Zero–THz Liquid Phase Absorptions and the Rotational Langevin Equation

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Solutions of the Langevin equation for rotational Brownian motion in the needle, sphere, symmetric top and asymmetric top are compared with experimental data over the MHz to THz frequency range. The liquids involved are 2-chloro-2-nitro-propane, the mono-halogenobenzenes, nitrobenzene and benzonitrile. While the microwave data are matched, the theoretical absorptions regain transparency too slowly compared with observations in the far infrared. The powerful mathematical techniques used in solving the Langevin equation should be applied to new types of stochastic equations of motion.

The problem of describing the far infrared and lower frequency absorptions caused by the rotational motions of dipolar molecules in fluids is one which cannot be solved without adequate considerations of the role of molecular inertia in the fundamental equation of motion.[1] This is a stochastic differential equation since the external torques vary in a manner too complicated to be amenable to analysis without large computers. Recently [2-5] there has been an intense theoretical effort at solving the Langevin equation for rotational Brownian motion in the needle, sphere, symmetric top and asymmetric top in order to obtain series expansions, continued fractions and other types of approximations to the complex polarisability. The complexity of these expressions vanishes without consideration of the molecular inertia and for the asymmetric top Perrin's equations are entirely adequate in this limit and are available in a closed form for the complex permittivity. Unfortunately, it is not possible to describe high frequency effects, such as the observed return to spectral transparency, with inertialess equations of motion. This is tantamount to saying that the Fick diffusion equation must be replaced by the Fokker–Planck equation.[6]

While the original Langevin equation was the starting point for the above investigations, an extension of this approach has been suggested [7] whereby a given molecule is bound harmonically to a cage (composed of its nearest neighbours) which is itself undergoing rotational Brownian motion. The motion of the rigid cage is then governed by a Langevin equation with an extra damping term. The system (known as the itinerant librator) is described, therefore, by two linked equations. Unfortunately, their solution in three dimensions is complicated,[8] but exists in a closed form in two dimensions, where the cage can be represented by a rigid annulus concentric and coplanar with a disc (the molecule carrying a dipole along one of its diameters).

The purpose of this paper is to compare and evaluate these theoretical approaches using the experimental absorptions of dipolar, spherical-like and disc-like molecules (which are, nevertheless, rigorously asymmetric tops) over the frequency range of interest (MHz to THz). First we need to consider factors which are known to affect the molecular motion but which are not included in the above equations of motion. They are as follows: (i) Electrostatic interactions between dipoles and multipoles on different molecules, giving rise [9, 10] to the so-called "dynamic internal field". (ii) Statistical cross-correlations of dipole vectors resulting from molecular motions of a cooperative nature which may result in a vortex motion connected *inter alia* with the conversion of spin to orbital angular momentum. This is essentially the problem of constructing hydrodynamic phenomena from molecular motions. Both of the formalisms presented in this paper may be used only to evaluate autocorrelation functions of various kinds, so that they cannot, without modification, give a natural description of collective motions and of macroscopic fluctuations.

Dipole–dipole interactions need for their adequate analysis a vector-cross-product term in the Langevin equation which, unfortunately, renders it insoluble without some iterative procedure as used by Scaife.[10] (However, there are alternative approaches exemplified by Cole,[12] Zwanzig [13] and Bellemans *et al.*[14] which do not use stochastic equations in the same way.) The effect of dilution in a non-dipolar solvent on the absorption profile of a strongly dipolar solute should help to estimate the relative importance of electrostatic effects as opposed to torques originating essentially from repulsive parts of the intermolecular potential. In the limit of infinite dilution, dipolar interactions and correlations between different solute molecules become negligible compared with those in the pure solute. Any Kirkwood g-factor and subsequent effect on the absorption cross-section per molecule in the pure solute may then be estimated. In this way it can be estimated whether any large discrepancy between the above theoretical descriptions and experiment is likely to be due merely to ignorance of these electrostatic interactions and cross-correlations, or whether there is first a need to develop further the fundamental dynamical equations.

Finally, the absorption cross-section per molecule throughout the MHz to THz range may be enhanced by temporary dipoles induced by the effect of one molecule on the resultant fields of the others. This complicated process gives rise to broad absorption bands in non-dipolar gases and liquids, which, however, rarely exceed 10 neper cm^{-1} in maximum absorption intensity. Thus the problem may be minimised by considering liquids with intense, permanent dipolar absorption predominant. Here we chose as models asymmetric tops of the pseudo-spherical molecule 2-chloro-2-nitropropane ($\mu = 2.87$ D) and the disc-like substituted benzenes studied by Poley.[16] Part of the reason for choosing these molecules is that their rotational absorptions in the far infrared are free of proper vibrational modes.

THEORETICAL CONSIDERATIONS

Consider the stochastic Liouville equation in the Mori form:

$$\dot{A}(t) = \mathrm{i}\Omega_A A(t) - \int_0^t \phi_A(t-\tau)A(\tau) + F_A(t).$$

Here A is a column vector of n linearly independent dynamical variables $A_j(t)$, Ω_A a resonance frequency operator and $\phi_A(t)$ the effective liouvillian. $F_A(t)$ is a stochastic vector with components force or torque Mori-propagated from $F_A(0)$.

We can consider special cases of the Mori equation which may be interpreted as dynamical models governed by the ensuing equations of motion. In the first case consider a null resonance operator and delta function liouvillian. The Mori equation then reduces to the Langevin equation for the Brownian motion of a particle which is in general an asymmetric top. The solution of the Mori equation in this case has recently been considered in great detail using graphical, matrix and operator methods [2-5, 17-19]

In this section we use the recent results of McConnell,[17] who has solved the rotational Langevin equation for the sphere with an embedded dipole and for the needle. The complex polarisability was calculated by use of a Bogoliubov–Mitropolsky method, yielding a series expansion for the sphere employing the following notation:

$$\beta = 2kT\tau_D/I \tag{1}$$

where τ_D is the Debye relaxation time and I the moment of inertia.

As $\omega \to \infty$ it may be shown that, if we neglect terms proportional to γ^3 (where $\gamma = kT/I\beta^2$) and denote $\omega' = \omega/\beta$, the complex polarisability is given by:

$$\frac{\alpha^*(\omega)}{\alpha(0)} = \frac{2\gamma}{\omega'^2} - \frac{2i\gamma}{\omega'^3} \tag{2}$$

which agrees with Sack.[18] The complex permittivity is given by:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = \frac{\alpha^*(\omega)}{\alpha(0)} \tag{3}$$

in the absence of an internal field correction.

For the case of a needle rotating in space, the Langevin equation yields [17] a similar result. Eqn (2) is obtained again as $\omega \to \infty$, again in agreement with the results of Sack if terms proportional to γ^3 are neglected. Since γ is usually much less than unity, this is an excellent approximation.

It is of interest to note that the correlation times appropriate to dielectric relaxation (τ_1) and to n.m.r. spin–spin relaxation, the dynamic Kerr effect, depolarised Rayleigh scattering or Raman line broadening (τ_2) are given for the spherical model in this context by:

$$\tau_1 = \frac{1}{2\gamma\beta}[1+\tfrac{3}{2}\gamma-\tfrac{5}{6}\gamma^2+\ldots] \tag{4}$$

$$\tau_2 = \frac{1}{6\gamma\beta}[1+\tfrac{11}{2}\gamma-\tfrac{83}{6}\gamma^2+\ldots] \tag{5}$$

and for the needle by:

$$\tau_1 = \frac{1}{2\gamma\beta}[1+\gamma-\tfrac{2}{3}\gamma^2+\ldots], \tag{6}$$

$$\tau_2 = \frac{1}{6\gamma\beta}[1+5\gamma-\tfrac{32}{3}\gamma^2+\ldots], \tag{7}$$

so that

$$\tau_1 = 3\tau_2 \quad \text{if} \quad \gamma \ll 1.$$

Morita has recently [5] solved the Euler–Perrin equations for a diffusing asymmetric top and for the symmetric top. We quote his results below. The complex permittivity for the asymmetric top is given by:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = 1-p\sum_{i=x,y,z}(m_i^2/\mu^2)A^{(i)}(p), \tag{8}$$

where $p = i\omega$ and $\mu^2 = m_x+m_y+m_z$; in which m_i is the permanent dipole moment along the principal axis denoted by i and β_i the corresponding frictional component. $A^{(i)}(p)$ is defined by Morita.

Eqn (8) reduces to Perrin's equation when inertial effects are neglected, *i.e.*,

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} \to \frac{1}{\mu^2}\left[\frac{m_x^2(D_y+D_z)}{\mathrm{i}\omega+D_y+D_z}+\frac{m_y^2(D_x+D_z)}{\mathrm{i}\omega+D_x+D_z}+\frac{m_z^2(D_x+D_y)}{\mathrm{i}\omega+D_x+D_y}\right], \tag{9}$$

where $D_i = kT/I_iB_i$. Eqn (9) thus defines three " Debye times ":

$$\tau_x^{-1} = D_y+D_z,$$
$$\tau_y^{-1} = D_x+D_z,$$
$$\tau_z^{-1} = D_x+D_y.$$

Note that eqn (9) or (8) may be used in extreme cases to produce two quite separate Debye type loss curves when $\tau_x \ll \tau_y+\tau_z$, the situation appertaining to an aligned mesophase, for example.

Morita's solution[5] of the Langevin equation for a symmetric top is, for the complex permittivity:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = 1-p/[p+B(p)] \tag{10}$$

where:

$$B(p) = \cfrac{2kT/I_x}{p+\beta_x+\cfrac{(2kT/I_x)}{p+2\beta_x+\cfrac{4kT/I_x}{p+3\beta_x}}+\cfrac{(kT/I_x)(I_z/I_x)}{p+\beta_x+\beta_z+\cfrac{(2kT/I_x)(I_z/I_x)}{p+\beta_x+2\beta_z+\cfrac{2kT/I_x}{p+2\beta_z}}}}.$$

An equation for asymmetric top diffusion in the Langevin limit has been developed[19] also by McConnell, Lewis and Ford. This is as follows for the complex polarisability:

$$\alpha^*(\omega) = \frac{1}{3kT}\sum_{x,y,z}\left[\frac{D_y(D_y+D_z+\beta_y)}{(D_y+D_z+\mathrm{i}\omega)(D_y+D_z+\beta_y+\mathrm{i}\omega)}+\frac{D_z(D_y+D_z+\beta_z)}{(D_y+D_z+\mathrm{i}\omega)(D_y+D_z+\beta_z+\mathrm{i}\omega)}\right]\mu_x^2. \tag{11}$$

Here, $D_x = kT/I_x\beta_x$ *etc.* The frictional couples with respect to the rotating principal axes of inertia are $I_x\beta_x\omega_x$, $I_y\beta_y\omega_y$ and $I_z\beta_z\omega_z$. Eqn (11) and (8) produce almost identical numerical results for all β_x, β_y and β_z of interest below. By numerical computation on the U.M.R.C.C. CDC 7600 it has been verified that in the appropriate limits the above equation yield identical results.

It is fully described elsewhere[1, 7, 8, 20] that the Mori equation may be solved approximately by constraining the asymmetric top dipole to librate in two dimensions. The Mori equation then becomes:

$$\frac{DJ}{Dt}+\int_0^t \mathrm{d}\tau\, \phi_J(t-\tau)J(\tau) = F_J(t)$$

where J is the angular momentum of the top about a fixed axis through the centre of mass perpendicular to the plane of rotation. D/Dt denotes the rate of change of the components of each vector referred to principal body-axes. In the case of the itinerant librator, which we discuss below, there is only one component and the equations of motion turn out to be identical with those constructed by a suitable continued fraction solution of the Mori equation.

ITINERANT LIBRATION

It is known [20] that the itinerant planar librator produces an angular velocity a.c.f. $\langle\dot{\theta}(t)\dot{\theta}(0)\rangle$ formally identical with that from Mori three-variable theory applied to the angular velocity as a variate. Furthermore, it is applicable to the reorientation of an asymmetric top provided that its dipole stays in a plane. In any comparison with experimental data made with this model there are three parameters: ω_0, Ω_0, and β which first have to be specified. ω_0 is the angular frequency of the disc relative to a stationary annulus. If I_2 is the moment of inertia of the disc and I_1 that of the annulus, then $\Omega_0^2 = (I_2/I_1)\omega_0^2$ and $\beta = kT\tau_D/I_1$ where τ_D is the Debye relaxation time.

TABLE 1.—PARAMETERS FOR FITTING THE 2-CHLORO-2-NITROPROPANE DATA WITH A MODEL OF ITINERANT LIBRATION

method	$I\omega_0^2/kT$	$I\Omega_0^2/kT$	$\beta(I/kT)^{\frac{1}{2}}$	molecule
variation of Ω_0^2	47.2	50	15.8	2-chloro-2-nitropropane
	47.2	100	15.8	2-chloro-2-nitropropane
	47.2	200	15.8	2-chloro-2-nitropropane
l.m.s. iteration on three parameters	206	3966	330	2-chloro-2-nitropropane
	169	654	64	1,1-dichloro-1-nitro-butane

$$I = \tfrac{1}{3}(I_x+I_y+I_z)$$

We have examined this model in relation to $C_{\text{exp}}(t)$ using two methods of estimating ω_0^2, Ω_0^2 and β. First, ω_0 was equated with the observed peak frequency in the far infrared and Ω_0 was set at different levels, thus determining β through the observed τ_D. The results for various Ω_0^2 are set out in fig. 2 and table 1. A rather unsatisfactory feature of this model is that we need $I_2 > I_1$ for a realistic result. This was first noticed for the translational, space-itinerant oscillator by Damle *et al.*[21] The theoretical $C_1(t)$ curves are oscillatory for $I_2 = I_1$, indicating that the corresponding power absorption spectra are sharp in comparison with the observed bandshape. Unfortunately, the model is not analytic in the frequency domain, but numerical methods of Fourier transformation are being developed. Secondly, an iterative procedure was employed to fit $C_1(t)$ to $C_{\text{exp}}(t)$ regarding ω_0^2, Ω_0^2 and β as adjustable parameters. The results of this least mean squares optimisation are shown in fig. 2(*b*) and (*c*) and in table 1. Whilst this l.m.s. fitting procedure undoubtedly produces the closest agreement between theory and experiment (*bandshape*, intensity being normalised), the optimised β is too high to be commensurate with the observed Debye time and the optimised ω_0 is much higher than the observed far infrared peak frequency.

We conclude, therefore, that in this case the planar itinerant librator is too simplified a mechanism for satisfactory description of the complete microwave and far infrared regions of the absorption profile. The complete profile can be more discriminating a test of any theory than that provided at present by molecular dynamics simulations [22] or by depolarised Rayleigh scattering.[7b, 23] However, use of molecular dynamics simulated velocity autocorrelation functions [24] (which display negative regions) quite clearly demonstrates the advantage of the space-itinerant oscillator over the translational Langevin equation (which predicts an exponential decay for the velocity a.c.f.). The same advantage presumably remains for rotational motions, in that the itinerant librator produces the more realistic angular velocity a.c.f. This is similar to, but not identical with, $C_1(t)$.

EXPERIMENTAL

Spectra were obtained mostly with a polarising interferometer at the P.O. Telecommunications H.Q. at Martlesham Heath. This instrument, specially built by one of us (G. J. D.) for work in the " difficult " decade, 1-10 cm^{-1}, is described elsewhere.[20] It is capable of producing data over this frequency range to within ± 1 % of the measured power absorption coefficient [$\alpha(\tilde{\nu})$ in neper cm^{-1}]. The upper frequency limit is normally $\approx$ 40 cm^{-1}, overlapping with a Grubb–Parsons phase modulated interferometer in use at Aberystwyth. Detectors were a Rollin InSb He(I) cooled instrument at Martlesham Heath and a diamond-windowed Golay at Aberystwyth. Each system was free of quartz or polythene which can cause spurious effects at 130 and 70 cm^{-1}, respectively. Typical resolution and spectrum noise characteristics are illustrated in fig. 1 and 2 where are displayed absorptions for 2-chloro-2-nitropropane and 1,1-dichloro-1-nitrobutane, each heavily absorbing in, and mainly characterised by, the 1-20 cm^{-1} window. The spectra of fluorobenzene, benzonitrile and nitrobenzene were taken with Grubb–Parsons mark III interferometer at Aberystwyth.

The liquids used were AnalaR or Spectroscopic grade, dried with type 3A zeolite, pre-baked at $\approx$ 674 K.

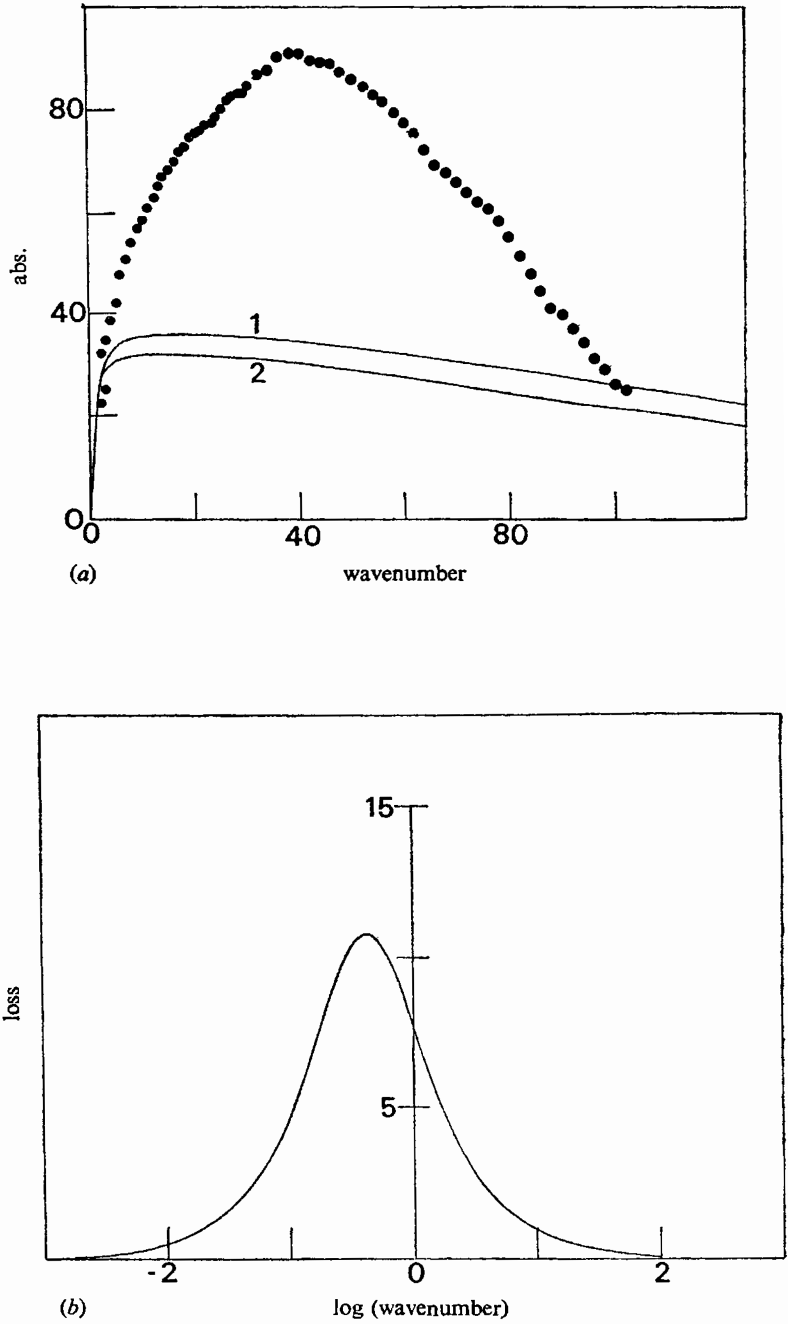
RESULTS AND DATA REFINEMENT

The absorption spectra from 1 cm^{-1} to higher frequencies are shown in fig. 1(*a*)-(*d*). The effect of dilution is to decrease the integrated absorption intensity (A) by an amount proportional to the molecular number density (N), so that there seems to be little effect of dipole–dipole coupling on A in the pure solutes. Furthermore, there is little discernible shift in the frequency of maximum absorption, fig. 1(*d*), although a more extensive analysis (with N varying) might show up such an effect more clearly. For our present purposes it is not necessary to measure with great accuracy the constancy or otherwise of A/N, but it is sufficient to indicate that any large discrepancy between the predictions of the Langevin equation and observation may not be attributed to the internal field or other electrostatic effect.

In order to compare our results with the itinerant librator theory the far infrared $\alpha(\tilde{\nu})$ profile has first to be Fourier transformed into the time domain. The resulting function, $C_{\mathrm{exp}}(t)$, is then normalised at the origin, $t = 0$ (fig. 2). The details of this procedure are given elsewhere;[26] suffice it here to indicate that $C_{\mathrm{exp}}(t)$ may be compared with the autocorrelation function:

$$C_1(t) = \frac{\left\langle \frac{\mathrm{d}}{\mathrm{d}t}\cos\theta(t)\left[\frac{\mathrm{d}}{\mathrm{d}t}\cos\theta(t)\right]_{t=0}\right\rangle}{\left\langle \left[\frac{\mathrm{d}}{\mathrm{d}t}\cos\theta(t)\right]^2_{t=0}\right\rangle}$$

calculable from the formalism of Coffey *et al.*[7] Here $O(t)$ is the angular velocity of the dipole vector under consideration, which for reasons of mathematical convenience is assumed to rotate in a plane. Full details are published elsewhere.[7]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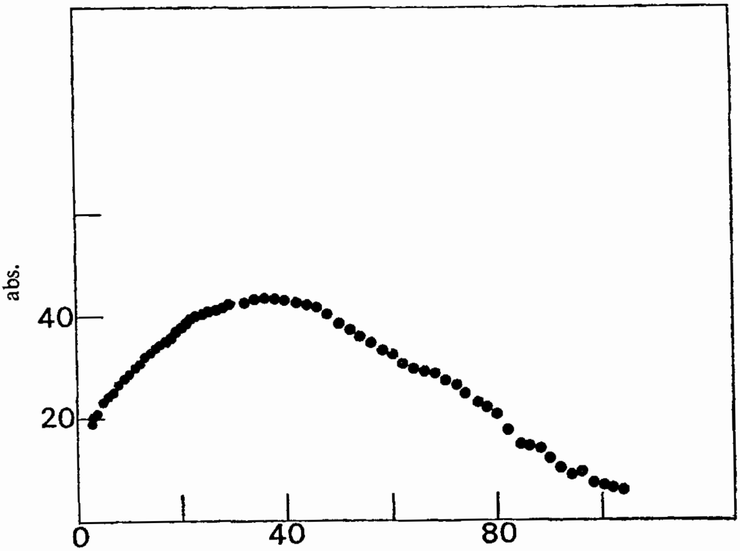
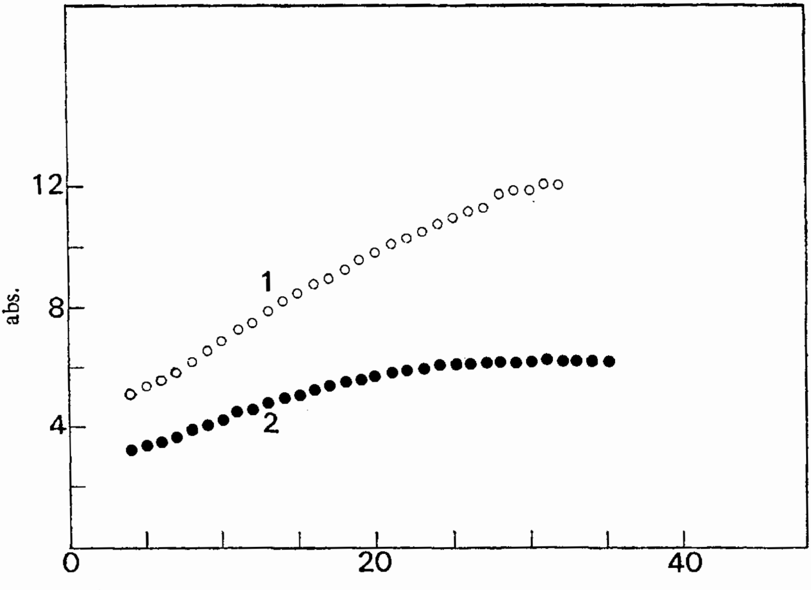
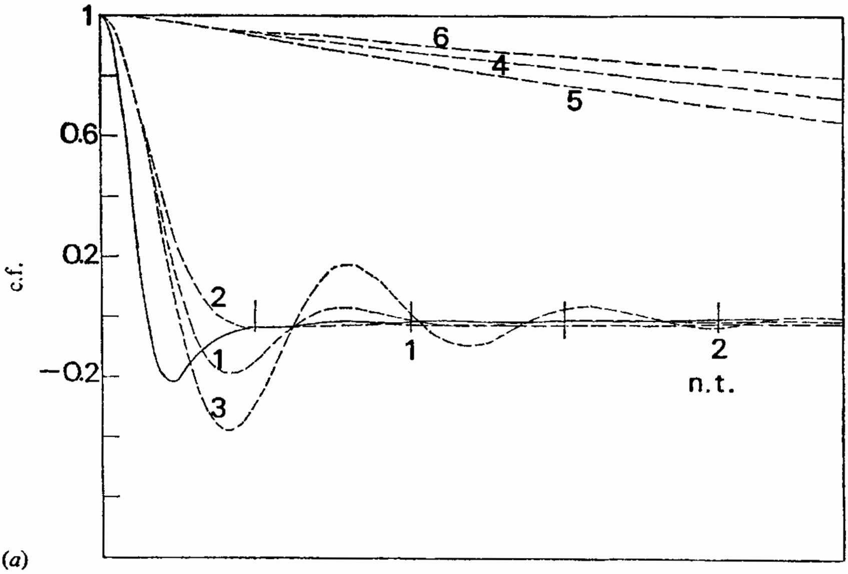


(*c*)



(*d*)

FIG. 1.—(*a*) ⊙, Absorption of 2-chloro-2-nitrobenzene at 293 K, taken with P.O. polarising interferometer. (—)(1) eqn (2). (—)(2) eqn (8) or (11). (*b*) Calculated loss curve for 2-chloro-2-nitropropane, using eqn (2), (8) or (11). (*c*) 1,1-dichloro-1-nitrobutane, far infrared absorption to 5 cm^{-1} (G. J. Davies). (*d*) Absorptions of bromobenzene [curve (1)] and a 50/50 v/v % solution in cyclohexane. Taken with a P.O. polarising interferometer.



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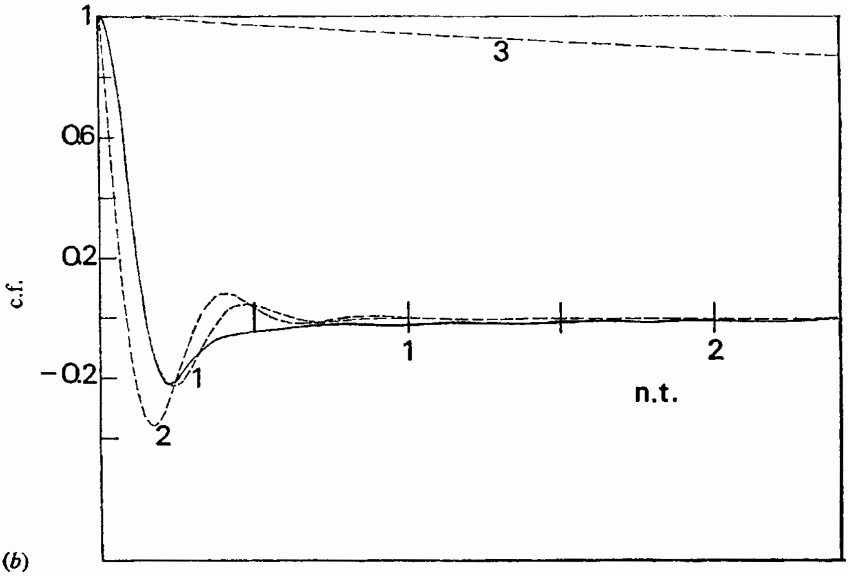

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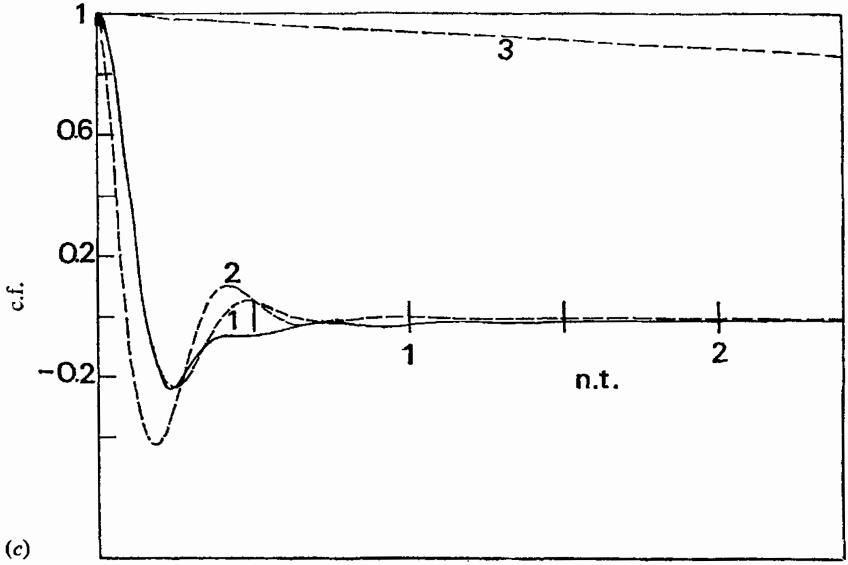

FIG. 2.—(*a*) 2-chloro-2-nitropropane, rotational velocity and orientational autocorrelation functions. (——) Direct Fourier transform of $\alpha(\tilde{\nu})$ from the far infrared (- - -)(1)-(3) itinerant librator function with Ω_0^2 decreasing. (- - -)(4)-(6) corresponding $\langle\cos\theta(t)\cos\theta(0)\rangle$. (*b*) As for fig. 2(*a*). (- - -)(1) least mean squares best fit obtained regarding ω_0, Ω_0 and β as variables, (- - -)(2) corresponding torque autocorrelation function $\langle\ddot{\theta}(t)\ddot{\theta}(0)\rangle$. The far i.r. peak frequency is proportional to a mean square torque. (*c*) As for fig. 2(*b*), 1,1-dichloro-1-nitrobutane. n.t. denotes $2(kT/I)^{\frac{1}{2}}t$.

DISCUSSION

2-CHLORO-2-NITROPROPANE

COMPARISON WITH THE LANGEVIN THEORY

For this asymmetric top the principal moments of inertia are in a frame (x, y, z) different from that (x', y', z') defining the resultant dipole moment along the y axis. The direction of the latter was estimated using group moments of C—CH$_3$ = 0, C—NO$_2$ = 3.5 D, C—Cl = 2.1 D. The origin of the (x, y, z) frame is taken to be the centre of mass, defined by approximating the NO$_2$ group by a mass of 46 as at the centre of mass of this group and the CH$_3$ groups similarly by masses of 15.

To facilitate implementation of eqn (8) and (11) the principal moments of inertia were used as a reference frame for the dipole components m_x, m_y and m_z and for the friction components β_x, β_y and β_z. The latter were estimated using a shape factor analysis (following Budo *et al.*[27]) in such a way that the diffusion coefficient and resultant Debye relaxation time equalled those observed in the liquid at 293 K by Clemett and Davies.[28] It was found that, approximately, $\beta_x = 29.1$ THz, $\beta_y = 39.5$ THz and $\beta_z = 23.3$ THz, so that the spherical top (with a mean moment of inertia and friction coefficient) is fairly satisfactory for this molecule. The power absorption coefficient $\alpha(\tilde{\nu})$ may now be calculated from both eqn (8) (asymmetric top) and eqn (3) and (11) by means of the relation:

$$\alpha(\tilde{\nu}) = \frac{2\sqrt{2}\pi\varepsilon''(\tilde{\nu})\tilde{\nu}}{\{[\varepsilon''(\tilde{\nu})^2+\varepsilon'(\tilde{\nu})^2]^{\frac{1}{2}}+\varepsilon'(\tilde{\nu})\}^{\frac{1}{2}}}.$$

Fig. 1 shows that the Langevin equation produces a return to transparency which is too slow compared with the observed high frequency part of the far infrared spectrum. There is, therefore, also a large discrepancy in intensity (despite use of the observed [28] $\varepsilon_0 = 24.0$, $\varepsilon_\infty = 3.00$, $n_D^2 = 2.05$) which, as explained above, may be attributable only in a small degree to electrostatic interactions of all kinds (including induction of temporary dipoles [15]). As expected, the difference between the spherical top and asymmetric top absorption is not large. The loss curves at low frequency are normal Debye curves.

TABLE 2.—PARAMETERS USED IN EQN (9) AND (11)

molecule			n_D	$10^{40}I_x$ /g cm	$10^{40}I_y$ /g cm	$10^{40}I_z$ /g cm	T/K	β_x /THz	β_y /THz	β_z /THz	μ/D	μ_x/D	μ_y/D	μ_z/D	τ_D/ps
2-chloro-2-nitropropane	24.0	3.00	2.05	348	254	434	293	29.1	39.5	23.3	2.87	0	2.87	0	12.5
s	24.0	3.00	2.05	345	345	345	293	29.3	29.3	29.3	2.87	0	2.87	0	12.5
ϕF	5.44	2.35	2.15	303	117	420	293	16.8	31.1	10.7	1.6	0	1.6	0	5.9
$\phi\mathrm{F}_s$	5.44	2.35	2.15	280	280	280	293	17.1	1.6	17.1	17.1	0	1.6	0	5.9
ϕCl	5.69	2.57	2.33	511	117	629	293	18.1	56.0	15.7	1.69	0	1.69	0	11.8
$\phi\mathrm{Cl}_s$	5.69	2.57	2.33	419	419	419	293	22.8	22.8	22.8	1.69	0	1.69	0	11.8
ϕBr	5.43	2.60	2.43	791	117	909	293	17.1	77.3	15.6	1.7	0	1.7	0	17.1
$\phi\mathrm{Br}_s$	5.43	2.60	2.43	606	606	606	293	22.8	22.8	22.8	1.7	0	1.7	0	17.1
ϕI	4.64	2.77	2.63	1089	117	1207	293	18.9	121.8	19.7	1.7	0	1.7	0	27.2
$\phi\mathrm{I}_s^-$	4.64	2.77	2.63	804	804	804	293	27.4	27.4	27.4	1.7	0	1.7	0	27.2
ϕCN	25.6	3.80	2.34	518	117	636	293	57.4	167.2	49.7	4.18	0	4.18	0	37.9
$\phi\mathrm{CN}_s$	25.6	3.80	2.34	424	424	424	293	72.6	72.6	72.6	4.18	0	4.18	0	37.9
ϕNO	35.7	4.10	2.40	636	179	814	293	57.7	167.2	49.7	4.22	0	4.22	0	45.3
$\phi\mathrm{NO}_s$	35.7	4.10	2.40	543	543	543	293	67.5	67.5	67.5	4.22	0	4.22	0	45.3

Subscript s = spherical top approximation (or needle approximation); $\phi = C_6H_5$.

It seems clear, therefore, that an extension of the fundamental Langevin combination of hydrodynamic friction and stochastic torque must be considered in order that the far infrared spectrum may be reproduced satisfactorily. A rigorous mathematical analysis and modification of the Mori–Kubo–Zwanzig formalism [29-31] seems the most promising line at present.

SUBSTITUTED BENZENES

These are the molecules (halogenobenzenes, cyano and nitrobenzene) for which Poley [16] detected a systematic discrepancy between the Cole–Cole arc and the square of the refractive index at $\approx 200\ \mathrm{cm}^{-1}$ or higher, indicating the existence of the far infrared absorption named after him. For these asymmetric tops only one component of the dipole moment remains non-zero in the frame of the principal moments of inertia. These were estimated from tables of bond lengths and angles using Hirschfelder's method [32] for minimising the dyadic. Friction components were estimated using Van der Waals radii and the method of Budó *et al.*[27] They were scaled to the observed [16] Debye relaxation times (table 2) using:

$$\frac{1}{\tau_y} = \frac{1}{\tau_D} = kT\left(\frac{1}{\beta_x I_x} + \frac{1}{\beta_z I_z}\right) \tag{12}$$

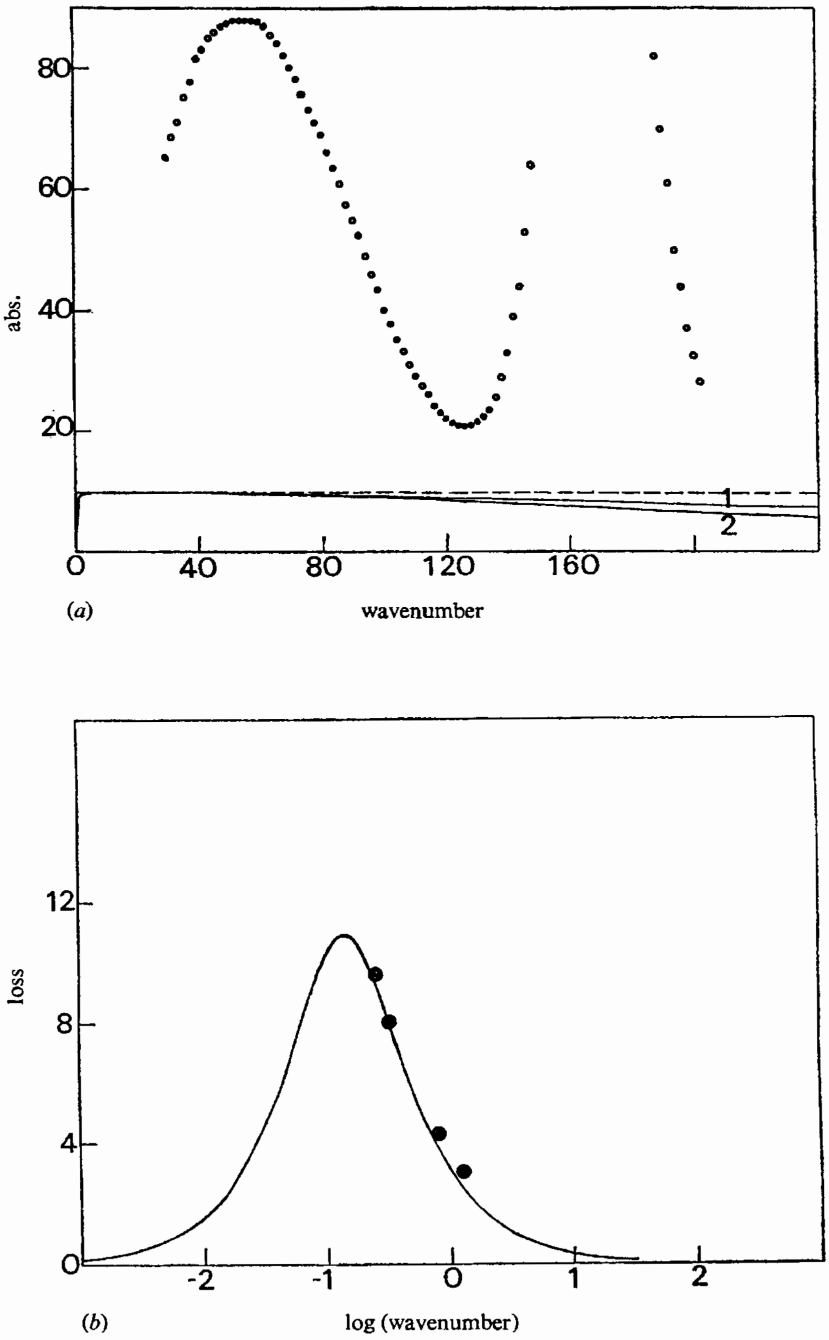

FIG. 3.—Comparison of Langevin equation with experimental data in the whole microwave/infrared range for mono substituted benzene, typified with benzonitrile. (*a*) ○, Experimental, Grubb–Parsons mark III. (—)(1) Langevin eqn, asymmetric top. (2) Langevin eqn, spherical top. (- - -) Debye plateau level. (*b*) (●), Loss data for benzonitrile. (—) Model fittings.

and are listed in table 2. There are also listed parameters for the " equivalent spherical tops ", which are hypothetical representations (or limiting approximations) governed by the conditions:

$$\begin{aligned} I_{\mathrm{Av}} &= \tfrac{1}{3}(I_x+I_y+I_z), \\ \beta_{\mathrm{Av}} &= 2kT\tau_{\mathrm{D}}/I_{\mathrm{Av}}. \end{aligned} \tag{13}$$

The limit imposed by eqn (13) is identical numerically with that of the rotating needle. Therefore, any intermediate variation of β_x, β_y and β_z [bearing in mind eqn (12)] must produce a far infrared absorption below that of the needle/sphere limit in fig. 1 and 3. For each substituted benzene the experimental absorption exceeds that predicted by the asymmetric top Langevin equation by an amount which cannot be attributed wholly to an electrostatic effect even in the weakly dipolar halogenobenzenes. (Since benzene itself absorbs [33] to a maximum of 5 neper cm^{-1} at 80 cm^{-1} then the far infrared absorption cross-section of iodobenzene, for example, must be largely collision induced, but by one estimate that of benzonitrile is over 80 % due to torsional oscillations of the permanent dipole alone.[34]) The integrated absorption intensity (A/N) of the C_6H_5X compounds are different in intensity even though the dipole moments are virtually identical (table 2). However, this does not mean that dipole rotation is not the dominant process because, by Gordon's sum rule, A/N is inversely proportional to the moment of inertia, and for constant μ therefore, A/N decreases across the series X = F, Cl, Br, I. Each solution of the Langevin equation yields an absorption coefficient which is characteristically slow in returning to transparency at high frequencies and which does not go above the so-called Debye plateau [1] in intensity, unlike the itinerant oscillator. This was discovered by Davies *et al.*[35] using the Rocard [36] and Powles [37] solutions of the inertial Langevin equation.

Numerically, therefore, eqn (1)-(11) are merely slight refinements of earlier solutions for higher molecular symmetries, but the powerful mathematical technique involved in their derivations may be used to solve more realistic, initial, stochastic differential equations such as those discussed recently by Ford [38] and by Wyllie.[39] These differ from the Kubo equation [40] in not being stochastic integro-differential Volterra type equations and may be capable of producing the required broad resonance effect making up the characteristic Poley band in dipolar liquids.

CONCLUSIONS

(i) Future work on extending the rotational Langevin equation should aim at improving the return to high frequency transparency of the calculated power absorption coefficient. The most unsatisfactory aspect of the traditional 1906 equation is its unrealistic and unphysical velocity autocorrelation function. This is probably also the case, certainly for libration in a plane, for the angular velocity autocorrelation function of this formalism.

(ii) The itinerant librator is by no means a satisfactory model over the whole frequency range of the absorption profile, but is more realistic than the Langevin equation. Further theoretical work in this area should concentrate on improving its far infrared characteristics by, for example, use of damping on both ring and annulus, following Singwi *et al.*[21]

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[1] M. W. Evans, G. J. Evans and A. R. Davies, *Adv. Chem. Phys.*, 1979, in press.

[2] J. T. Lewis, J. R. McConnell and B. K. P. Scaife, *Phys. Letters*, 1974, **49A**, 303; *Proc. Rep. Irish Acad.*, 1976, **76A**, 43.

[3] G. W. Ford, J. T. Lewis and J. R. McConnell, *Proc. Roy. Irish Acad.*, 1976, **76**, 117.

[4] J. R. McConnell, *Proc. Roy. Irish Acad.*, 1977, **77A**, 13.

[5] A. Morita, *J. Phys. C.*, 1978, in press.

[6] S. A. Adelman, *J. Chem. Phys.*, 1976, **64**, 124; A. R. Davies and M. W. Evans, *Mol. Phys.*, 1978, **35**, 857.

[7] J. H. Calderwood and W. T. Coffey, *Proc. Roy. Soc. A*, 1977, **356**, 269; W. T. Coffey, G. J. Evans, M. W. Evans and G. H. Wegdam, *J.C.S. Faraday II*, 1978, **74**, 310.

[8] M. W. Evans, *Mol. Phys.*, 1977, **34**, 963.

[9] C. Brot in *Dielectric and Related Molecular Processes*, vol. 2 (Chem. Soc., London, 1975).

[10] B. K. P. Scaife, *Complex Permittivity* (Eng. Univ. Press, London, 1971), p. 35.

[11] N. K., Ailawadi, B. J. Berne and D. Forster, *Phys. Rev.*, 1971, **3A**, 1472.

[12] R. H. Cole, *Mol. Phys.*, 1974, **27**, 1.

[13] R. W. Zwanzig, *J. Chem. Phys.*, 1963, **38**, 2766.

[14] A. Bellemans, J-C. Bernard, M. Kohler, and E. Kestemont, *Physica*, 1965, **31**, 1291; M. Kohler and A. Bellemans, *J. Chem. Phys.*, **47**, 1261; A. Bellemans, M. Kohler and M. Gancberg *J. Chem. Phys.*, 1969, **51**, 2578.

[15] M. Evans in *Dielectric and Related Molecular Processes*, vol. 3 (Chem. Soc., London, 1977).

[16] J. Ph. Poley, *Appl. Sci. Res.*, 1955, **4**, 337.

[17] J. K. McConnell, Preprint DIAS-TP-77-19 (1977), published in *Conf. on Electrical Insulation and Dielectric Phenomena*, Colonie, N.Y., 1977.

[18] R. A. Sack, *Proc. Phys. Soc.*, 1957, **76**, 43; 1960, **79**, 402.

[19] G. W. Ford, J. T. Lewis and J. K. McConnell, *Physica*, 1979, in press.

[20] M. W. Evans, *Chem. Phys. Letters*, 1977, **48**, 385.

[21] P. S. Damle, A. Sjölander and K. S. Singwi, *Phys. Rev.*, 1968, **165**, 277.

[22] A. R., Davies, G. J. Evans, M. W. Evans and G. H. Wegdam, XIIIth European Conference on Molecular Spectroscopy, *J. Mol. Struct.*, 1978, **46**, 395.

[23] M. W. Evans, *J.C.S. Faraday II*, 1977, **73**, 485.

[24] A. Rahman, *Phys. Rev.*, 1964, **136**, 405; B. J. Berne and G. D. Harp, *Adv. Chem. Phys.*, 1970, **17**, 63.

[25] G. J. Davies, G. J. Evans and M. W. Evans, *J.C.S. Faraday II*, 1977, **73**, 1071; G. J. Davies and M. W. Evans, *J.C.S. Faraday II*, 1979, **75**, in press.

[26] M. W. Evans, *J.C.S. Faraday II*, 1975, **71**, 2051.

[27] A. Budó, E. Fischer and S. Miyamoto, *Phys. Z.*, 1939, **40**, 337.

[28] C. Clemett and M. Davies, *Trans. Faraday Soc.*, 1962, **58**, 1705.

[29] H. Mori, *Progr. Theor. Phys.*, 1965, **33**, 423.

[30] R. Zwanzig, *J. Chem. Phys.*, 1964, **40**, 2527.

[31] J. M. Deutch, *Faraday Symp. Chem. Soc.*, 1976, **11**.

[32] J. O. Hirschfelder, *J. Chem. Phys.*, 1940, **8**, 431.

[33] G. J. Davies, *Thesis* (Univ. of Wales, 1971), G. W. F. Pardoe, *Thesis* (Univ. of Wales, 1969), G. J. Davies and M. W. Evans, *J.C.S. Faraday II*, 1976, **72**, 1194, 1206.

[34] S. G. Kroon and J. Van der Elsken, *Chem. Phys. Letters*, 1967, **1**, 285.

[35] M. Davies, G. W. F. Pardoe, J. E. Chamberlain and H. A. Gebbie, *Trans. Faraday Soc.*, 1968, **64**, 847.

[36] Y. Rocard, *J. Phys. Rad.*, 1933, **4**, 247.

[37] J. G. Powles, *Trans. Faraday Soc.*, 1948, **44**, 802.

[38] G. W. Ford, 1976, D.I.A.S. conference on Brownian motion.

[39] G. Wyllie, *Phys. Letters*,, 1977, **61A**, 285.

[40] R. Kubo, *Statistical Mechanics of Equilibrium and Non-equilibrium* (North Holland, Amsterdam, 1965).

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