

# Experimental Measure of the Planar Itinerant Oscillator

BY WILLIAM T. COFFEY,

School of Engineering, Trinity College, Dublin, Eire

GARETH JOHN EVANS AND MYRON EVANS,\*

Department of Chemistry, University College of Wales, Aberystwyth SY23 INE

AND

GERARD H. WEGDAM

Laboratory for Physical Chemistry, University of Amsterdam,  
Nieuwe Prinsengracht 126, Amsterdam, The Netherlands

*Received 27th June, 1977*

The two-dimensional itinerant oscillator model for reorientational molecular motion in fluids has been reformulated recently to take account of inertial effects by Coffey *et al.* The new theory is here matched with experimental data from Rayleigh scattering in the depolarised mode (Litovitz *et al.*); original far infrared data on a highly dipolar species ( $\text{CH}_2\text{Cl}_2$ ) in dilute solution and with molecular dynamics computations (of Tildesley and Streett *et al.*) using the atom-atom potential. In most cases studied experimentally and by molecular dynamical computation the angular velocity a.c.f. proves to be an oscillatory function of the time. This behaviour may be simulated closely by means of the present model. Furthermore, this short time oscillatory behaviour of the a.c.f. value appears to be a general feature of the reorientational motion of small molecules, even though the associated decay functions retain their familiar exponential forms at long times.

---

Much interest has centred on the application of relaxation techniques to the study of molecular motions at short times in dipolar fluids. The molecular dynamics in this interval are of theoretical and practical significance, for they reveal clearly the short-comings of the Debye theory<sup>1</sup> of rotational diffusion of dipolar molecules. The far infrared plateau absorption<sup>2</sup> is a consequence of this model and arises from neglect of inertial effects in the initial equation of motion. Deviations from this theory of rotational diffusion are observable also in the bandshape of depolarised, scattered light,<sup>3, 4</sup> where the classical Lorentzian function is no longer followed by the high frequency experimental data. A technique which is capable of yielding<sup>5-8</sup> detailed information on reorientational motions over the whole of the range is that of computer molecular dynamics. This intermediary between analytical theory and experimental observation has the especial advantage of bringing the problems of internal field, dipole-dipole coupling and cross-correlations under strict control, since there is no need of an external probe in order to attain response functions which describe the reorientational motions.

In this paper autocorrelation functions (a.c.f.) computed by means of this technique are compared with (a) a.c.f. values calculated analytically from a model of the molecular behaviour based on the Langevin equation<sup>9</sup> for rotational Brownian motion; and with (b) experimental observations of far infrared/microwave absorptions<sup>10</sup> and depolarised light scattering.

## MODELS FOR THE SHORT TIME BEHAVIOUR

The first attempt to explain the shape of the dielectric absorption spectrum in the far infrared region was made by Hill<sup>11</sup> who, following a suggestion of Poley<sup>12</sup> (and earlier inferences by Frenkel), postulated that the far infrared absorption arises from the perturbation of the rotation of a molecule by an external mechanical potential. This led Hill to propose what is now called the itinerant oscillator model. The central feature of the model is that a molecule is supposed to execute torsional oscillations arising from a mechanical potential generated by the rigid cage of its neighbours which itself undergoes rotational Brownian motion. The torsional oscillations of the central molecule are deemed to account for the far infrared absorption while the Debye absorption is modified by the harmonic link between it and the cage. The Hill treatment, and a further paper by Wyllie,<sup>13</sup> produced results where the high frequency return to optical transparency was found by Larkin *et al.*<sup>14</sup> to be much too gradual in relation to experimental absorption bands<sup>15</sup> in the far infrared. The underlying cause is probably the partial neglect of inertial effects in the calculations. Recently a two dimensional form of the model has been given.<sup>16-18</sup> This treatment is summarised briefly. The model consists of an annulus (the cage) of moment of inertia  $I_1$ , free to rotate about a central axis perpendicular to itself; concentric with the annulus and constrained to rotate about the same central axis is a disc (the molecule) of moment of inertia  $I_2$  carrying a dipole  $\mu$  along one of its diameters. The dipolar position is specified by an angle  $\theta(t)$  relative to a fixed axis (which for convenience is taken to coincide with the direction of a steady electric field  $E$ ). It is supposed that the steady field  $E$  has been applied for a long time so that statistical equilibrium has been attained and that  $E$  is suddenly switched off at a time  $t = 0$ . The equations governing the motion of the system at any time  $t > 0$  are:

$$I_1 \ddot{\psi}(t) + \zeta \dot{\psi}(t) - \gamma[\theta(t) - \psi(t)] = \lambda(t), \quad (1)$$

$$I_2 \ddot{\theta}(t) + \gamma[\theta(t) - \psi(t)] = 0. \quad (2)$$

In eqn (1) and (2)  $\gamma$  is the restoring torque constant,  $\zeta \dot{\psi}$  is the frictional couple acting on the annulus arising from the surroundings, and  $\lambda(t)$ , which is represented by a Wiener process,<sup>16, 19</sup> is the couple caused by random collisions of the Brownian motion type. After a long calculation,<sup>17</sup> the dielectric after-effect function<sup>20</sup>  $b(t)$  for the system is given by:

$$\begin{aligned} b(t) &= \frac{\mu^2}{kT} \langle \cos \theta(t) \cos \theta(0) \rangle_0 \\ &= \frac{\mu^2}{2kT} \exp \left[ - \int_0^t (t-\tau) \langle \dot{\theta}(\tau) \dot{\theta}(0) \rangle_0 d\tau \right] \\ &= \frac{\mu^2}{2kT} \exp \left[ - \frac{1}{2} \langle (\Delta\theta)^2 \rangle_0 \right], \end{aligned} \quad (3)$$

where  $\Delta\theta = [\theta(t) - \theta(0)]$ . The angular brackets  $\langle \rangle_0$  denote an ensemble average taken in the absence of an applied field. In eqn (3)

$$\frac{\langle \dot{\theta}(t) \dot{\theta}(0) \rangle}{\langle \dot{\theta}^2(0) \rangle} = \mathcal{L}^{-1} \left[ \frac{s(s+\beta) + \Omega_0^2}{s^3 + \beta s^2 + (\omega_0^2 + \Omega_0^2)s + \beta \omega_0^2} \right]; \quad (4)$$

$$\frac{\langle (\Delta\theta)_0^2 \rangle}{2} = \mathcal{L}^{-1} \left[ \frac{kT}{I_2} \left( \frac{s(s+\beta) + \Omega_0^2}{s^2 [s^3 + \beta s^2 + (\omega_0^2 + \Omega_0^2)s + \beta \omega_0^2]} \right) \right]; \quad (5)$$

with

$$\langle \dot{\theta}^2(0) \rangle_0 = kT/I_2, \quad (6)$$

$$\beta = \zeta/I_1, \quad (7)$$

$$\omega_0^2 = \gamma/I_2, \quad (8)$$

$$\Omega_0^2 = (I_2/I_1)\omega_0^2. \quad (9)$$

In eqn (4) and (5)  $\mathcal{L}^{-1}$  denotes the inverse Laplace transform operator and  $s$  is the usual Laplace variable. It is important to note that equations formally *identical* to the Laplace transforms of eqn (4) and (5) have been obtained by Evans<sup>21</sup> from a modification of the Langevin equation proposed by Mori.<sup>22</sup> In the notation used by Evans:

$$\omega_0^2 = K_0(0), \quad (10)$$

$$\beta = \gamma, \quad (11)$$

$$\Omega_0^2 = K_1(0). \quad (12)$$

$K_0(0)$  is proportional to the mean square torque, and  $K_1(0)$  is related to this factor and the mean square value of the torque time derivative. It is clear that  $\gamma$  of three variable Mori theory (applied to the angular velocity autocorrelation function) is proportional [via eqn (7)] to the Debye relaxation time. Furthermore, eqn (9), (10) and (12) show that  $K_0(0)$  is the square of the peak librational (or far infrared) frequency ( $\omega_0$ ), and  $K_1(0)$  of three variable theory is related to  $K_0(0)$  by means of a ratio of a phenomenological moment of inertia (that of the rigid annulus) to that of the disc representing the central molecule.

When the discriminant of the denominator in eqn (4) is negative, the Laplace transform theorem gives the angular velocity a.c.f. as:

$$\frac{\langle \dot{\theta}(t)\dot{\theta}(0) \rangle_0}{\langle \dot{\theta}(0)\dot{\theta}(0) \rangle_0} = (1+\Gamma)^{-1} \left[ \left( \cos \omega_1 t + \frac{(\sigma_1 + \Gamma\sigma_2)}{\omega_1} \sin \omega_1 t \right) e^{-\sigma_1 t} + \Gamma e^{-\sigma_2 t} \right]. \quad (13)$$

In eqn (13)  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  are the roots of the secular determinant of the system of eqn (1) and (2), namely:

$$s^3 + \beta s^2 + (\omega_0^2 + \Omega_0^2)s + \beta\omega_0^2 = 0, \quad (14)$$

and

$$\lambda_1 = -\sigma_1 + i\omega_1, \quad \lambda_2 = -\sigma_1 - i\omega_1, \quad \lambda_3 = -\sigma_2. \quad (15)$$

The factor  $\Gamma$  is given by:

$$\Gamma = \frac{-2\sigma_1(\sigma_1^2 + \omega_1^2)}{\sigma_2(3\sigma_1^2 - \sigma_2^2 - \omega_1^2)}. \quad (16)$$

Eqn (13) provides a basis for the calculations of all the necessary reorientational and torque a.c.f.s to be used later in comparison with data obtained from molecular dynamics and from electro-optical sources. The corresponding set of equations for the less common case of a positive discriminant ( $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  distinct and real), are given in the Appendix. Eqn (13) also provides the normalised linear velocity a.c.f. for the *three-dimensional translational* itinerant oscillator,<sup>23</sup> with appropriate changes in notation. From eqn (13) and (14) the orientational a.c.f. characterising the decay of the electric polarisation consequent upon the sudden removal of a constant electric field is:<sup>20</sup>

$$b(t)/b(0) = \rho_1(t) = \exp[-\gamma(t)], \quad (17)$$

where  $y(t)$  is given by:<sup>21</sup>

$$y(t) = \frac{kT}{I_2}(1+\Gamma)^{-1} \left\{ \left[ \frac{2\sigma_1\sigma_2 + \Gamma(\sigma_1^2 + \sigma_2^2 + \omega_1^2)}{\sigma_2(\sigma_1^2 + \omega_1^2)} \right] t - \left[ \frac{\Gamma}{\sigma_2^2} + \frac{3\sigma_1^2 + 2\sigma_1\sigma_2\Gamma - \omega_1^2}{(\sigma_1^2 + \omega_1^2)^2} \right] + \left[ \frac{3\sigma_1^2 + 2\sigma_1\sigma_2\Gamma - \omega_1^2}{(\sigma_1^2 + \omega_1^2)^2} \right] \times \left[ \cos \omega_1 t + \frac{[\sigma_1^3 - 3\sigma_1\omega_1^2 + \sigma_2\Gamma(\sigma_1^2 - \omega_1^2)]}{\omega_1(3\sigma_1^2 + 2\sigma_1\sigma_2\Gamma - \omega_1^2)} \sin \omega_1 t \right] e^{-\sigma_1 t} + \frac{\Gamma}{\sigma_2^2} e^{-\sigma_2 t} \right\}.$$

In a similar way one may deduce the orientational a.c.f. appropriate to depolarised Rayleigh scattering,<sup>24</sup> spin-spin n.m.r. relaxation, or Kerr-effect relaxation.<sup>25</sup> One finds that:

$$\rho_2(t) = \exp[-4y(t)] = \langle \cos 2\theta(t) \cos 2\theta(0) \rangle / \langle \cos^2 2\theta(0) \rangle \quad (18)$$

in two-dimensions. An attempt at extending eqn (17) to three dimensions has been made by Evans<sup>26</sup> for the spherical top carrying a dipole, following Lewis *et al.*<sup>27</sup> The torque a.c.f. may be obtained by differentiating eqn (13) twice and reversing signs. Thus:

$$\frac{\langle \ddot{\theta}(t)\ddot{\theta}(0) \rangle}{\langle \ddot{\theta}(0)\ddot{\theta}(0) \rangle} = \frac{\Xi}{1+\Gamma} \left[ (\omega_1^2 + \sigma_1^2 + 2\Gamma\sigma_1\sigma_2) \cos \omega_1 t + \left( \Gamma\omega_1\sigma_2 - \frac{\sigma_1}{\omega_1} [\omega_1^2 + \sigma_1^2 + \Gamma\sigma_1\sigma_2] \sin \omega_1 t \right) e^{-\sigma_1 t} - \sigma_2^2 \Gamma e^{-\sigma_2 t} \right], \quad (19)$$

where

$$\Xi = [(\omega_1^2 + \sigma_1^2 + 2\Gamma\sigma_1\sigma_2 - \sigma_2^2\Gamma)/(1+\Gamma)]^{-1}.$$

It is important to note that these a.c.f. values may be strictly comparable with absorption and scattering data only where these latter are extrapolated to infinite dilution. In addition, any collision-induced absorption<sup>28</sup> or scattering<sup>29</sup> must be subtracted (or reduced to insignificance by suitable choice of molecular species) before a comparison can be attempted. However, using three techniques as in this paper provides a stringent test for our model, despite the assumptions made in refining the raw experimental data.

#### COMPARISON OF MODEL WITH EXPERIMENT

##### (a) MOLECULAR DYNAMICS—THE ATOM-ATOM POTENTIAL

This involves the *ab initio* computation of orientation, angular velocity, and torque (or angular acceleration) a.c.f. values for a cubic ensemble of 256 interacting atom-atom potentials.<sup>30</sup> The advantage of this method is that it gives realistic a.c.f. values without the complications of the internal field,<sup>2</sup> dipole-dipole coupling,<sup>20</sup> induced absorption or induced polarizability anisotropy. The Lennard-Jones parameters  $\epsilon/k$  and  $\sigma$  are always those corresponding to nitrogen, so that we have a "real" N<sub>2</sub> molecule only when the interatomic separation (in reduced units<sup>8</sup>)  $d^* = 0.3292$ . The thermodynamic stability of the system is judged by the constancy of total pressure calculated by the virial theorem, and by the total internal or configurational energy per molecule. 400 time steps of  $5 \times 10^{-15}$  s were sufficient to give stable, excellently reproducible a.c.f. values after rejecting the first 100 or so in the averaging. These statistics are adequate since most of the computed a.c.f. values are damped to zero in  $\approx 50$  or 100 steps (fig. 4). The effect of using the two

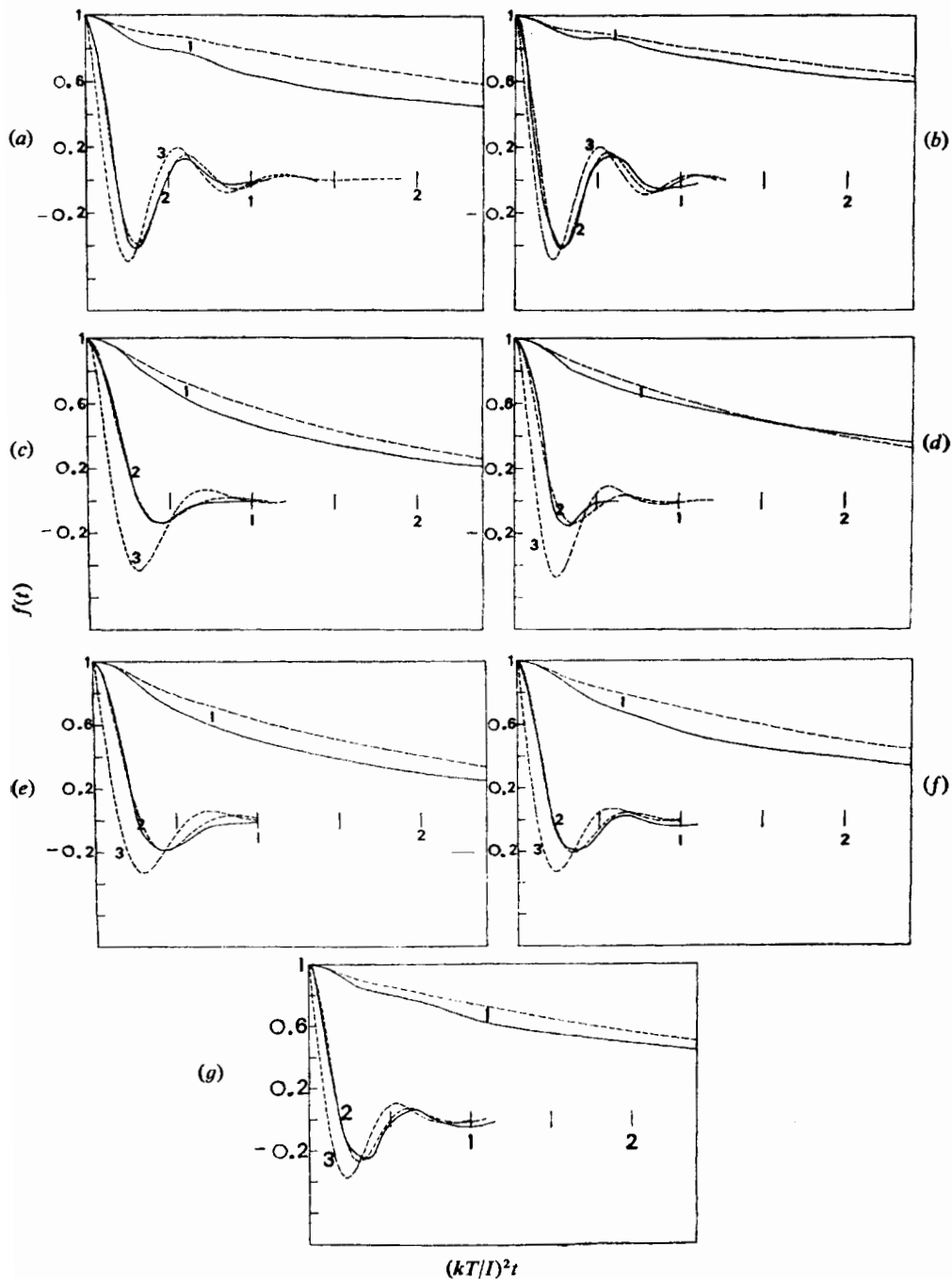


FIG. 1—(a) — (1) Experimental  $\rho_2(t)$ ; — (2) experimental  $-d^2 \rho_2(t)/dt^2$ . - - - (1) Theoretical  $\rho_2(t)$  predicted from fit to eqn (2); - - - (2) theoretical  $\langle \hat{\theta}(t)\hat{\theta}(0) \rangle / \langle \hat{\theta}(0)\hat{\theta}(0) \rangle$  fitted to eqn (2); - - - (3) theoretical  $\langle \hat{\theta}(t)\hat{\theta}(0) \rangle / \langle \hat{\theta}(0)\hat{\theta}(0) \rangle$  for liquid benzene at 1 bar. Data of Litovitz *et al.*<sup>3</sup> (b) As for (a), benzene at 601 bar. (c) As for (a), acetone at 1 bar. (d) As for (a), acetone at 2 kbar. (e) As for (a), methyl iodide at 1 bar. (f) As for (a), methyl iodide at 1 kbar. (g) As for (a), methyl iodide at 2.5 kbar.

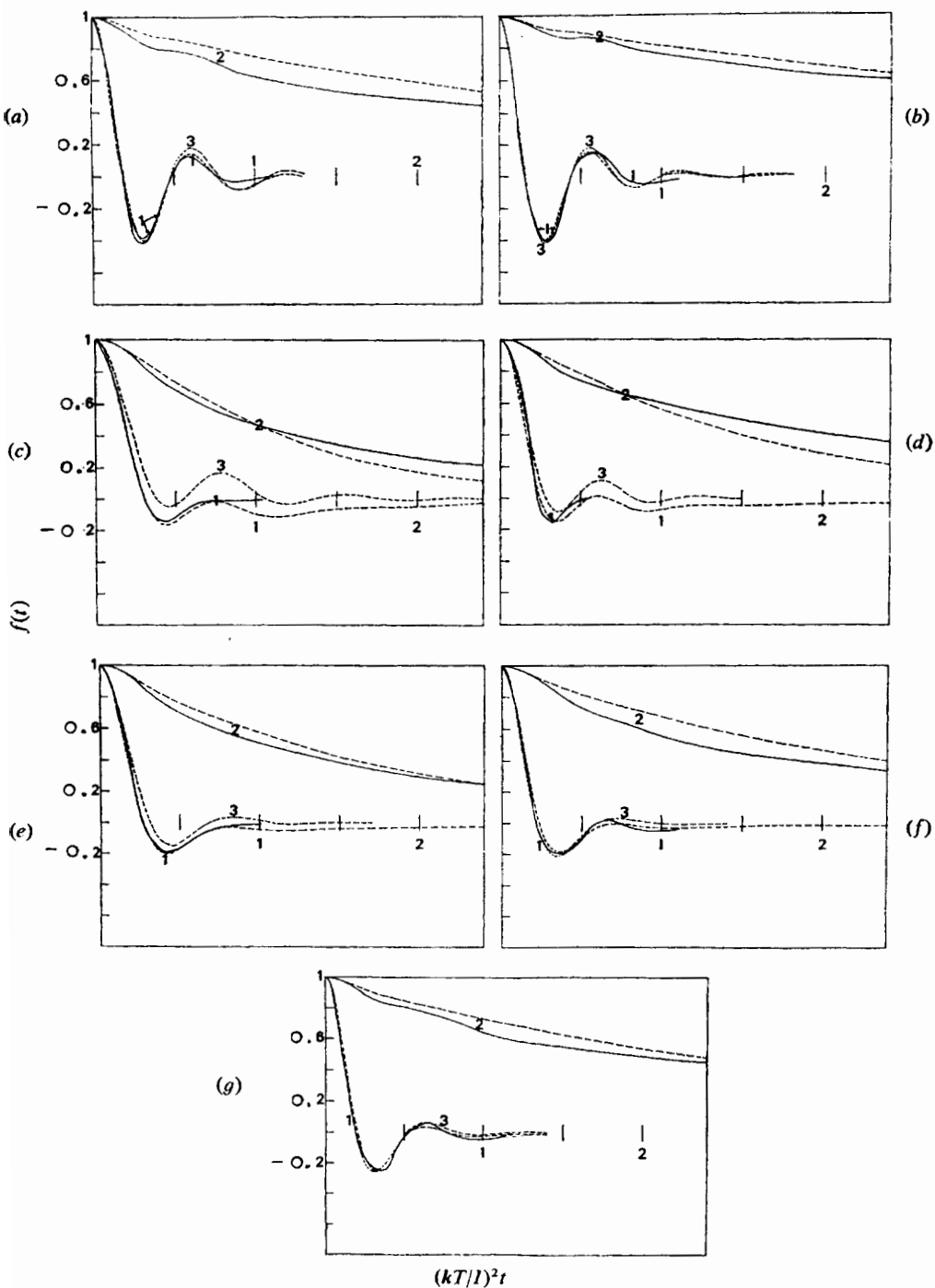


FIG. 2.—(a) — (1) Experimental  $-\frac{d^2 \rho_2(t)}{dt^2}$ , — (2) Experimental  $\rho_2(t)$ , --- (1)  $\langle \frac{d}{dt}[\cos 2\theta(t)] \rangle / \langle \frac{d}{dt}[\cos 2\theta(t)] \rangle_{t=0}$  fitted to eqn (1), --- (2)  $\langle \cos 2\theta(t) \cos 2\theta(0) \rangle$ , --- (3)  $\langle \dot{\theta}(t)\dot{\theta}(0) \rangle / \langle \dot{\theta}(0)\dot{\theta}(0) \rangle$ . (2) and (3) both calculated from the fitting for liquid benzene at 1 bar. Data of Litovitz *et al.*<sup>3</sup> (b)-(g), as in fig. (1).

centre potential is to build in an anisotropic repulsion core and a dispersive part cut off at  $3.2\sigma$ . (The classical theory of the translational Brownian movement for a free body<sup>31</sup> is equivalent to using a hard core spherical potential alone.) The parameter  $\omega_0^2 = K_0(0)$  provides a means of comparing the predictions of the itinerant oscillator model with the mean square torque calculated from our predictor-corrector algorithm.

### (b) DEPOLARISED RAYLEIGH SCATTERING

The results of Litovitz *et al.*<sup>3</sup> for liquid acetone, methyl iodide and benzene are used to provide experimental decay functions for depolarised Rayleigh scattered light and also the equivalent second derivative a.c.f. values with which to compare our model. Three *caveats* are: (1) the experimental data are complicated by cross-correlations and induced scattering; (2) the correlation function labelled "angular velocity" by these authors is in reality the negative of the second derivative of  $\rho_2(t)$  which reduces to the former only as a limit;<sup>37</sup> (3) the data are, of course, for molecules which may rotate in 3D.

The method adopted is to fit the experimental "angular velocity" a.c.f. with eqn (13) or with  $-\dot{\rho}_2(t)$ , (see below) and, therefrom, generate an orientational a.c.f.  $\rho_2(t)$  (fig. 1 and 2). Since the liquids were subject experimentally to the order of kilobars of external pressure we are also able to observe the dependence of the predicted mean square torque  $[K_0(0)]$  on molecular number density.

### (c) FAR INFRARED/MICROWAVE ABSORPTION

Choice of the absorption of a highly dipolar species,  $\text{CH}_2\text{Cl}_2$ , in dilute solution in  $\text{CCl}_4$  removes to a great extent the influence of the dipole-dipole coupling term (which badly complicates<sup>20</sup> the initial Langevin equation), and also reduces induced absorption to insignificance. These results still apply, of course, to rotation in space and not in a plane. It is striking that, experimentally, the position of the maximum

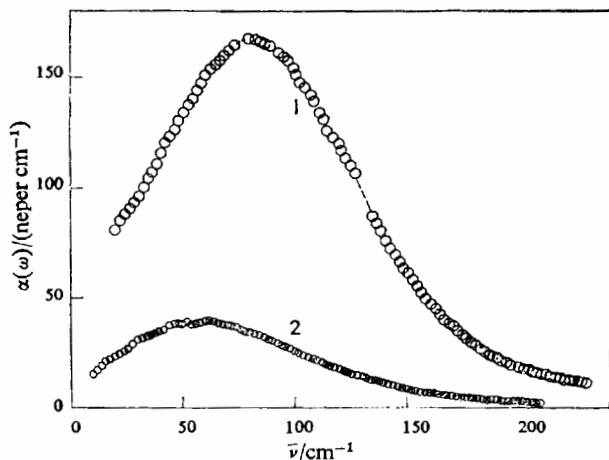


FIG. 3.—(1) Neat  $\text{CH}_2\text{Cl}_2$  at 296 K, 1 bar. Far infrared spectrum. (2)  $1.97 \times 10^{21}$  molecules  $\text{CH}_2\text{Cl}_2$   $\text{ml}^{-1}$  in  $\text{CCl}_4$ . Far infrared spectrum.

absorption in the far infrared shifts  $\approx 30 \text{ cm}^{-1}$  between the neat liquid and a dilute solution (fig. 3) although the mechanism is still far from free rotation. The quantity  $-\dot{\rho}_1(t)$  is obtained by Fourier transformation<sup>32</sup> of  $\omega g''(\omega)$ , the second intensity

moment, into the time domain. This function is then fitted and an orientational a.c.f. generated therefrom, no experimental function  $\rho_1(t)$  being available because of lack of microwave data.

## EXPERIMENTAL

The discrimination of increasingly sophisticated theoretical models requires well-substantiated experimental results. To this end a representative liquid (neat and in a dilute solution of  $\text{CCl}_4$ ) has been studied in the high frequency ( $10\text{--}200\text{ cm}^{-1}$ ) spectroscopic region using a Mark III, Grubb-Parsons/N.P.L. Fourier transform spectrometer. Phase modulation of the detected signal was employed. This both discriminates in favour of the interferogram, resulting in a high signal to noise ratio, and utilises all the radiation passing through the source aperture. The signal was detected with a low noise infrared detector type IR50, a redesigned Golay pneumatic cell in which solid state active devices replace the hot filament lamps, vacuum photocells and thermionic amplifiers in the old Golay design, resulting in an improved stability.

The synchronously amplified, periodically fluctuating detector output was Fourier transformed digitally, and a power absorption coefficient  $\alpha(\omega)/\text{neper cm}^{-1}$  calculated from the ratio of intensities penetrating two sample thicknesses. This procedure removes spurious effects arising from refractive index changes.

Particular care is taken to reduce limitations in the calculated spectra arising from beam divider and convergent beam effects. The first is achieved by matching the phase modulation characteristic and wave-number of maximum transmittivity of the interferometer. In the present study the latter is insignificant, small sample thicknesses only being possible for highly dipolar  $\text{CH}_2\text{Cl}_2$ .

Using an amplitude modulated spectrometer with a diamond-windowed Golay detector, different interferometric beam dividers with overlapping frequency ranges and different cells and cell window materials virtually eliminated residual systematic uncertainties in the band shapes. The results were reproducible in absolute intensity to within  $\pm 1\%$  over 90% of the frequency range, the maximum resolution being  $2\text{ cm}^{-1}$ .

The samples, spectroscopic grades, were contained in one of two VC-01 cells with T.P.X., quartz or polyethylene windows.

TABLE 1.—RAYLEIGH SCATTERING: PARAMETERS FOR BEST FIT TO EQN (13)

liquid	pressure/bar	temp./K	$I\omega_0^2/kT^*$	$I\Omega_0^2/kT^*$	$(I/kT)^{1/2}\beta^*$
acetone	1	296	47.9	148.6	21.8
acetone	$2 \times 10^3$	296	67.9	172.6	21.3
methyl iodide	1	296	68	1 414	185
methyl iodide	$1 \times 10^3$	296	107	30 247	3285
methyl iodide	$2.5 \times 10^3$	296	122	34 284	4028
benzene	1	296	109	551	94
benzene	$6.01 \times 10^2$	296	137	39 496	6291

\*  $I$  is the mean moment of inertia used, but not quoted, by the authors in ref. (3).

## DISCUSSION

### RAYLEIGH SCATTERING

The a.c.f. labelled "angular velocity" by Litovitz *et al.* was fitted initially with eqn (13) using the N.A.G. non-linear least mean squares procedure E04FAA; the results are illustrated in fig. 1. The optimum values of  $\omega_0^2$ ,  $\Omega_0^2$  and  $\beta$  are listed in table 1. It is clear that  $\omega_0^2$  (proportional to the mean square torque  $\langle T_q^2 \rangle$ ) increases with molecular number density in each species. The values of  $\beta$  and  $\Omega_0^2$  vary much



more rapidly, and the latter (which is related to  $\langle \dot{T}_q^2 \rangle / \langle T_q^2 \rangle - \langle T_q^2 \rangle$ ) increases a thousandfold in a few instances as the external pressure is increased over the same range. It seems that an interpretation of  $\Omega_0^2$  as  $(I_2/I_1)\omega_0^2$  is not useful in practice, but in general a very high value for  $\Omega_0^2/\omega_0^2$  means that  $\langle T_q^2 \rangle$  changes very rapidly with time at certain points in its domain of definition. The correlation frequency  $\beta$  also increases rapidly with applied pressure in some instances.

Using these optimum values the predicted  $\rho_2(t)$  function decays consistently more slowly than the experimental response function (corrected by Litovitz *et al.* for induced polarizability effects). This is due in some measure to our use of a planar model. Also, the form of the correction of Litovitz *et al.* is open to criticism. For instance, to use the theoretical second moment for the non-collisional component implies a Kirkwood factor of unity; it seems doubtful that the high frequency collisional contribution parallels the non-collisional. The separation of collisional from non-collisional effects is a major undertaking, and remains largely an unsolved problem. To develop the i.o. theory for space fluctuations is a formidably difficult mathematical exercise,<sup>33</sup> even for the needle and spherical top, for which  $\rho_1$  and  $\rho_2$  have been developed in an open-ended time series recently<sup>34</sup> from a purely exponential angular velocity a.c.f. These latter calculations suggest strongly that  $\rho_1$  and  $\rho_2$  would decay generally rather more quickly in space than in a plane.

TABLE 2.—RAYLEIGH SCATTERING: PARAMETERS FOR BEST FIT TO THE FUNCTION  $-\dot{d}^2\rho_2(t)/\dot{d}r^2$

liquid	pressure/bar	temp./K	$I\omega_0^2/kT$	$I\Omega_0^2/kT$	$(I/kT)^{1/2}\beta$
acetone	1	296	31.2	52.8	6.7
acetone	$2 \times 10^3$	296	53.4	93.8	10.4
methyl iodide	1	296	43.4	102.9	16.1
methyl iodide	$1 \times 10^3$	296	97.7	30 187	3254
methyl iodide	$2.5 \times 10^3$	296	115.2	36 451	4250
benzene	1	296	86.8	108.9	19.8
benzene	$6.01 \times 10^2$	296	137.3	39 496	6391

Considering the *caveats* listed above it would be naive to expect more of the present model than a reasonable prediction of  $\rho_2(t)$  given an oscillatory  $\langle \omega(t) \omega(0) \rangle$ , and to predict a sensible dependence of  $\langle T_q^2 \rangle$  upon the applied pressure. This alone is a considerable improvement on the classical theory. However, it is certainly more accurate to fit the experimental Rayleigh scattering data with

$$-\rho_2(t) = \left\langle \frac{d}{dt} \cos 2\theta(t) \left( \frac{d}{dt} \cos 2\theta(t) \right)_{t=0} \right\rangle$$

this yields the results of fig. 2 and table 2. The predicted angular velocity a.c.f. is little different from  $-\dot{\rho}_2(t)$ , *i.e.*, oscillatory. Comparison of tables 1 and 2 reveals similar overall variations in  $\omega_0^2$ ,  $\Omega_0^2$  and  $\beta$  with molecular number density, although the absolute values for best fit are different.

#### MOLECULAR DYNAMICS

In this case the computed angular velocity a.c.f. values were fitted and the torque a.c.f. predicted for the interatomic separations  $d^* = 0.7$  and  $d^* = 0.5$ , but the reverse procedure is more convenient for  $d^* = 0.3$ . The results are shown in fig. 4 and table 3. The computed and itinerant oscillator  $\langle T_q^2 \rangle$  factors are compared in fig. 4(d) on a normalised scale. In all three cases the l.m.s. best fits are acceptable, signifying that the planar oscillator is capable of matching results in 3-dimensional space over

the range of dumb-bell geometries studied here. It might be more consistent to fit the results of rough hard disc simulations<sup>35</sup> in two dimensions, but these have always led to an almost purely exponential angular velocity a.c.f., as do rough sphere computations,<sup>36</sup> and are thus restricted in scope in comparison with the atom-atom

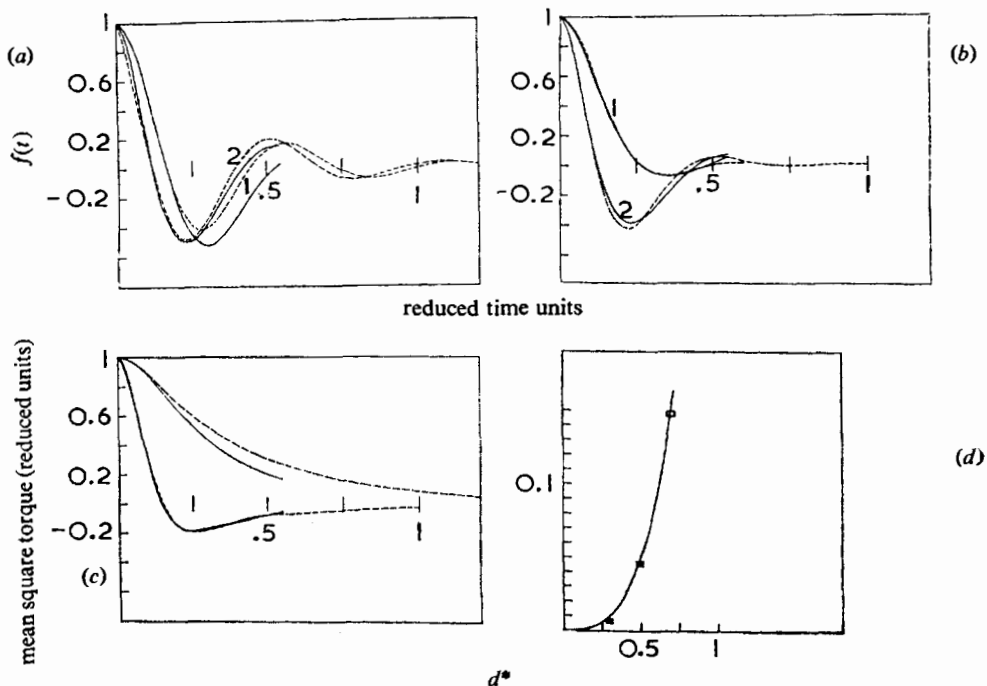


FIG. 4.—(a) — (1) Angular velocity a.c.f. computed with the atom-atom potential for  $d^* = 0.7$ , at a reduced number density of 0.643 and reduced temperature of 2.3; using L.-J. atom parameters from nitrogen. — (2) Torque a.c.f. likewise computed. - - - (1) best fit of  $\langle \dot{\theta}(t)\dot{\theta}(0) \rangle$  to eqn (1). - - - (2) theoretical  $\langle \dot{\theta}(t)\dot{\theta}(0) \rangle$ , corresponding to the computed curve (2), normalised at  $t = 0$ . (b) As for (a),  $d^* = 0.5$ , (c) As for (a),  $d^* = 0.3$ , (d) Variation of mean square torque with  $d^*$ . Itinerant oscillator predictions of  $\omega_0^2 = K_0(0)$ ; normalised at  $d^* = 0.7$ .

TABLE 3.—COMPUTER MOLECULAR DYNAMICS: PARAMETERS FOR BEST FIT TO EQN (13)

interatomic separation, $d^*$	$\omega_0^*$	$\rho_0^*$	$\beta^*$
0.7	134.9	31 136	6520
0.5	80.9	252.8	25.2
0.3	26.4	309.2	26.9

\* denotes reduced units. The time unit used corresponds to  $200(kT/I)^{\frac{1}{2}}$  time steps. A time step is  $\approx 5 \times 10^{-15}$  s.

algorithm. Nevertheless it would be instructive to reproduce the conditions assumed initially in the itinerant oscillator formalism in a molecular dynamics run, replacing the random torque  $\lambda(t)$  with deterministic interactions of the rough disc type between the annuli. In the case of linear motion the translational itinerant oscillator ought to match the force and linear velocity a.c.f. (as well as the kinetic energy a.c.f.) calculated by the atom-atom method. This will be the subject of a forthcoming article.

## FAR INFRARED ABSORPTION

In this case, data for a highly dipolar molecule,  $\text{CH}_2\text{Cl}_2$ , in dilute  $\text{CCl}_4$  solution, were used to calculate by Fourier transformation the space a.c.f.  $F_1 = \langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle / \langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(0) \rangle$ , where  $\mathbf{u}$  is the dipole unit vector  $\boldsymbol{\mu}/|\boldsymbol{\mu}|$ . The uncertainty in the experimental data is small. The function  $F_1$  calculated using Simpson's rule, ought then to be well defined and essentially free of cross-correlations, *i.e.*, it is virtually a true autocorrelation function. If  $\mathbf{u}$  were to fluctuate angularly in a plane, then  $F_1$  would reduce to  $\dot{\rho}_1(t)/\dot{\rho}_1(0)$ . This makes clear the assumptions made in fitting the data (fig. 5). The match is less satisfactory than those for the other sources considered

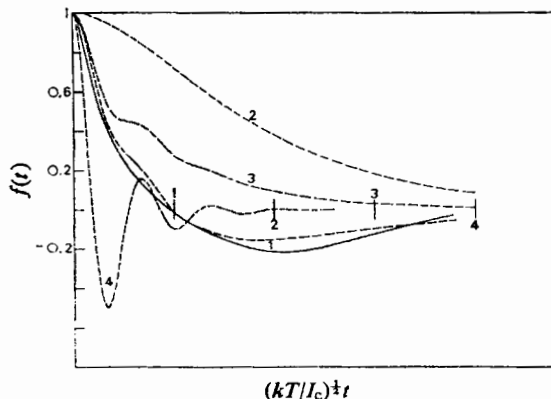


FIG. 5.—(1) — (1) Experimental  $\langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle / \langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(0) \rangle$  obtained from Fourier transforming curve 2 of fig. 3.

$$\left. \begin{array}{l} \text{--- (1) } \left\langle \frac{d}{dt} [\cos \theta(t)] \left( \frac{d}{dt} [\cos \theta(t)] \right)_{t=0} \right\rangle \text{ fitted to (1).} \\ \text{--- (2) } \langle \cos \theta(t) \cos \theta(0) \rangle. \\ \text{--- (3) } \langle \dot{\theta}(t) \dot{\theta}(0) \rangle. \\ \text{--- (4) } \langle \ddot{\theta}(t) \ddot{\theta}(0) \rangle. \end{array} \right\} \text{normalised to unity at } t = 0.$$

here, [optimum values:  $\omega_0^2 = 16.4 (kT/I_c) \text{ s}^{-2}$ ;  $\Omega_0^2 = 80.7 (kT/I_c) \text{ s}^{-2}$ ;  $\beta = 6.2 (kT/I_c)^{1/2} \text{ s}^{-1}$ ] but still within about  $\pm 10\%$  over much of the interval considered. At short times it is far closer than is the case<sup>15</sup> for the Wyllie/Larkin version<sup>14</sup> of the same basic model. From fig. 5, the rich variety of dynamical information (embodied in four separate a.c.f. values) is clearly apparent. In particular, the angular velocity a.c.f. is oscillatory. From a consideration of the very extensive data presented in ref. 15 (on some fifty different  $F_1$  functions), it seems that  $F_1$  is often markedly oscillatory, and so the angular velocity a.c.f. for real molecules is rarely a single exponential.

## CONCLUSIONS

(i) Itinerant oscillation in a plane represents fairly accurately the angular reorientations of molecules as revealed by the three separate probes used here.

(ii) The experimental angular velocity a.c.f. is rarely anything but oscillatory in fluids consisting of small molecules.

The Ramsay Memorial Trust is thanked for a Fellowship to M. W. E. The S.R.C. is thanked for an equipment grant and a studentship to G. J. E.

## APPENDIX 1

## A.C.F. VALUES FOR A POSITIVE DISCRIMINANT

In this case all the roots of the secular determinant are distinct and real. It can be shown using the elementary theory of cubic equations that the roots  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  are all negative and take the form:

$$\alpha_1 = 2(-A/3)^{\frac{1}{2}} \cos(\theta/3),$$

$$\alpha_2 = 2(-A/3)^{\frac{1}{2}} \cos[(\theta+2\pi)/3],$$

$$\alpha_3 = 2(-A/3)^{\frac{1}{2}} \cos[(\theta+4\pi)/3],$$

where

$$\theta = \cos^{-1}[-(B/2)/(-A^3/27)^{\frac{1}{2}}].$$

The factors  $A$  and  $B$  are related elsewhere to  $\beta$ ,  $\omega_0^2$  and  $\Omega_0^2$  by Evans *et al.*,<sup>21</sup> for all values of the discriminant, using Cardan's formula. The required a.c.f. of angular velocity is now the inverse Laplace transform of:

$$\frac{A_0}{s+\alpha_1} + \frac{B_0}{s+\alpha_2} + \frac{C_0}{s+\alpha_3}$$

where  $A_0$ ,  $B_0$ ,  $C_0$  are determined by the matrix equation:

$$\begin{bmatrix} 1 & 1 & 1 \\ \alpha_2 + \alpha_3 & \alpha_1 + \alpha_3 & \alpha_1 + \alpha_2 \\ \alpha_2\alpha_3 & \alpha_1\alpha_3 & \alpha_1\alpha_2 \end{bmatrix} \begin{bmatrix} A_0 \\ B_0 \\ C_0 \end{bmatrix} = \begin{bmatrix} 1 \\ \beta \\ \Omega_0^2 \end{bmatrix}.$$

Solving, we have:

$$A_0 = (\alpha_2 - \alpha_3)[\alpha_1(\alpha_1 - \beta) + \Omega_0^2]/D_0,$$

$$B_0 = (\alpha_3 - \alpha_1)[\alpha_2(\alpha_2 - \beta) + \Omega_0^2]/D_0,$$

$$C_0 = (\alpha_1 - \alpha_2)[\alpha_3(\alpha_3 - \beta) + \Omega_0^2]/D_0,$$

where

$$D_0 = \alpha_1^2(\alpha_2 - \alpha_3) + \alpha_2^2(\alpha_3 - \alpha_1) + \alpha_3^2(\alpha_1 - \alpha_2).$$

Therefrom:

$$\frac{\langle \dot{\theta}(t)\dot{\theta}(0) \rangle}{\langle \dot{\theta}(0)^2 \rangle} = A_0 e^{-\alpha_1 t} + B_0 e^{-\alpha_2 t} + C_0 e^{-\alpha_3 t},$$

$$\rho_1(t) = \exp \left\{ -\frac{kT}{I_2} \left[ \left( \frac{A_0}{\alpha_1} + \frac{B_0}{\alpha_2} + \frac{C_0}{\alpha_3} \right) t - \left( \frac{A_0}{\alpha_1^2} + \frac{B_0}{\alpha_2^2} + \frac{C_0}{\alpha_3^2} \right) + \left( \frac{A_0 e^{-\alpha_1 t}}{\alpha_1^2} + \frac{B_0 e^{-\alpha_2 t}}{\alpha_2^2} + \frac{C_0 e^{-\alpha_3 t}}{\alpha_3^2} \right) \right] \right\};$$

$$\frac{\langle \ddot{\theta}(t)\ddot{\theta}(0) \rangle}{\langle \ddot{\theta}(0)^2 \rangle} = \frac{\alpha_1^2 A_0 e^{-\alpha_1 t} + \alpha_2^2 B_0 e^{-\alpha_2 t} + \alpha_3^2 C_0 e^{-\alpha_3 t}}{\alpha_1^2 A_0 + \alpha_2^2 B_0 + \alpha_3^2 C_0}.$$

## APPENDIX 2

Since the direct Fourier transform of the power absorption coefficient  $\alpha(\omega)$ , setting aside internal field and induced absorption factors, yields  $-d^2\rho_1(t)/dt^2$ , and not strictly the angular velocity a.c.f., we give here the rather cumbersome expression

for the combinatorial function represented by the second derivative above. For a negative or zero discriminant:

$$-\frac{d^2}{dt^2} [\rho_1(t)] = [f_1(t) - f_2^2(t)] \exp[-y(t)]$$

where

$$f_1(t) = \frac{kT}{I_2} \left( e^{-\sigma_1 t} \left\{ [\omega_1(B_1\sigma_1 - A_1\omega_1) + \sigma_1(B_1\omega_1 + A_1\sigma_1)] \cos \omega_1 t + \right. \right. \\ \left. \left. [\omega_1(B_1\omega_1 + A_1\sigma_1) - \sigma_1(B_1\sigma_1 - A_1\omega_1)] \sin \omega_1 t \right\} + \Gamma e^{-\sigma_2 t} / (1 + \Gamma) \right);$$

$$f_2(t) = \frac{kT}{I_2} \left\{ e^{-\sigma_1 t} [(B_1\sigma_1 - A_1\omega_1) \sin \omega_1 t - (B_1\omega_1 + A_1\sigma_1) \cos \omega_1 t] - \right. \\ \left. \Gamma e^{-\sigma_2 t} / (1 + \Gamma) + C_1 \right\};$$

$$A_1 = \frac{3\sigma_1^2 + 2\sigma_1\sigma_2\Gamma - \omega_1^2}{(\sigma_1^2 + \omega_1^2)^2(1 + \Gamma)};$$

$$B_1 = \frac{2\omega_1^2\sigma_1 + (\sigma_1 + \Gamma\sigma_2)(\omega_1^2 - \sigma_1^2)}{\omega_1(\sigma_1^2 + \omega_1^2)^2(1 + \Gamma)};$$

$$C_1 = \frac{2\sigma_1}{(\sigma_1^2 + \omega_1^2)(1 + \Gamma)} + \frac{\Gamma}{1 + \Gamma} \left( \frac{\sigma_2}{\sigma_1^2 + \omega_1^2} + \frac{1}{\sigma_2^2} \right).$$

For a positive discriminant:

$$-\frac{d^2}{dt^2} [\rho_1(t)] = \frac{kT}{I_2} \left[ A_0 e^{-\alpha_1 t} + B_0 e^{-\alpha_2 t} + C_0 e^{-\alpha_3 t} + \right. \\ \left. \left( \frac{A_0}{\alpha_1} (1 - e^{-\alpha_1 t}) + \frac{B_0}{\alpha_2} (1 - e^{-\alpha_2 t}) + \frac{C_0}{\alpha_3} (1 - e^{-\alpha_3 t}) \right)^2 \right] \rho_1(t).$$

- <sup>1</sup> P. Debye, *Polar Molecules* (Dover, N.Y., 1929).
- <sup>2</sup> N. E. Hill, A. H. Price, W. E. Vaughan and M. Davies, *Dielectric Properties and Molecular Behaviour* (van Nostrand, London, 1969).
- <sup>3</sup> J. F. Dill, T. A. Litovitz and J. A. Bucaro, *J. Chem. Phys.*, 1975, **62**, 3839.
- <sup>4</sup> M. Evans, *J.C.S. Faraday II*, 1977, **73**, 485.
- <sup>5</sup> J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1976), chap. 3.
- <sup>6</sup> J. Barojas, D. Levesque and B. Quentrec, *Phys. Rev.*, 1973, **A7**, 1092.
- <sup>7</sup> P. S. Y. Cheung and J. G. Powles, *Mol. Phys.*, 1975, **30**, 921.
- <sup>8</sup> (a) W. B. Streett and D. J. Tildesley, *Proc. Roy. Soc. A*, 1976, **348**, 485; (b) G. H. Wegdam, G. J. Evans and M. Evans, *Mol. Phys.*, 1977, **33**, 1805.
- <sup>9</sup> *Selected Papers on Noise and Stochastic Processes*, ed. N. Wax (Dover, N.Y., 1954).
- <sup>10</sup> M. Evans, *Adv. Molecular Relaxation Int. Proc.*, 1977, **10**, 203, (review); *Dielectric and Related Molecular Processes*, Specialist Periodical Report (Chem. Soc. London, 1977), vol. 3, p. 1.
- <sup>11</sup> N. E. Hill, *Proc. Phys. Soc.*, 1963, **82**, 723.
- <sup>12</sup> J. P. Poley, *J. Appl. Sci. Res. B*, 1955, **4**, 337.
- <sup>13</sup> G. A. P. Wyllie, *J. Phys. C.*, 1971, **4**, 564.
- <sup>14</sup> (a) I. W. Larkin, *Faraday Symp. Chem. Soc.*, 1972, **6**, 112; (b) R. Haffmanns and I. W. Larkin, *J.C.S. Faraday II*, 1972, **68**, 1729; (c) M. Evans, M. Davies and I. W. Larkin, *J.C.S. Faraday II*, 1973, **69**, 1011; (d) I. W. Larkin, *J.C.S. Faraday II*, 1973, **69**, 1278; (e) I. W. Larkin and M. Evans, *J.C.S. Faraday II*, 1974, **70**, 477; (f) I. W. Larkin, *J.C.S. Faraday II*, 1974, **70**, 1457.
- <sup>15</sup> M. Evans, *J.C.S. Faraday II*, 1975, **71**, 2051.
- <sup>16</sup> W. T. Coffey, T. Ambrose and J. H. Calderwood, *J. Phys. D.*, 1976, **9**, L115.

- <sup>17</sup> J. H. Calderwood and W. T. Coffey, *Proc. Roy. Soc. A*, 1977, **356**, 269.
- <sup>18</sup> W. T. Coffey, J. G. Pearce and J. H. Calderwood, *J. Phys. D.*, submitted.
- <sup>19</sup> E. Nelson, *Dynamical Theories of Brownian Motion* (Princeton Univ. Press, N.J., 1967).
- <sup>20</sup> B. K. P. Scaife, *Complex Permittivity* (English Univ. Press, London, 1971).
- <sup>21</sup> M. Evans, *Chem. Phys. Letters*, 1976, **39**, 601.
- <sup>22</sup> H. Mori, *Prog. Theor. Phys.*, 1965, **33**, 423.
- <sup>23</sup> V. F. Sears, *Canad. J. Phys.*, 1967, **45**, 237.
- <sup>24</sup> J. S. Rowlinson and M. Evans, *Ann. Rep. Chem. Soc.*, 1975, **72**, 5.
- <sup>25</sup> M. S. Beevers and G. Williams, *J.C.S. Faraday II*, 1976, **72**, 2171.
- <sup>26</sup> M. Evans, *Mol. Phys.*, 1977, **34**, 963.
- <sup>27</sup> J. T. Lewis, J. R. McConnell and B. K. P. Scaife, *Phys. Letters*, 1974, **49A**, 303; *Proc. Roy. Irish Acad.*, 1976, **76A**, 543.
- <sup>28</sup> G. J. Davies and M. Evans, *J.C.S. Faraday II*, 1976, **72**, 1194, 1206.
- <sup>29</sup> S.-C. An, C. J. Montrose and T. A. Litovitz, *J. Chem. Phys.*, 1976, **64**, 3717; P. Madden, *Chem. Phys. Letters*, 1977, in press.
- <sup>30</sup> G. J. Evans, G. H. Wegdam and M. Evans, *Adv. Molecular Relaxation Int. Proc.*, 1977, **11**, 295.
- <sup>31</sup> G. E. Uhlenbeck and L. S. Ornstein, *Phys. Rev.*, 1930, **36**, 823.
- <sup>32</sup> A. Gerschel, *Mol. Phys.*, 1976, **31**, 209; 1977, **32**, 679.
- <sup>33</sup> J. R. McConnell, *Proc. Roy. Irish Acad.*, 1977, **77A**, 13.
- <sup>34</sup> J. R. McConnell, personal communication.
- <sup>35</sup> E. Kestemont and A. Bellemans, *J. Comp. Phys.*, 1971, **7(3)**, 515.
- <sup>36</sup> E. Kestemont, *J. Phys. C.*, 1976, **9**, 2651.
- <sup>37</sup> C. Brot, *Dielectric and Related Molecular Processes*, Specialist Periodical Report (Chem. Soc., London, 1975), vol. 2, p. 1.

(PAPER 7/1117)