

THE PLANAR ITINERANT OSCILLATOR MODEL. A DISCUSSION OF ITS USE IN REPRODUCING EXPERIMENTAL DATA FROM THREE SEPARATE SOURCES

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Autocorrelation functions calculated from the itinerant oscillator model are compared with experimental data from far infrared absorption measurements, depolarised Rayleigh scattering measurements and molecular dynamics computations. It is concluded that the model represents the reorientational motion of a molecule in the fluid (at short times) satisfactorily. The predicted angular velocity acf is not a pure exponential but rather an oscillatory function of time. This seems to be the case generally for small molecules.

1. Introduction and theory

In this letter we shall attempt to compare autocorrelation functions (acf's) calculated from the itinerant oscillator model of reorientational molecular motion developed recently by Coffey et al. [1-3] with experimental results from three separate fields. These are (a) depolarised light scattering [4] from liquids subject to kilobars of external pressure, (b) molecular dynamics results using the atom-atom potential of Tildesley and Streett [5], (c) far infrared absorption of a highly dipolar species in dilute solution. Several interrelated autocorrelation functions are obtained by using these three techniques simultaneously, thus providing a stern test for the model.

For details of this planar mechanism see refs. [1-3]. Here we state merely that the librations of a molecule within a cage of its neighbours are represented by the angular motion of a disk harmonically bound within an annulus or ring which is itself undergoing rotational brownian motion. The equations of motion governing this system lead to an angular velocity acf, $C_\omega(t)$, of the form

$$C_\omega(t) = \langle \dot{\theta}(t)\dot{\theta}(0) \rangle_0 / \langle \dot{\theta}^2(0) \rangle_0 \quad (t > 0)$$

$$= (1 + \Gamma)^{-1} \{ [\cos \omega_1 t + (\sigma_1 + \Gamma\sigma_2)\omega_1^{-1} \sin \omega_1 t] e^{-\sigma_1 t} + \Gamma e^{-\sigma_2 t} \}, \quad (1)$$

where θ is a coordinate which specifies the angular position of a dipole μ lying along the axis of the disk at any time $t > 0$. For convenience, $\theta(0)$ is taken to be coincident with the direction of a steady electric field E , and it is assumed that this field is suddenly removed at the time $t = 0$. Further, λ_1 , λ_2 and λ_3 are the roots of the equation:

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

i.e. $\lambda_1 = \sigma_1 + i\omega_1$, $\lambda_2 = \sigma_1 - i\omega_1$, $\lambda_3 = \sigma_2$. The factor Γ is given by:

$$\Gamma = -2\sigma_1(\sigma_1^2 + \omega_1^2)/\sigma_2(3\sigma_1^2 - \sigma_2^2 - \omega_1^2). \quad (3)$$

If $\psi(t)$ is the angle which a point on the rim of the annulus makes with the reference direction at time t and if I_1 is the moment of inertia of the annulus, then $I_1\beta\dot{\psi}$ is the frictional couple acting on the annulus due to the surroundings. ω_0 is the angular frequency of oscillation of the disk when the annulus is held in a fixed position and $\Omega_0^2 = (I_2/I_1)\omega_0^2$, where I_2 is the moment of inertia of the disk. By means of a theorem about characteristic functions of gaussian distributions [1-3], it may be shown from eq. (1) that the orientational acf's appropriate to dielectric relaxation and depolarised Rayleigh scattering of light are given by:

$$\rho_1(t) = \langle \cos \theta(t) \cos \theta(0) \rangle / \langle \cos^2 \theta(0) \rangle = \exp[-\gamma(t)],$$

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

respectively, where $\gamma(t)$ is defined as follows.

$$\begin{aligned} \gamma(t) = & \frac{1}{1+\Gamma} \frac{kT}{I_2} \left[\frac{-2\sigma_1\sigma_2 + \Gamma(\sigma_1^2 + \sigma_2^2 + \omega_1^2)}{\sigma_2(\sigma_1^2 + \omega_1^2)} \right] t - \left[\frac{\Gamma}{\sigma_2^2} + \frac{3\sigma_1^2 + 2\sigma_1\sigma_2\Gamma - \omega_1^2}{(\sigma_1^2 + \omega_1^2)^2} \right] \\ & + \frac{3\sigma_1^2 + 2\sigma_1\sigma_2\Gamma - \omega_1^2}{(\sigma_1^2 + \omega_1^2)^2} \left[\cos \omega_1 t + \frac{\sigma_1^3 - 3\sigma_1\omega_1^2 + \sigma_2\Gamma(\sigma_1^2 - \omega_1^2)}{\omega_1(3\sigma_1^2 + 2\sigma_1\sigma_2\Gamma - \omega_1^2)} \sin \omega_1 t \right] e^{-\sigma_1 t} + \frac{\Gamma}{\sigma_2^2} e^{-\sigma_2 t}. \end{aligned} \quad (5)$$

One may readily calculate from eqs. (1) and (3) the quantity $\langle \dot{\theta}(t)\dot{\theta}(0) \rangle / \langle \dot{\theta}(0)\dot{\theta}(0) \rangle$, which we shall call the torque acf, and the quantities $-\ddot{\rho}_1(t)$ and $-\ddot{\rho}_2(t)$ needed [6] to fit the raw experimental data.

2. Experimental

The original data for this letter consists of the far infrared spectrum of the highly dipolar species CH_2Cl_2 in dilute CCl_4 solution. This spectrum was chosen to eliminate: (i) dipole-dipole coupling [7]; (ii) collision induced effects [8]. The data were obtained with a Mark 3 Grubb-Parsons/N.P.L. Fourier transform interferometer using phase modulation of the radiation arriving at a solid-state Golay IR50 detector. In comparison with the pure liquid CH_2Cl_2 the solution absorption band peaks 30 cm^{-1} lower in frequency. Solute and solvent were Analar spectroscopic grade.

3. Results and discussion

Least mean squares fits (N.A.G. system E04FAA) to some depolarised light scattering data of Litovitz et al. [4], to our own molecular dynamics data and far infrared spectrum are shown in figs. 1-3. The optimum values of ω_0^2 , Ω_0^2 and β (regarded as variables), are tabulated in table 1.

3.1. Rayleigh scattering

The function $-\ddot{\rho}_2(t)$ was used to fit the "angular velocity acf" of Litovitz et al. [4]. It is seen that ω_0^2 (which is proportional [9] to the mean square torque, $\langle T_q^2 \rangle$, in the system) increases with molecular number density as this

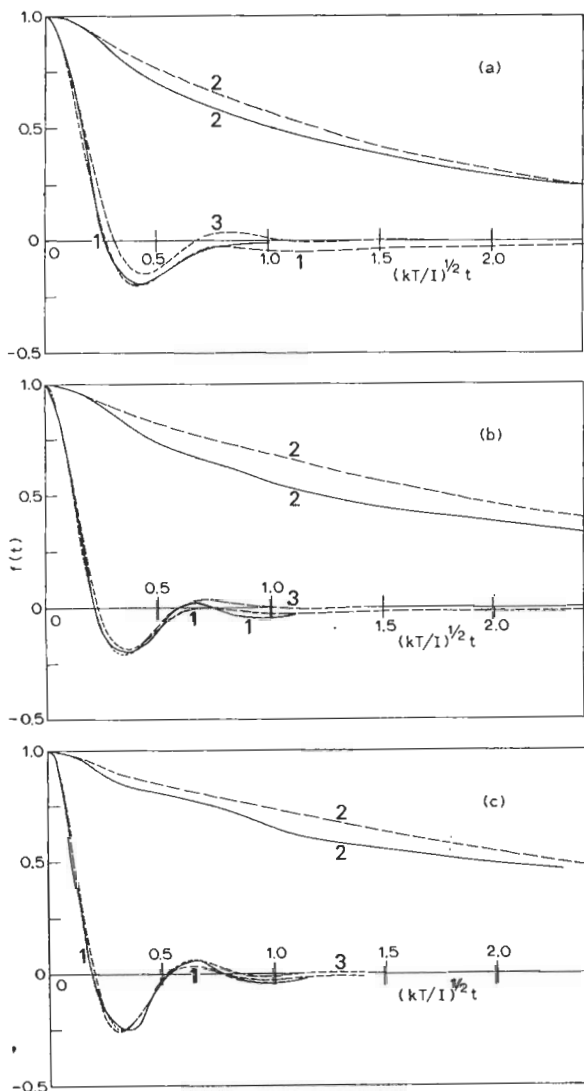


Fig. 1. (a) — (1) Experimental $-d^2\rho_2(t)/dt^2$ for 3-D reorientations, (2) Experimental $\rho_2(t)$; --- (1) $\langle [d \cos 2\theta(t)/dt] [d \cos 2\theta(0)/dt] \rangle$ fitted to (1), (2) $\langle \cos 2\theta(t) \cos 2\theta(0) \rangle$ and (3) $\langle \dot{\theta}(t)\dot{\theta}(0) \rangle$ calculated from the fitting for liquid methyl iodide at 1 bar, 296 K. Data of Litovitz et al. [4]. (b) As for (a), 1 kbar. (c) As for (a), 2.5 kbar.

is increased a thousandfold by application of external hydraulic pressure. The values of β and Ω_0^2 vary much more rapidly, and the latter (which is related to $\langle T_q^2 \rangle / \langle T_q^2 \rangle - \langle T_q^2 \rangle$) increases a thousandfold in a few instances as the external pressure is increased over the same range. It seems that the interpretation of Ω_0^2 as $(I_2/I_1)\omega_0^2$ is not meaningful experimentally, but in general, a very high value of Ω_0^2/ω_0^2 means that $\langle T_q^2 \rangle$ changes very rapidly with time at certain points in its domain of definition. The $\rho_2(t)$ function predicted by this fitting decays consistently more slowly than the experimental response function (corrected by Litovitz et al. for collision induced polarisabilities). This is due in some measure to our use of a planar model.

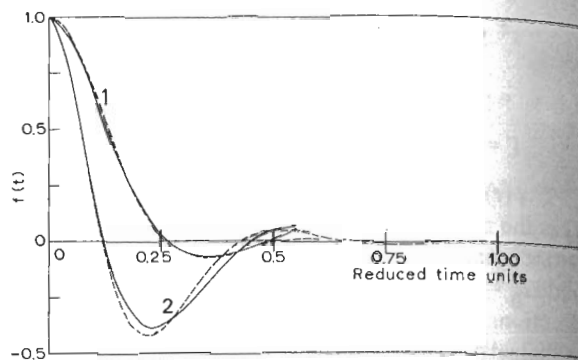


Fig. 2. — (1) Angular velocity acf computed with the atom-atom potential for a reduced interatomic separation, $d^* = 0.5$, at a reduced number density of 0.643 and reduced temperature of 2.3. — (2) Torque acf likewise computed. --- (1) Best fit of $\langle \dot{\theta}(t)\dot{\theta}(0) \rangle / \langle \dot{\theta}(0)\dot{\theta}(0) \rangle$ to (1). --- (2) Predicted itinerant oscillator torque acf from the fitting with the parameters tabulated in the text.

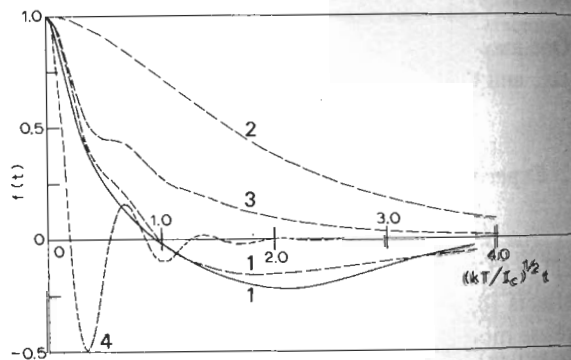


Fig. 3. (1) — Experimental $\langle \dot{u}(t) \cdot \dot{u}(0) \rangle / \langle \dot{u}(0) \cdot \dot{u}(0) \rangle$ obtained [6] from Fourier transforming the far infrared power absorption coefficient. --- (1) $\langle [d \cos \theta(t)/dt] [d \cos \theta(0)/dt] \rangle$ fitted to (1), (2) $\langle \cos \theta(t) \cos \theta(0) \rangle$, (3) $\langle \dot{\theta}(t)\dot{\theta}(0) \rangle / \langle \dot{\theta}(0)\dot{\theta}(0) \rangle$, (4) $\langle \ddot{\theta}(t)\ddot{\theta}(0) \rangle / \langle \ddot{\theta}(0)\ddot{\theta}(0) \rangle$.

Table 1
Values of ω_0^2 , Ω_0^2 and β for best fit

Liquid	Experimental function	Pressure (bar)	Temperature (K)	$\frac{I\omega_0^2}{kT}$	$\frac{I\Omega_0^2}{kT}$	$(I/kT)^{1/2}\beta$
methyl iodide	Rayleigh scattering	1	296	43.4	102.9	16.1
		1000	296	97.7	30187	3254
		2500	296	115.2	36451	4250
dumbbell potential	molecular dynamics, torque acf	$\rho^* = 0.643$	$T^* = 2.3$	80.9 *	252.8 *	25.2 *
CH ₂ Cl ₂ /CCl ₄	far infrared	1.97×10^{21} molecules cm ⁻³	298	16.4	80.7	6.2

* Reduced units corresponding to $200 (kT/I)^{1/2}$ time steps per time unit.

3.2. Molecular dynamics

In this case angular velocity and torque acf's were computed for a dumbbell potential using an atom-atom algorithm (described fully by Evans et al. [10] and by Tildesley and Streett [5]) under the conditions described in the caption to fig. 2. For an interatomic separation of $d^* = 0.5$ in reduced units [5] the computed angular velocity acf is fitted accurately by the analytical model and the torque acf realistically predicted. This work will be expanded in a forthcoming publication in order to evaluate the underlying dependence of $\langle T_q^2 \rangle$ on interatomic separation d^* . This result indicates that a planar molecule is capable of reproducing the molecular dynamics results, which are derived from 3-D space reorientations. It might be interesting to use an algorithm based on an ensemble of rough disks, but previous computations have shown that in this case the angular velocity acf is always exponential. This indicates that an atom-atom potential is the more realistic, since an oscillatory angular velocity acf is needed to fit both Rayleigh scattering and far infrared data.

3.3. Far infrared data

In this case, data for a highly dipolar species, CH₂Cl₂, in dilute solution were used to evaluate the experimental function:

$$F_1 = \langle \dot{u}(t) \cdot \dot{u}(0) \rangle / \langle \dot{u}(0) \cdot \dot{u}(0) \rangle,$$

where u is the unit dipole vector. In a plane, this would be $-\ddot{\rho}_1(t)$. This is true regardless of molecular symmetry. The match is less satisfactory than for the results of the other two techniques considered here but still within about $\pm 10\%$ [6] over most of the time interval up to 4 reduced units. At short times the fit is far closer than in the case of the Wyllie/Larkin version [8,11] of the same model. From fig. 3 the rich variety of dynamical information obtainable is clearly apparent. In particular the angular velocity acf is oscillatory. This seems to be true generally [11], since F_1 experimentally becomes negative at intermediate times.

4. Conclusions

- (i) The 2-D itinerant oscillator model reproduces closely the molecular dynamics of molecules in fluids as manifested by the three different probes used here.
- (ii) The predicted angular velocity acf is not a pure exponential but rather an oscillatory function of time. This seems to be the case generally for small molecules.

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References

- [1] W.T. Coffey, T. Ambrose and J.H. Calderwood, *J. Phys.* D9 (1976) L115.
- [2] J.H. Calderwood and W.T. Coffey, *Proc. Roy. Soc. A* (1977), to be published.
- [3] W.T. Coffey, J.G. Pearce and J.H. Calderwood, *J. Phys. D*, to be published.
- [4] J.F. Dill, T.A. Litovitz and J.A. Bucaro, *J. Chem. Phys.* 62 (1975) 3839.
- [5] W.B. Streett and D.J. Tildesley, *Proc. Roy. Soc.* 348A (1976) 485.
- [6] C. Brot, in: *Dielectric and related molecular processes*, Vol. 2 (The Chemical Society, London, 1975) p. 1.
- [7] B.K.P. Scaife, *Complex permittivity* (English Univ. Press, London, 1971).
- [8] M. Evans, *Advan. Mol. Rel. Int. Proc.* 10 (1977) 203.
- [9] M. Evans, *Chem. Phys. Letters* 39 (1976) 601.
- [10] G.J. Evans, G.H. Wegdam and M. Evans, *Mol. Phys.* (1977), to be published; *Advan. Mol. Rel. Int. Proc.* (1977), to be published.
- [11] M. Evans, *J. Chem. Soc. Faraday II* 71 (1975) 2051.