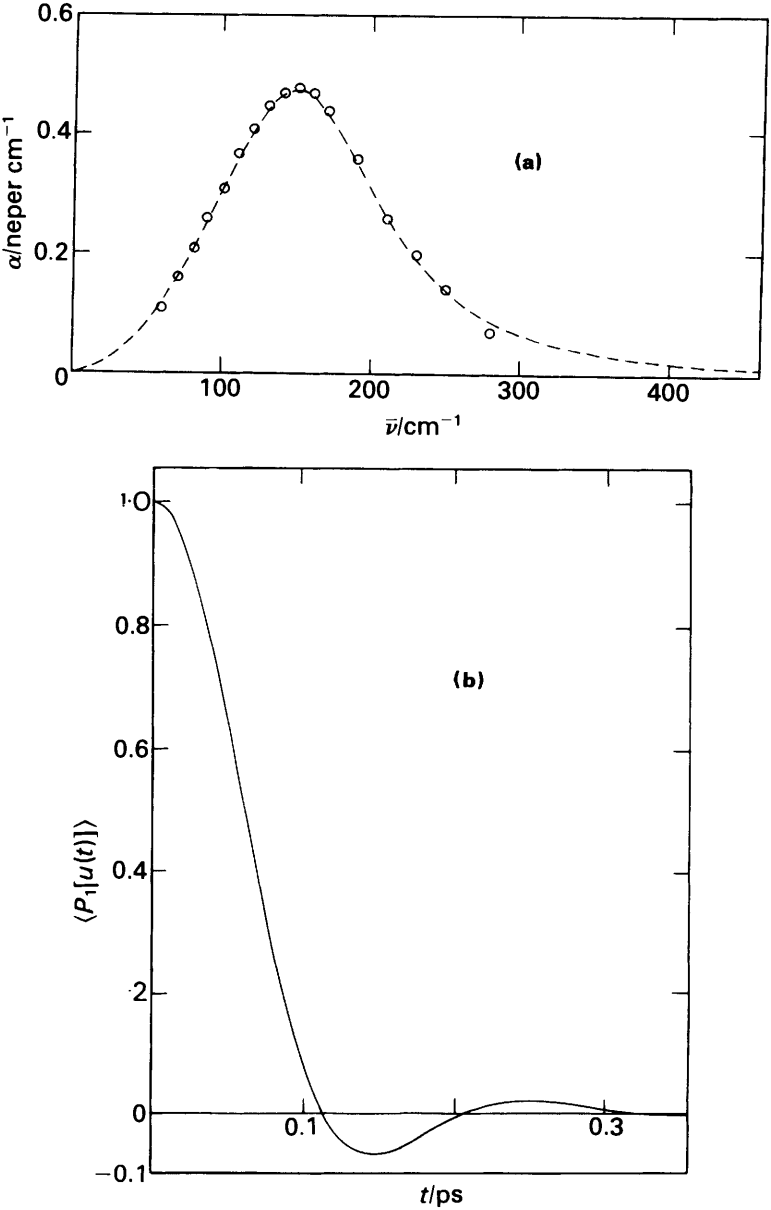
[105] M Evans, *J.C.S. Faraday II*, 1976, **72**, 2138.

cases the short-time behaviour of the correlation function resembles that of a free rotator (or a librator for the liquid-crystal case) and at longer times the influence of molecular collisions is seen. As one example, Figure 4 shows $\alpha(\omega)$



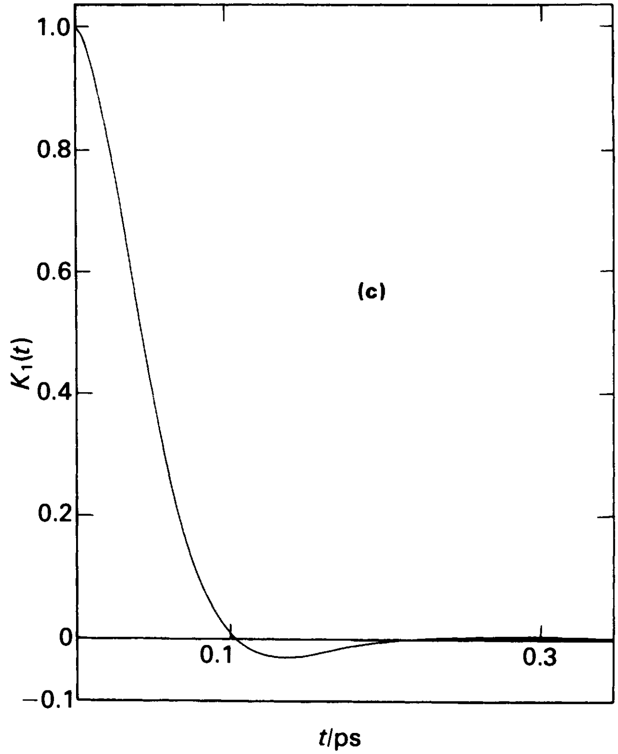


Figure 4 (a) *Infrared absorption coefficient* $\alpha(\omega)$ *against wavenumber* (cm^{-1}) *for an* 0.011% w/w *solution of water in cyclohexane at* 296 K, *corrected for solvent absorption.* (b) $\langle P_1[u(t)]\rangle$ *calculated from the data of Figure* 4 (a). (c) *The normalized memory-function* $K_1(t)$ *calculated from the data of Figure* 4 (a).
(Reproduced from *J.C.S. Faraday II*, 1976, **72**, 2138)

for water in cyclohexane together with the derived $\langle P_1[u(t)]\rangle$ and its memory function $K_0(t)$. Note the short time-scale for the reorientation process of H_2O in this system.

The dielectric relaxations of viscous molecular liquids and solid polymers may occur in the range 10^{-4}—10^{6} Hz, and are characterized by loss curves which are asymmetric in shape and are far broader than that for a single relaxation time process. As one example, Figure 5 shows $\epsilon''(\omega)$ data, in normalized form, for anthrone in *o*-terphenyl in the supercooled liquid state[84] together with the derived $\langle P_1[u(t)]\rangle$ obtained using equation (35). These data are well fitted by the empirical relation of Williams and Watts,[106,107] $\phi(t) = \exp[-(t/\tau_0)^{\bar{\beta}}]$, with $\bar{\beta} = 0.55$. Such a relation with $\bar{\beta} = 0.55$ is numerically very similar to a relaxation

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[106] G. Williams and D. C. Watts, *Trans. Faraday Soc.*, 1970, **66**, 80.

[107] G. Williams, D. C. Watts, S. B. Dev, and A. M. Notth, *Trans. Faraday Soc.*, 1971, **67**, 1323.

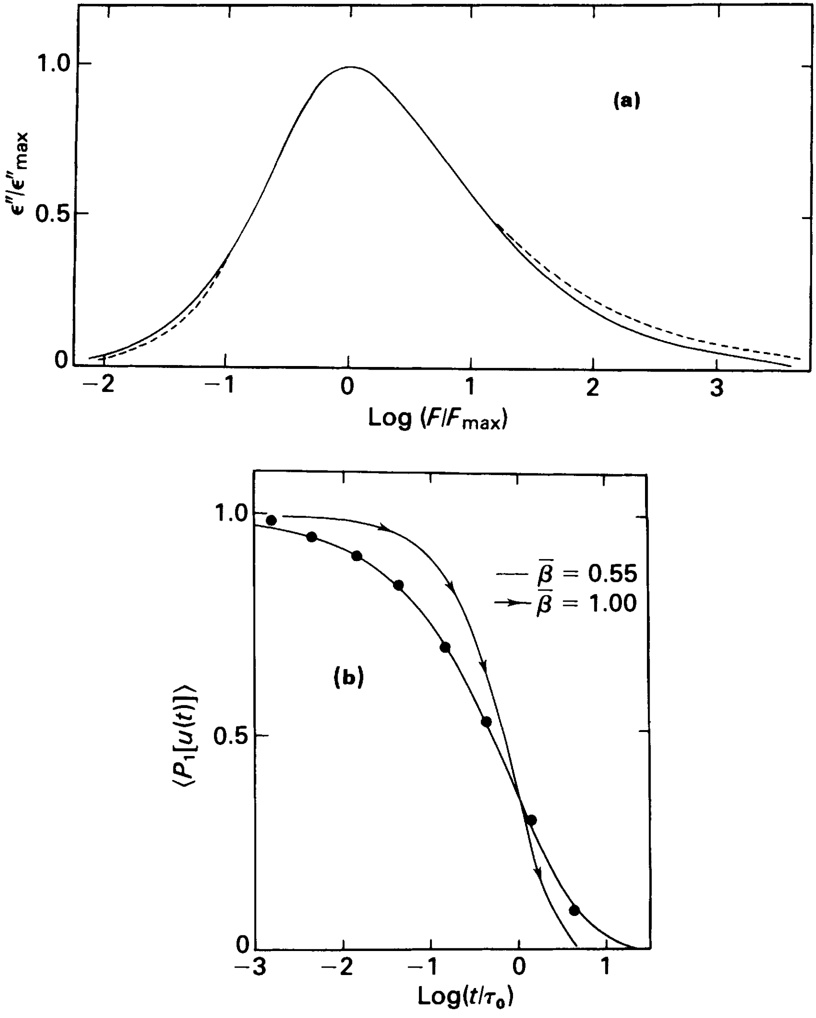

Figure 5 (a) *Normalized dielectric-loss factor* (ϵ''/ϵ_m) *against* $\log(f/f_m)$ *for anthrone in* o-*terphenyl in the supercooled liquid state. The dashed curve* (– – – –) *is calculated using the Williams–Watts relation with* $\bar{\beta} = 0.55$. (b) $\langle P_1[u(t)]\rangle$ *calculated from the data of Figure* 5 (a). ● *experimental data; continuous curve* (——) *calculated with* $\bar{\beta} = 0.55$; *arrowed curve* (→→) *single relaxation-time process*

(Reproduced from *Faraday Symposia Chem. Soc.*, 1972, No. 6, p. 14)

function deduced by Phillips and co-workers[108] for the model of relaxation in which a molecule moves as a result of the 'defect-diffusion' of nearest and next-nearest neighbour 'defects' in the liquid state. For solid amorphous polymers

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[108] M. C. Phillips, A. J. Barlow, and J. Lamb, *Proc. Roy. Soc.*, 1972, **A329**, 193.

the form of the dielectric α relaxation process[6] is found[13,83,109] to be very similar to that in small-molecule glass-forming systems and this implies that the time-dependence of $\Phi(t)$, equation (89), for polymers is quite similar to the auto-correlation function $\langle P_1[u(t)]\rangle$ for dipoles in highly viscous molecular liquids. It has been reasoned[109] that this means that the dipole moment auto- and cross-correlation functions have the same time-dependence in solid amorphous polymers, owing to the co-operative nature of the α-process.

C. Kerr-effect Relaxation.—Dynamic Kerr-effect experiments involve the measurement of the optical birefringence, Δn, of a material subjected to a directing electric field.[19–24,81,82,110] Experiments may be conducted in the frequency or time domains and although most studies have been made in the range 10^{-2}—10^7 Hz, measurements have recently been made on liquids in the 5—40 ps range[111,112] using picosecond laser techniques. Beevers and co-workers[23] have shown for the simple case of axially symmetrical molecules of dipole moment μ and polarizability anisotropy Δg that the decay-transient for Δn following the step-withdrawal of a directing electric field is characterized by $\langle P_2[u(t)]\rangle$, where $u = \cos\theta$ and θ is the angle of reorientation of the dipole vector. Since the Kerr effect is a non-linear optical effect ($\Delta n \propto E^2$), the rise transient for a step-applied directing electric field may be very different from the decay transient, this being so for the case where the molecule moves by rotational diffusion.[19,23] As one example of $\langle P_2[u(t)]\rangle$ being obtained from Kerr-effect experiments, we refer to the work of Benoit[19] and of O'Konski and co-workers[20,21] for tobacco-mosaic virus in aqueous media, where they observed rise and decay transients which are a direct measure of

$$\langle P_2[u(t)]\rangle = \exp(-6D_r t)$$

for the rotational diffusion of this ellipsoidal macromolecule (rod 3000 Å × 180 Å diameter[35]). For this system the rise and decay transients are symmetrical, both giving $\langle P_2[u(t)]\rangle$, since the Kerr-effect arises in this case from the induced moment of the molecule. Transient data for dipolar macromolecules, involving $\langle P_1[u(t)]\rangle$ and $\langle P_2[u(t)]\rangle$, are reviewed by Fredericq and Houssier[22] while recent studies include those by Beevers and co-workers[110] for poly-n-alkyl isocyanates in non-polar solvents. As a further example of this technique, Figure 6 shows the normalized birefringence transients for fluorenone in *o*-terphenyl in the supercooled liquid state.[82] The rise and decay transients are symmetrical at each temperature and correspond to $\{1 - \langle P_2[u(t)]\rangle\}$ and $\langle P_2[u(t)]\rangle$, respectively, for the reorientation of the dipole vector of fluorenone. $P_2\langle[u(t)]\rangle$ is far removed from a single exponential decay in time, ruling out rotational diffusion, but is adequately represented by the Williams–Watts function with $\bar{\beta} \simeq 0.6$. Dielectric measurements on the same system[82] yield

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[109] G. Williams, M. Cook, and P. J. Hains, *J.C.S. Faraday II*, 1972, **68**, 1045.

[110] M. S. Beevers, D. C. Garrington, and G. Williams, *Polymer*, 1977, **18**, 540.

[111] M. Duguay and J. Hansen, *Appl. Phys. Letters*, 1969, **15**, 192; *Opt. Comm.*, 1969, **1**, 254.

[112] P. P. Ho, W. Yu, and R. R. Alfano, *Chem. Phys. Letters*, 1976, **37**, 91.

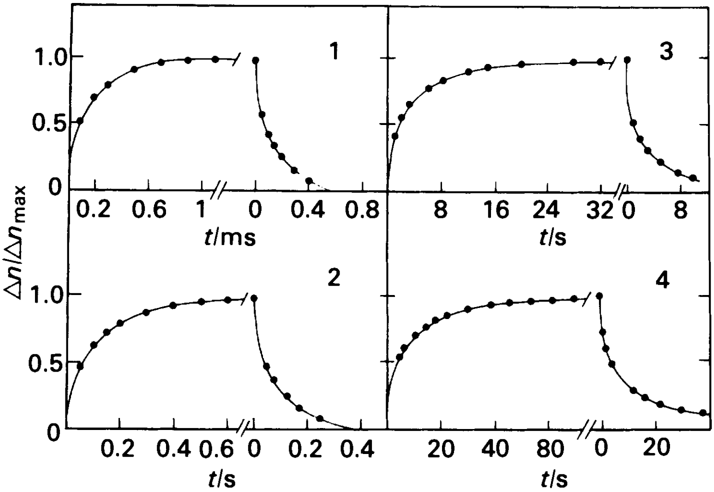

Figure 6 *Normalized birefringence against time for* 22.5% *fluorenone in* o-*terphenyl in the supercooled liquid state. Curves* 1, 2, 3, *and* 4 *refer to* 259.6, 246.9, 241.2, *and* 239.9 K *respectively*

(Reproduced from *Faraday Symposia Chem. Soc.*, 1976, No. 11)

$\langle P_1[u(t)]\rangle$, which is found to have the same time-dependence and the same average relaxation time as the Kerr-effect relaxation at each given temperature. These results are consistent[82] with the 'fluctuation-relaxation' model[23] discussed above (Section 2G).

Note that the interpretation of Kerr-effect relaxations may be made complicated by cross-correlation terms,[113] as is the case for dielectric relaxation. It seems likely that in liquid-crystal forming systems, both in their liquid-crystal and isotropic phases, equilibrium and dynamic cross-correlation terms make a substantial contribution to equilibrium and dynamic Kerr-effect quantities.[114–117] Cross-correlations are also of importance for the Kerr-effect of alcohols[118] (intermolecular correlations) and of dipolar polymers[119] (intramolecular correlations).

D. Depolarization of Fluorescence.—The steady-state and time-dependent fluorescence depolarization of fluorophores incorporated into macromolecules has been shown[26–30,41] to be a useful method of studying the rotational motions of macromolecules. $\langle P_2[u(t)]\rangle$ for the reorientation of the axis of the transition moment of a fluorophore may be obtained in favourable cases from measure-

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[113] S. Kielich, in ref. 8, p. 192.
[114] M. S. Beevers, *Mol. Crystals Liquid Crystals*, 1975, **31**, 333.
[115] H. J. Coles and B. R. Jennings, *Mol. Phys.*, 1976, **31**, 571.
[116] M. S. Beevers and G. Williams, *J.C.S. Faraday II*, 1976, **72**, 2171.
[117] T. D. Gierke and W. H. Flygare, *J. Chem. Phys.*, 1974, **61**, 2231.
[118] C. G. LeFevre and R. J. W. LeFevre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[119] K. Nagai and T. Ishikawa, *J. Chem. Phys.*, 1965, **43**, 4508.

ments of the components $I_{\parallel}(t)$ and $I_{\perp}(t)$ for the intensity of fluorescence which emerges from a sample following its irradiation with a fast pulse of (vertically) polarized light. The time-dependent depolarization ratio (or emission anisotropy), $r(t)$ is defined as

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \tag{90}$$

If $\mathbf{x}_a$ and $\mathbf{x}_e$ are unit vectors along the direction of the absorption and emission transition dipole moments respectively, then,[41] $r(t) = (2/15)\langle P_2[\mathbf{x}_a(0).\mathbf{x}_e(t)]\rangle$. If $\mathbf{x}_a$ and $\mathbf{x}_e$ are parallel then $r(t) = (2/15)\langle P_2[u(t)]\rangle$. Experimentally, the range of the technique is limited to $t < 10^{-8}$ s by the lifetimes of the fluorophores, and to $t > 10^{-10}$ s by instrumental factors. As examples we refer to the work of Monnerie and co-workers[29,30] for fluorophores contained in flexible polymer chains. Figure 7 shows $r(t)$ for anthracene units contained in polystyrene for solvent mixtures of different viscosity. The data are not accurate at short times owing to the problem of deconvolution of the pulse excitation and fluorescence functions. Valeur and Monnerie[29] have fitted these data with a model for chain motion[120,121] which gives, for a bond in the chain,

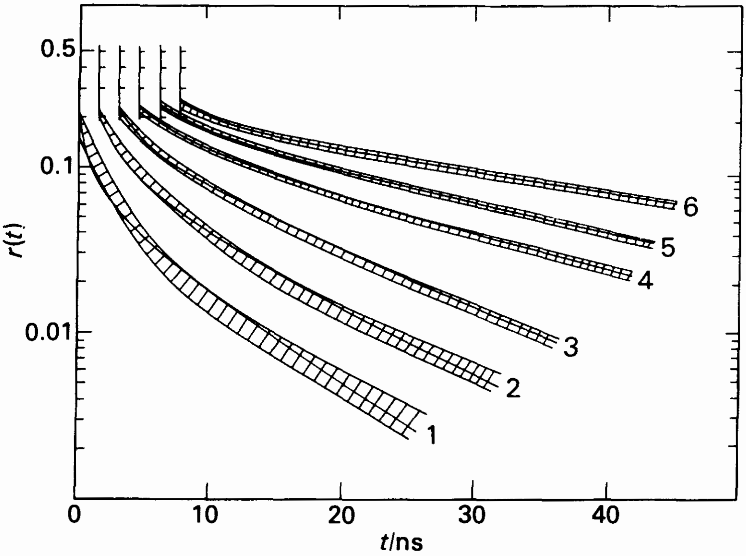

Figure 7 *The time-dependence of polarization anisotropy r(t) for anthracene–styrene polymer in various ethyl acetate–tripropionin mixtures. The theoretical curves [equation* (91) *of text] are drawn as bold lines. Viscosities* (cp): 0.43, 100% *ethyl acetate* (*curve* 1); 0.89 (*curve* 2); 1.50 (*curve* 3); 2.88 (*curve* 4); 4.35 (*curve* 5); 7.45, 100% *tripropionin* (*curve* 6) (after Valeur and Monnerie[29])

(Reproduced by permission from *J. Polymer Sci., Polymer Phys.*, 1976, **14**, 11)

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[120] B. Valeur, L. Monnerie, and J. P. Jarry, *J. Polymer Sci., Polymer Letters*, 1975, **13**, 667, 675.

[121] E. Duboise-Violette, F. Geny, L. Monnerie, and O. Parodi, *J. Chim. phys.*, 1969, **66**, 1865.

$$\langle P_2[u(t)]\rangle = [\exp(-\,t/\sigma)]\,[\exp(t/\rho)]\,\operatorname{erfc}(t/\rho)^{\frac{1}{2}} \tag{91}$$

where ρ is a characteristic time for jumps on a tetrahedral lattice and σ is a relaxation time for random fluctuations of the direction of the co-ordinates which define the lattice. Valeur and Monnerie[30] have also examined the effects of quenching agents on the observed $r(t)$ for fluorophore/polystyrene in 1,2-dichloroethane and chloroform as solvent.

E. Nuclear Magnetic Resonance.—N.m.r. studies, involving the spin–lattice relaxation time T_1, the spin–spin relaxation time T_2, the rotating frame relaxation time $T_{1\rho}$, and line-broadening techniques, have been very successful in characterizing molecular motions in liquids and solids. Key references are to Abragam,[31] Slichter,[32] Connor,[33,122] Powles,[123] Waugh,[124] and Cole.[34] Experimentally, n.m.r. studies are commonly and conveniently carried out at a fixed resonance frequency ω_0 and over a range of temperature. Although such measurements may give information on average correlation times for molecular motion, they do not allow the form of the various spherical harmonic correlation functions which are involved[31,125] to be obtained without making assumptions regarding the mechanism for motion and/or its dependence on temperature. The difficulties arising from measurements made at a single frequency may be illustrated with the model of two equivalent nuclear dipoles, of gyromagnetic ratio γ_N and spin quantum number I_N, separated by an internuclear vector $\boldsymbol{r}$ of fixed length. The spin–lattice relaxation time T_1 is given by[31,34,125]

$$\frac{1}{T_1} = \frac{3}{2}\gamma_N^4\,\frac{\hbar^2 I_N(I_N + 1)}{r^6}\cdot[J_1(\omega_0) + 4J_2(2\omega_0)] \tag{92}$$

where, in general, J_1 and J_2 are Fourier transforms of time-correlation functions of second-order spherical harmonics $Y_{mn}(\theta,\phi)$ describing the reorientation of $\boldsymbol{r}$. For the special case where the reorientation occurs with axial symmetry from any initial orientation of $\boldsymbol{r}$, the ϕ-dependence goes out and J_1 and J_2 become Fourier transforms of $\langle P_2[u(t)]\rangle$, where $u = \cos\theta$ and $\theta(t)$ is the angle between $\boldsymbol{r}(0)$ and $\boldsymbol{r}(t)$. Assuming $\langle P_2[u(t)]\rangle = \exp(-t/\tau_2)$, equation (92) becomes[125,126]

$$\frac{1}{T_1} = \frac{3}{2}\gamma_N^4\,\frac{\hbar^2 I_N(I_N + 1)}{r^6}\cdot\left[\frac{\tau_2}{1 + (\omega_0\tau_2)^2} + \frac{4\tau_2}{1 + (2\omega_0\tau_2)^2}\right] \tag{93}$$

From equation (92) it is clear that the form of the correlation functions cannot be obtained from T_1 measurements at a fixed ω_0. Equation (93) is only applicable if $\langle P_2[u(t)]\rangle$ is exponential in time which, for most solid polymers or viscous liquids, is not the case.[32,33,122]

F. Quasi-elastic Light Scattering.—Owing to the wide frequency range, the

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[122] T. M. Connor, *Trans. Faraday Soc.*, 1964, **60**, 1574.

[123] J. G. Powles, *Polymer*, 1960, **1**, 219.

[124] J. S. Waugh, in 'Molecular Relaxation Processes', Chemical Society Special Publication No. 20, The Chemical Society and Academic Press, London, 1966.

[125] N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 1948, **73**, 679.

[126] R. Kubo and K. Tomita, *J. Phys. Soc.* (*Japan*), 1954, **9**, 888.

alternatives of polarized and depolarized scattering, and the wide application to systems of chemical and biochemical interest, dynamic quasi-elastic laser light-scattering has emerged as one of the most used techniques for studies of the motions of molecules and larger species. The reader is referred to reviews,[35–39], texts,[40,41] and key papers[90–97] where many examples of experimental time-correlation functions for molecular motion are given. For the purposes of this review we refer to only a few examples taken from photon-correlation and frequency-domain (Rayleigh line-broadening) experiments.

Of the many studies of the diffusion of macromolecules in solution using photon-correlation methods[35–41,92–95,127] we refer to the work of Pusey and co-workers[89,95,127] and of King and co-workers[93–95] on monodisperse polystyrenes of different molecular weight in several solvents. Their data for polarized scattering are entirely consistent with translational diffusion, equations (4) and (8), and D_t values are obtained with good precision. In such studies the polymer molecules are of smaller dimension than the wavelength λ_0 of the incident light. For molecules whose dimension is comparable with, or greater than, λ_0 modes of motion additional to centre-of-mass (c.o.m.) motion may contribute to $G^{(1)}(k,t)$ and $I(k,\omega)$. For a rod-like macromolecule of length l, if the c.o.m. motion and rotation about the c.o.m. are uncoupled and obey simple translational diffusion and rotational diffusion, then[35,128]

$$G^{(1)}(k,t) = N(A_0V)^2 \exp(-i\omega_0 t) \sum_{\substack{m=0\\ m\text{ even}}}^{\infty} \mathscr{B}_m \exp\{-[D_t k^2 + m(m+1)D_r]t\} \tag{94}$$

$$I(k,\omega) = \frac{N(A_0V)^2}{2\pi} \sum_{\substack{m=0\\ m\text{ even}}}^{\infty} \mathscr{B}_m L_m[D_t k^2 + m(m+1)\, D_r] \tag{95}$$

where $\mathscr{B}_m = (2m+1)\left[\frac{1}{h}\int_0^h J_m(y)\mathrm{d}y/y\right]^2$, $h = kl/2$, and $J_m(y)$ is a spherical Bessel function of y (see ref. 60, p. 407). The integral arises from the summation of scattering elements along the rod. $L_m(\cdot)$ denotes a Lorentzian of a given m centred on ω_0 [see equation (10)]. In practice only the first two terms in each series, of relative magnitude $\mathscr{B}_0 : \mathscr{B}_2$, are significant. Thus equation (94) involves two weighted exponential decays and equation (95) involves two Lorentzians where the variation with k suffices to determine D_t and D_r. This was used by Cummins and co-workers[35] and King and co-workers[94] for tobacco-mosaic virus in aqueous solution, yielding[35] $D_t = 2.8 \times 10^{-6}$ cm^2 s^{-1} and $D_r = 320$ s^{-1}. King and co-workers[94] and Frederick and co-workers[129–131] have interpreted deviations from simple translational diffusion behaviour for

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[127] P. N. Pusey, in ref. 39, p. 387—428.
[128] R. Pecora, *J. Chem. Phys.*, 1964, **40**, 1604.
[129] T. F. Reed and J. E. Frederick, *Macromolecules*, 1971, **4**, 72.
[130] O. Kramer and J. E. Frederick, *Macromolecules*, 1972, **5**, 69.
[131] W. N. Huang and J. E. Frederick, *Macromolecules*, 1974, **7**, 34.

very high molecular weight polystyrenes in cyclohexane and butanone in terms of Rouse–Zimm-type internal relaxation modes[41] for these spherical macromolecules.

The equilibrium and dynamic correlations for charged polystyrene spheres (radius ~ 250Å) in dilute aqueous dispersion have been studied by Brown and co-workers[97] using conventional and photon-correlation light-scattering methods. $\langle I \rangle$, when plotted as a function of scattering angle, exhibited maxima which could be interpreted in terms of a definite structure for the medium, and the derived radial distribution function indicated short-range ordering due to repulsive Coulombic interactions. $G^{(1)}(k,t)$ results were non-exponential in time, but the short-time behaviour gave an effective diffusion coefficient $D_t(k)$ which was k-dependent in a manner which exactly paralleled the k-dependence of the equilibrium structure factor $S(k)$. Brown and co-workers give theoretical support to this result. The motion is similar to that of a particle in a well. At short times it moves in free translational motion [equation (4)]. At longer times the particles move collectively and these motions are influenced by interparticle interactions.

The light-scattering arising from fluctuations associated with structural relaxation in pure liquids has been studied for glycerol[98] and other viscous liquids.[100–102] Phenomenologically, the form of the time-dependence of $g^{(1)}(k,t)$ is found to be similar to dielectric and viscoelastic relaxation functions for such media, being fitted with a Davidson–Cole function or Williams–Watts function. An interpretation of such scattering is given by Demoulin and co-workers[99] and by Berne and Pecora[41] in terms of generalized hydrodynamics.

The fast reorientational motions of simple non-viscous molecular liquids may be studied by light-scattering methods in the frequency domain in terms of the width and shape of the depolarized Rayleigh-scattered line. Of the many recent studies we refer to the work of Pecora and co-workers[91] and of Litovitz and co-workers.[63,90,132–135] For optically anisotropic molecules which possess cylindrical symmetry, the scattered light intensity for the depolarized spectrum is proportional to $(g_{\parallel} - g_{\perp})^2$ where g is the optical molecular polarizability. The spectrum is given by a Fourier transform of correlation functions for translational and reorientational modes of motion[41,91,92] but if it is assumed (i) that the translational motions occur on a much longer time-scale than the reorientational motions, so that $Dk^2 \ll 6D_r$ and (ii) that the reorientational motions follow the simple rotational diffusion model, equation (16), then the spectrum is a Lorentzian centred on ω_0 with a half-width $6D_r$ (independent of k and so independent of scattering angle). This approach has been applied very successfully by Pecora and co-workers[91] to obtain rotational relaxation times τ_2 for benzene, toluene, p-xylene, chloroform, nitrobenzene, and certain carboxylic acids in solvents composed of optically isotropic molecules (*e.g.* CCl_4). In this

[132] J. A. Bucaro and T. A. Litovitz, *J. Chem. Phys.*, (*a*) 1971, **54**, 3846; (*b*) 1971, **55**, 3585.

[133] C. J. Montrose, J. A. Bucaro, J. Marshall-Coakley, and T. A. Litovitz, *J. Chem. Phys.*, 1974, **60**, 5025.

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

[135] H. Dardy, V. Volterra, and T. A. Litovitz, *Faraday Symposia Chem. Soc.*, 1972, No. 6, p. 71.

work it is assumed that $\langle P_2[u(t)]\rangle = \exp(-6D_r t)$, and since the lineshape is analysed in the 'low-frequency, long-time' region satisfactory results are achieved. Litovitz and co-workers[63,135] have extended measurements of the depolarized Rayleigh spectrum of benzene into the high-frequency 'wings' in order to obtain information on $\langle P_2[u(t)]\rangle$ at short as well as at long times. Following corrections for the finite resolution of the spectrometer and, importantly, for an estimated collisional contribution to the spectrum, the Fourier inversion of the corrected spectrum yields[63] $\langle P_2[(t)]\rangle$, as shown in Figure 8. At short times the correlation function is that for a free rotator (see Section 2D above) while at long times the correlation function is an exponential decay in time with a correlation (or relaxation) time τ_2. The simple interpretation regards the benzene molecule as a symmetric top.[41,135]

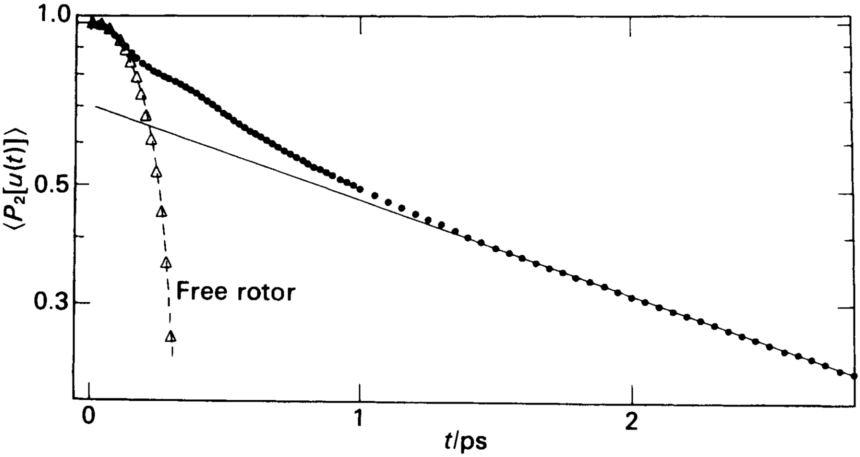

Figure 8 $\langle P_2[u(t)]\rangle$ *for liquid benzene at* 293.5 K *obtained from a Fourier inversion of the corrected depolarized scattered Rayleigh line;* ● *experimental data,* – – – △ – – – *calculated for a free rotator*

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G. Quasi-elastic Neutron Scattering.—In recent years there have been several publications describing quasi-elastic scattering of mono-energetic slow neutrons from solids and liquids for which molecular motion plays an important part in determining the lineshape of the scattered neutron energy at a given scattering angle. The reader is referred to reviews[42-45] and key papers[45,46,136] for details of experiment and theory. The theory for quasi-elastic scattering from molecules capable of c.o.m. motion and rotation about the c.o.m. is quite similar to that for quasi-elastic light scattering,[2,35,41,92] equation (95), and has been reviewed by White[43,44] and by Allen and Higgins.[44] The co-ordinate $\boldsymbol{R}$ for each molecule is expanded in terms of the c.o.m. co-ordinate and the (θ,ϕ) co-ordinates of the

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[136] Ref. 45, discussion therein pp. 165—168.

molecular axes. For a rigid molecule for which translational and reorientational modes of motion are uncoupled the incoherent scattering function $S(k,t)$ may be written as a product of translational and rotational functions and for the case where translational diffusion occurs more rapidly than rotational diffusion, so that $D_tk^2 \gg D_r$, the scattering cross-section is given by[43,45]

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \frac{Nb^2k}{\pi k_x}\left[\frac{D_tk^2}{(\omega - \omega_0)^2 + D_tk^2}\right] \tag{96}$$

where b is the scattering length for incoherent scattering from the assumed equivalent nuclei. For the case where rotational diffusion is the primary cause of incoherent scattering, *e.g.* for a rotator-phase crystal,[43,45]

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \frac{Nk}{\pi k_x}\sum_{m=0}^{\infty}(2m + 1)\, b_m{}^2 J_m{}^2(kr)\left[\frac{m(m + 1)\, D_r}{\{m(m + 1)\, D_r\}^2 + (\omega - \omega_0)^2}\right] \tag{97}$$

which corresponds to a sum of Lorentzians centred on ω_0 involving spherical Bessel functions $J_m(kr)$, where r is the radius of gyration of the molecule. In general the observed scattering cross-section will be due to a convolution of translational and rotational contributions. For the rapid motions of small molecules, inertial effects will be important, as discussed above, and the assumptions of simple translational diffusion and/or translational diffusion which lead to equations (96) and (97) may not be acceptable.

Experimentally it appears difficult to obtain, with good accuracy, the material scattering function from the observed scattering function. This is due to several factors[136] prominent among which are corrections for background levels, multiple scattering from the sample-cell, and the deconvolution of the sample lineshape from that of the incident beam and the instrument itself. Consequently current interpretations have relied on assumed models for motion, equations (96) and (97), giving the transport coefficients D_t and D_r. For examples we refer to the work of Aldred and co-workers[45] for D_t for liquid methanol and toluene and to that of Leadbetter and co-workers[46] for D_r for rotator-phase solids of the substituted cyclohexanes $C_6F_9H_3$ and C_6F_{12}. The fact that the quasi-elastic scattering spectrum in general involves a convolution of translational and reorientational modes of motion suggests that it would be highly desirable to make use of experimental data on time-correlation functions for translational motions, from tracer diffusion or n.m.r. experiments, and for reorientational motions, from microwave, dielectric, far-i.r. and Raman absorption, and picosecond Kerr-effect and depolarized laser-light scattering experiments, in order to obtain a consistent interpretation of motion in a given system.

H. Infrared and Raman Vibration–Rotation Spectra.—The rotational broadening of vibrational lines, as observed for i.r. and Raman vibrational spectra, may be interpreted[2,47–56,137] for simple molecules possessing a degree of symmetry in terms of correlation functions $\langle P_1[u(t)]\rangle$ and $\langle P_2[u(t)]\rangle$ for the reorien-

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[137] F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, (*a*) 1972, **56**, 404; (*b*) 1972, **56**, 413.

tation of particular molecular axes. It is recognized that many processes other than reorientation may contribute to the broadening of vibrational lines. Van Konynenberg and Steele[51] have given a critical assessment of these and they include cross-correlation terms, vibrational relaxation, isotope effects, 'hot-bands', and collision-induced processes. As one example of the use of vibration–rotation spectra for the evaluation of $\langle P_1[u(t)]\rangle$ and $\langle P_2[u(t)]\rangle$ we refer to the work of Rothschild and co-workers[50] on the i.r. and Raman spectra of $CHCl_3$, $CDCl_3$, and isotopically pure $CH^{35}Cl_3$. Figure 9 shows the time-correlation functions

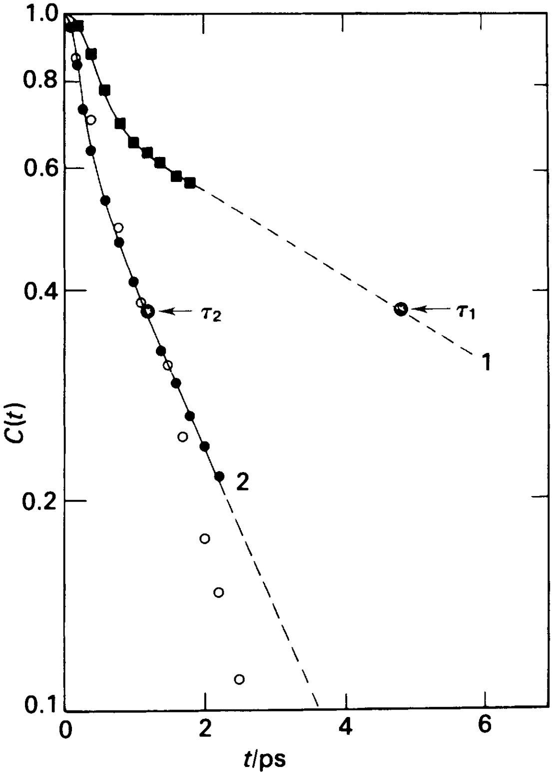

Figure 9 $\langle P_1[u(t)]\rangle$ *(curve* 1) *and* $\langle P_2[u(t)]\rangle$ *(curve* 2), *obtained from i.r. and Raman vibration–rotation spectra respectively, describing the orientational motion of the* C_3 *symmetry axis in liquid chloroform at ambient temperature. Points '*τ_1*' and '*τ_2*' obtained from microwave dielectric and nuclear quadrupole resonance spectra respectively*
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for reorientational motion of the C_3 symmetry axis. The correlation functions have zero slope at $t = 0$ (*i.e.* they are even functions of time), resemble a classical symmetric-top free rotator at short times, and become exponential in time at long times. Also $\langle P_2[u(t)]\rangle$ decays faster than $\langle P_1[u(t)]\rangle$ which is expected for a 'smooth' distribution function $f(\Omega,t)$ (see Section 2G above). Such behaviour is interpreted in terms of the free reorientations of molecules interrupted by collisions and many models have been proposed.[2,8,9,52–57,138]

5 Computer Simulations of Dynamical Behaviour

As indicated in Section 2F, computer simulations of the dynamics of assemblies of molecules yield both equilibrium and dynamic data, where the dynamic data are in the form of translational and reorientational time-correlation functions and their memory functions. Simulations have been made for argon,[65] for diatomic molecules,[2,57,58,66,67,139,140] for liquid water,[68] and for ionic melts,[141,142] and all relate to 'fast' motions with $t < 10^{-10}$ s. The translational motions [as expressed by *e.g.* $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$] and the reorientational motions, as expressed by $\langle P_1[u(t)]\rangle$ and $\langle P_2[u(t)]\rangle$, generally exhibit free-particle behaviour at short times, complicated behaviour at intermediate times due to collisions, and exponential behaviour at long times where the process may be regarded as stochastic. A good example of such behaviour is afforded by the calculations of $\langle P_1[u(t)]\rangle$ and $\langle P_2(u(t)]\rangle$ for CO by Berne and co-workers.[143] As one example of the results of simulations, Figure 10 shows $\langle P_1[u(t)]\rangle$ for a model of liquid water.[68] At short times there is a sharp oscillatory drop of about 20% of the total correlation function, followed by the exponential decay having $\tau_1 = 6.7 \times 10^{-12}$ s. The short-time behaviour corresponds to oscillatory motions of the hydrogen-bonded molecules, the long-time behaviour to the gross rearrangements of molecular orientations *via* co-operative processes involving a sequence of finite stochastic jumps. Rahman and Stillinger also simulated $\langle P_2[u(t)]\rangle$, which is found to be rather similar to $\langle P_1[u(t)]\rangle$ (Figure 10), but decays more rapidly with $\tau_1/\tau_2 = 2.7$ [compared with $\tau_1/\tau_2 = 3$ for rotational diffusion, equation (27)].

Such simulations should provide a valuable means whereby experimental data may be reconstructed using molecular parameters and intermolecular potential functions. Up to the present a qualitative and semi-quantitative understanding of fast molecular motions has been sought with the aid of computer simulation. The results obtained clearly demonstrate the inadequacies of simple models for motion [*e.g.* equations (5), (16), and (37)] and will, no doubt, lead to new generations of models for motion which are based on quantities having a physical interpretation.

6 Conclusions

The material presented in this review has been selected so that it will act as an introduction to the time-correlation function approach to molecular motion,

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[138] R. E. D. McClung, *J. Chem. Phys.*, 1972, **57**, 5478.

[139] W. Streett and D. Tildesley, *Proc. Roy. Soc.*, 1976, **A348**, 485.

[140] M. Evans, G. Evans, and G. Wegdam, (*a*) *Mol. Phys.*, 1977, **33**, 1805; (*b*) *Adv. Mol. Relaxation Processes*, 1977, **11**, 295.

[141] Ref. 84, p. 163.

[142] J. W. E. Lewis and K. Singer, *J.C.S. Faraday II*, 1975, **71**, 41, and refs. therein.

[143] Ref. 2, p. 697, Figure 29.

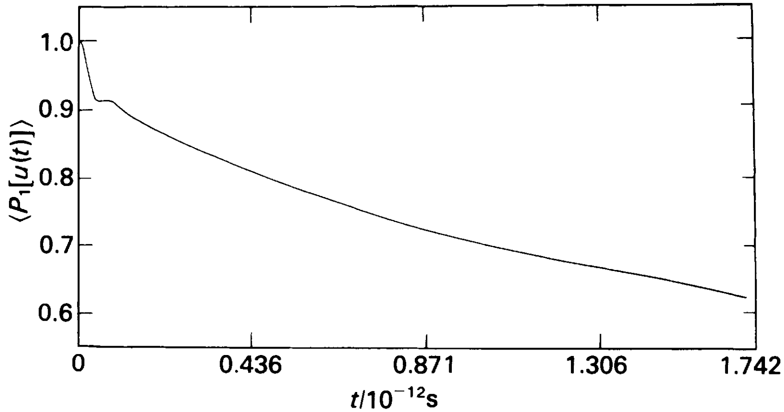

Figure 10 ⟨$P_1[u(t)]$⟩, *calculated by the method of molecular dynamics, for a model of liquid water at* 307.5 K
(Reproduced by permission from *J. Chem. Phys.*, 1971, **55**, 3336)

will clarify through examples how time-correlation functions may relate to experimentally determined quantities, and will make chemists more aware that studies of liquids and solids using the diverse experimental techniques listed in Table 1 may have common interpretations through the underlying time-correlation functions for molecular motion. Up to the present, data from a given experimental technique have largely been interpreted without recourse to information from other experiments. In recent years some comparisons have been made, usually in terms of averaged relaxation times which, being integrals over time-correlation functions, only reflect a limited aspect of the dynamical process. In order that a more satisfactory understanding of the nature and form of motions in liquids and solids may be achieved, the writer suggests that greater effort should be made to obtain experimental time-correlation functions for a given system from as many experimental techniques as possible and that the interpretation of such data be made using all the results. This is now a practical possibility and is very necessary when a given experiment involves several time-autocorrelation functions, *e.g.* neutron-scattering, light-scattering (Sections 4F, 4G), or several cross-correlation functions, *e.g.* dielectric relaxation, Kerr-effect relaxation (Sections 4B, 4C).