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 calculations. It is concluded that the model represents the rotational motion of a molecule in the fluid (at short times) satisfactorily. The predicted angular velocity autocorrelation function 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 calculated from the itinerant oscillator model of rotational 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 liquid paraffins at kilohertz of external pressure, (b) molecular dynamics results using the stator-stator potential of Tildesley and Streit [5], and (c) far infrared absorption of a highly dopable 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 neighbors are represented by the angular motion of a disk harmonically bound within an annular or ring which is itself undergoing rotational brownian motion. The equations of motion governing this system lead to an angular velocity autocorrelation function, \( C_\omega(t) \), of the form

\[
C_\omega(t) = \delta(\theta(0)) \langle \delta^2(\theta) \rangle_0 \quad (t > 0)
\]

\[
\times (1 + \Gamma)^{-1} \left[ (\cos \omega t + (\epsilon_1 + \Gamma \omega_3) \sin \omega t) e^{-\Gamma t} + \Gamma e^{-\delta t} \right],
\]

where \( \theta \) is a coordinate which specifies the angular position of a dipole \( \mu \) 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, \( \lambda_1, \lambda_2 \) and \( \lambda_3 \) are the roots of the equation...
\[ \dot{\theta}^2 + \ddot{\theta}^2 + (\omega_1^2 + \omega_2^2) \dot{\theta} + \omega_1 \dot{\theta} = 0. \] (2)

i.e. \( \lambda_1 = \omega_1 + i\omega_2, \lambda_2 = \omega_1 - i\omega_2, \lambda_3 = \omega_3. \) The factor \( \Gamma \) is given by:

\[ \Gamma = -2\omega_1 \left( \omega_1^2 + \omega_2^2 \right) \omega_1 \left( 3\omega_1^2 - \omega_2^2 \right). \] (3)

If \( \alpha(t) \) is the angle which a point on the rim of the annulus makes with the reference direction at time \( t \) and if \( \omega_2 \) is the moment of inertia of the annulus, then \( \tau(t) \) is the frictional couple acting on the annulus due to the surroudings. \( \omega_1 \) is the angular frequency of oscillation of the disk when the annulus is held in a fixed position and \( \omega_2^2 = (\omega_1/\omega_2)^2 \omega_0^2 \), where \( \omega_2 \) 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 orientations \( \alpha \) with appropriate drielectric relaxation and depolarized Rayleigh scattering of light are given by:

\[ p_1(t) = \cos \theta(t) \cos \theta(0) / \cos^2 \theta(0) \exp(-\alpha(t)) \],

\[ p_2(t) = \cos 2\theta(t) \cos 2\theta(0) / \cos^2 2\theta(0) \exp(-4\alpha(t)) \],

respectively, where \( \alpha(t) \) is defined as follows:

\[ \alpha(t) = \frac{1}{1 + \Gamma \omega_2^2} \left[ \frac{2\omega_1 \omega_2 + \Gamma (\omega_1^2 + \omega_2^2)}{\omega_1^2 + \omega_2^2} \right] \left[ \frac{\Gamma + 3\omega_1^2 + 2\omega_1 \omega_2 \Gamma - \omega_2^2}{(\omega_1^2 + \omega_2^2)^2} \right] \left[ \frac{-3\omega_1^2 + 2\omega_1 \omega_2 \Gamma - \omega_2^2}{(\omega_1^2 + \omega_2^2)^2} \right] \left[ \frac{\omega_1 \left( \omega_1^2 + \omega_2^2 \right) \left( \omega_1^2 + \omega_2^2 \right)^2}{\omega_1 \left( 3\omega_1^2 + 2\omega_1 \omega_2 \Gamma - \omega_2^2 \right) \left( \omega_1^2 + \omega_2^2 \right)^2} \right]. \] (5)

One may readily calculate from eqns. (1) and (3) the quantity \( \partial p_1(\theta)/\partial \theta(\theta) \partial \theta(0) \), which we shall call the torque \( \alpha \), and the quantities \( -\dot{\theta}_1(t) \) and \( -\dot{\theta}_2(t) \) 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 CH₃OH in dibutyl ether 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 Grobb-Pansoni/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 CH₃OH the solution absorption bandwidth peaks 30 cm⁻¹ lower in frequency. Solution and solvent were Analar spectrograde.

3. Results and discussion

Least mean squares fits \( (N.A.G. \text{ system E04FNA}) \) to some depolarized 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 \( \Lambda(\omega_1^2,\omega_2^2) \) and \( \beta \) (regarded as variables), are tabulated in table 1.

3.1. Rayleigh scattering

The function \( p_2(t) \) was used to fit the "angular velocity \( \alpha \)" of Litovitz et al. \([4]\). It is seen that \( \omega_2^2 \) (which is proportional \([9]\) to the mean square torque, \( \langle \gamma^2 \rangle \), in the system) increases with molecular number density in this
Fig. 1. (a) Experimental $-\frac{d\psi_2(2t)}{d\omega}$ for 3-D rotorizations. (b) Experimental $\psi_2(2t)$.

- (1) $\alpha(\cos(\theta/2)\cos(\theta/2))$ fitted to (1), (2) $\cos(\theta/2)\cos(\theta/2)$ and (3) $\cos(\theta/2)$, calculated from the fitting for liquid methyl iodide at 1 bar. 296 K. Data of Litovitz et al. [4].
- As for (a), 1 kbar. (c) As for (a), 2.5 kbar.

It increased a thousandfold by application of external hydraulic pressure. The values of $\beta$ and $\Omega_2$ vary much more rapidly, and the latter (which is related to $\Omega_2^2/(T_2^2 - T_2^2)$) increases a thousandfold in a few instances as the external pressure is increased over the same range. It seems that the interpretation of $\Omega_2^2$ as $(T_2^2/\gamma_1)$ is not meaningful experimentally, but in general, a very high value of $\Omega_2^2/\gamma_2$ means that $T_2^2$ changes very rapidly with time at certain points in its domain of definition. The $\mu(t)$ function predicted by this fitting decays sufficiently now slowly than the experimental response function (corrected by Litovitz et al. for collision-induced polarizabilities). This is due in some measure to our use of a planar model.
### Table 1

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Experimental function</th>
<th>Pressure (bar)</th>
<th>Temperature (K)</th>
<th>$kT/k_B$</th>
<th>$U/k_B$</th>
<th>$(U/k_B)^{1/3}$ $\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl iodide</td>
<td>Rayleigh scattering</td>
<td>1</td>
<td>296</td>
<td>43.4</td>
<td>102.9</td>
<td>16.1</td>
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<tr>
<td></td>
<td>scattering</td>
<td>1000</td>
<td>296</td>
<td>97.7</td>
<td>3018T</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td>scattering</td>
<td>2500</td>
<td>296</td>
<td>115.2</td>
<td>36451</td>
<td>42.00</td>
</tr>
<tr>
<td>dumbbell potential</td>
<td>molecular dynamics, torque acf</td>
<td>$a^* = 0.643$</td>
<td>$J^* = 2.3$</td>
<td>80.9</td>
<td>252.8</td>
<td>25.2</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$/CCl$_4$</td>
<td>far infrared</td>
<td>1.97 x 10$^{21}$ molecules cm$^{-3}$</td>
<td>298</td>
<td>16.4</td>
<td>80.7</td>
<td>6.2</td>
</tr>
</tbody>
</table>

* Reduced units corresponding to 200 (kT/$\pi$)$^3$ 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. [7]) and by Tildeney 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 $[7]$ 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, CH$_2$Cl$_2$, in dilute solution were used to evaluate the experimental function:

$$P_1 = \langle \vec{d}(t) \cdot \vec{d}(0) \rangle \langle \dot{\vec{d}}(0) \cdot \ddot{\vec{d}}(0) \rangle,$$

where $\vec{d}$ is the unit dipole vector. In a plane, this would be $-\vec{\gamma}(t)$. 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 ±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 Wylie/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 $P_1$ experimentally becomes negative at intermediate times.

### 3.4. Conclusions

(i) The 2D itinerant oscillator model reproduces closely the molecular dynamics of molecules in fluids as stimulated 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