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CYBERNETIC SPECTROSCOPY OF MOLECULAR ROTOTRANSLATION IN THE LIQUID STATE

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SYNOPSIS

We introduce (following Ciccotti et al.) the subject of cybernetic spectroscopy with reference to the computer simulation of rototranslational mixed a.c.f.'s in the molecule-fixed frame of CH_2Cl_2 in the liquid state (E.M.L.G. pilot project). The detailed acquisition of such "signatures" is possible only via numerical methods using fast computers and provides a corroborative challenge both in the fields of experimental spectroscopy and phenomenological theory. Up to nine elements each of the mixed a.c.f. matrices are observable depending on molecular symmetry. The properties of these elements are basically important in the interpretation of molecular diffusion and broad-band spectroscopy of liquids and mesophases.

INTRODUCTION

The effect of molecular rotation on molecular translation and vice-versa is a subject which has eluded both experimentalist and theoretician ever since Debye [1] propounded his theory of rotational diffusion in 1913. There have been many attempts to extend Debye's phenomenological approach to describe the

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rototranslation of real molecules as opposed to the rotation of Debye's spherical entities, but these inevitably end in a morass of supermatrices with too many coefficients to be useful. It is a truism that the outcome of every experiment on liquid phase molecular motion is the observation of rototranslation in a time averaged form, but with no theory the details of rototranslation remain obscure.

Computer simulation [2,3] is therefore important in this area in a new and fundamental sense. In this paper we demonstrate that rototranslation must be investigated in the molecular frame [3a], and not in the laboratory frame, for useful results. Depending on the molecular symmetry there are up to nine observable components of the relevant mixed auto-correlation functions [4] (a.c.f.'s) in the molecule fixed farme which make up a "signature" of rototranslation. We may, of course, construct other signatures using different mixed a.c.f.'s and build up an entirely new subject area of cybernetic spectroscopy. The epistomological importance of this is that these functions are directly observable neither by experimentation nor by phenomenological theory, and accordingly the numerical method stands on its own until other methods are developed to corrborate its indications. These will probably be based on laser spectroscopy on a picosecond time scale [5].

The subject of cybernetic spectroscopy is illustrated here by reference to a molecular dynamics simulation of dichloromethane liquid. The molecule CH_2Cl_2 is C_{2v} in symmetry and out of the nine elements mentioned already only two exist by symmetry in the molecule frame a.c.f. of linear centre of mass momentum ($\underline{p}$) with the resultant molecular angular momentum ($\underline{J}$) at the instant t in time. The mixed laboratory frame a.c.f. $\langle \underline{p}(0).\underline{J}(t)\rangle_{lab.}$ vanishes for all t in an isotropic molecular liquid except in the presence of a magnetic field. This is because the parity of $\underline{p}$ to time reversal is opposite in sign to that of $\underline{J}$. In the molecule-fixed frame two elements of $\langle \underline{p}(0)\underline{J}^T(t)\rangle_{mol.}$, (or $\langle \underline{p}(t)\underline{J}^T(0)\rangle_{mol.}$) exist. These are observable only by computer simulation until present-day experimental methods are refined accordingly. The existence of such functions implies that Debye's theory of 1913 is correct only in a very narrow and rather unuseful sense. Further progress may be aided by computer simulation. The paper is arranged as follows.

In section 1 we provide a brief description of the algorithm and methods used to calculate $\underline{p}$ and $\underline{J}$ in the molecule frame as opposed to the usual laboratory frame. In section 2 we illustrate the cybernetic spectroscopy of rototranslation with mixed a.c.f.'s of more than one type. In a new and original sense, this is the results and interpretation section. The conclusions are outlined for convenience in section 3.

Section 1: Description of Algorithm

We have chosen to base the investigation on one of the most rigorously tested algorithms available. This is developed from the TETRA listing of SERC CCPS originally written by Singer and co-workers [6,7]. Elsewhere [8,9] we have reported its performance against a range of experimental data (such as f.i.-r. bandshapes [3]) in the context of the E.M.L.G. pilot project [10]. This performance is already at a level higher than any available phenomenological theory [2-4,11] (including generalised Langevin equations) and this provides us with a solid basis on which to pursue the more subtle and interesting statistics associated with rototranslation.

The weak point of any molecular dynamics algorithm in absolute measure is the necessity to model the intermolecular potential energy [12]. The results of section 2 are not, however, in any sense critically dependent on the model we take provided that this has the elements of realism (e.g. reflects the known C_{2v} symmetry in some sense). In detail we have used a 5 x 5 atom-atom Lennard-Jones model with point charges at the atomic sites. The Lennard-Jones parameters are as follows: σ (H-H) = 2.75 Å; σ (Cl-Cl) = 3.35 Å; σ (C-C) = 3.20 Å; ε/k(H-H) = 13.4 K; ε/k(Cl-Cl) = 175.0 K; ε/k(C-C) = 51.0 K. These were taken directly from the available literature [7]. The dipole moment of CH_2Cl_2 was reproduced with del Re's point charges [13] of $q_H = 0.131|e|$; $q_c = 0.056|e|$; $q_{Cl} = -0.063|e|$. TETRA was modified to involve a force cut-off criterion [8,9] based on molecule centre of mass distance. In modified TETRA the equations of motion are solved with a third-order predictor routine based on the Verlet algorithm and rotation is integrated using as coordinates the angular momenta components and the three unit vectors along the principal axes of the molecular moment of inertia matrix. Dynamical vectors in this molecular frame of reference may be calculated from the frame transformation relations described below (indices x, y, z refer to the lab. frame and A, B, C to the molecule frame):

$$V_A = V_x e_{Ax} + V_y e_{Ay} + V_z e_{Az} \tag{1}$$

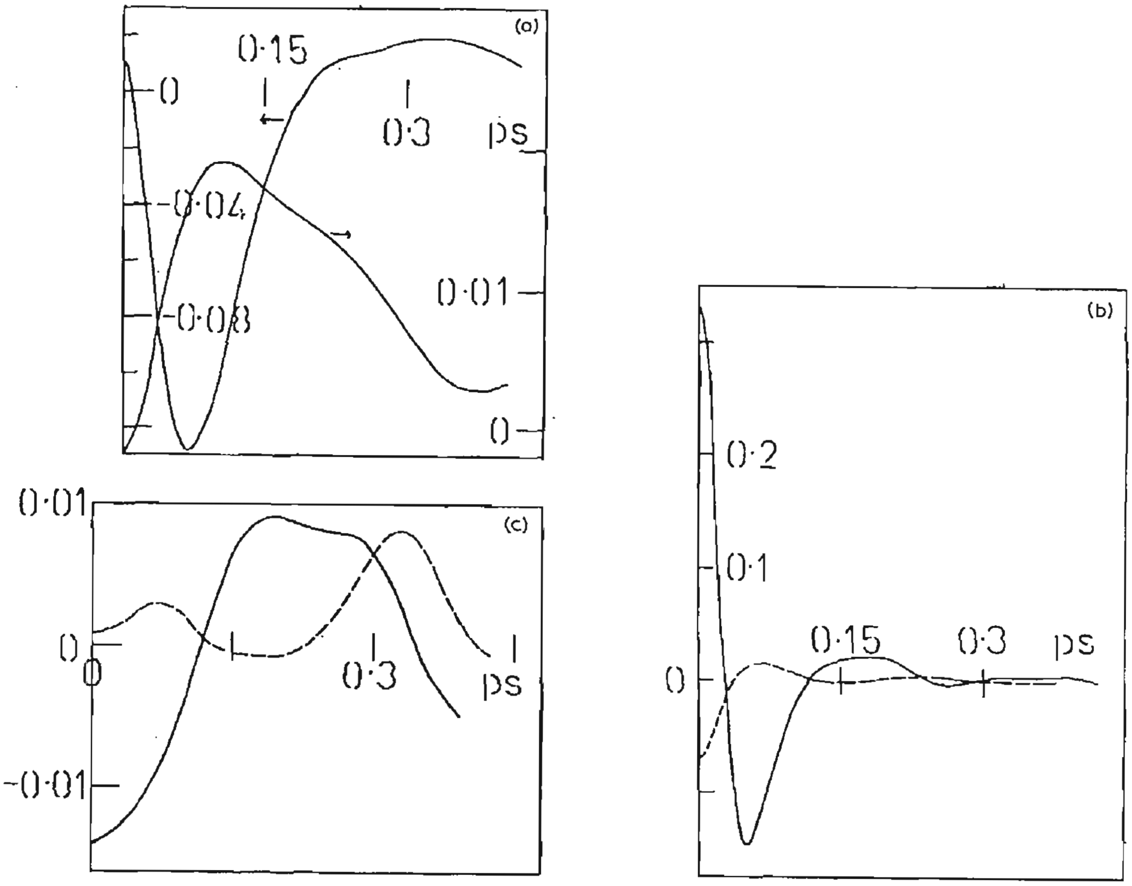
$$V_B = V_x e_{Bx} + V_y e_{By} + V_z e_{Bz} \tag{2}$$

$$V_C = V_x e_{Cx} + V_y e_{Cy} + V_z e_{Cz} \tag{3}$$

Here $\underline{e}_A$, $\underline{e}_B$ and $\underline{e}_C$ are unit vectors along the principal moment of inertia frame defined in fig. (1). Thus e_{Ax} is the x component of $\underline{e}_A$ in the lab. frame etc. In eqns. (1) to (3) $\underline{V}$ is the centre of mass resultant velocity. Thus (V_x, V_y, V_z) are its components in the laboratory frame and (V_A, V_B, V_C) those in the principal molecular moment of inertia frame. The force $(\underline{F})$, torque $(\underline{T}_q)$ and angular momentum $(\underline{J})$ may be transferred similarly to $\underline{V}$ in eqns. (1) to (3). We denote the mixed a.c.f.'s by $\langle\,\rangle_{lab.}$ or $\langle\,\rangle_{mol.}$ as the case may be. Cybernetic spectroscopy may then be defined as the detailed study of either $\langle\,\rangle_{lab.}$ or $\langle\,\rangle_{mol.}$ for vectors such as these.

Section 2: Results and Discussion

The C_{2v} symmetry of CH_2Cl_2 implies that only the $\langle p_1(0)J_2(t)\rangle_{mol.}$ and $\langle p_2(0)J_1(t)\rangle_{mol.}$ elements of $\langle \underline{p}(0)\underline{J}^T(t)\rangle_{mol.}$ exist for $t>0$. In the lab. frame all elements vanish. The same is true for the force-torque mixed a.c.f. $\langle \underline{F}(0)\underline{T}_q^{\,T}(t)\rangle_{mol.}$. Fig. (1) shows that the (2,1) and (1,2) components are not symmetric for either types of a.c.f.



On the other hand the second moment a.c.f.'s $\langle p^2(0)J^2(t)\rangle$ and $\langle F^2(0)T_q{}^2(t)\rangle$ are invariant to frame transformation, (i.e. are the same in the molecule and laboratory frames) and all the components (i,j) exist. These are illustrated in figs. (2) to (3) and provide us with a detailed description of molecular rototranslation.

These results may now be used to suggest how phenomenological theory ought to be extended to involve rototranslation. In the <u>simplest</u> case the basic Langevin and Fokker/Planck equations [2-4,11] should be written in the molecule frame as follows [14]:

$$\dot{\omega}_i = (I_i - I_k)\omega_j\omega_k/I_i - \sum_{\ell=1}^{3} (\gamma_{i\ell}^{(r)}\omega_\ell + \gamma_{i\ell}^{(rt)}V_\ell) + T_i(t)$$

$$\dot{V}_i = V_j\omega_k - \omega_j V_k - \sum_{\ell=1}^{3} (\gamma_{i\ell}^{(t)}V_\ell + \gamma_i^{(tr)}\omega_\ell) + F_i(t) \qquad (4)$$

<u>Figure (1) (a)</u>

The non-vanishing elements of the molecule frame correlation matrix

$$< \underline{p}(0)\underline{J}^T(t) >_{mol}.$$

Left hand scale: $$\frac{[< p_1(o)J_2(t) > + < p_1(t)J_2(o) >]\ \mathrm{mol.}}{2 < p_1{}^2 >^{\frac{1}{2}} < J_2{}^2 >^{\frac{1}{2}}}$$

Right hand scale: $$\frac{[< p_2(o)J_1(t) > + < p_2(t)J_1(o) >]\ \mathrm{mol.}}{2 < p_2{}^2 >^{\frac{1}{2}} < J_1{}^2 >^{\frac{1}{2}}}$$

<u>Figure (1) (b)</u>

—— (1,2) element of the molecule frame force/torque mixed a.c.f., normalised as in fig. (1) (a).

- - - (2,1) element.

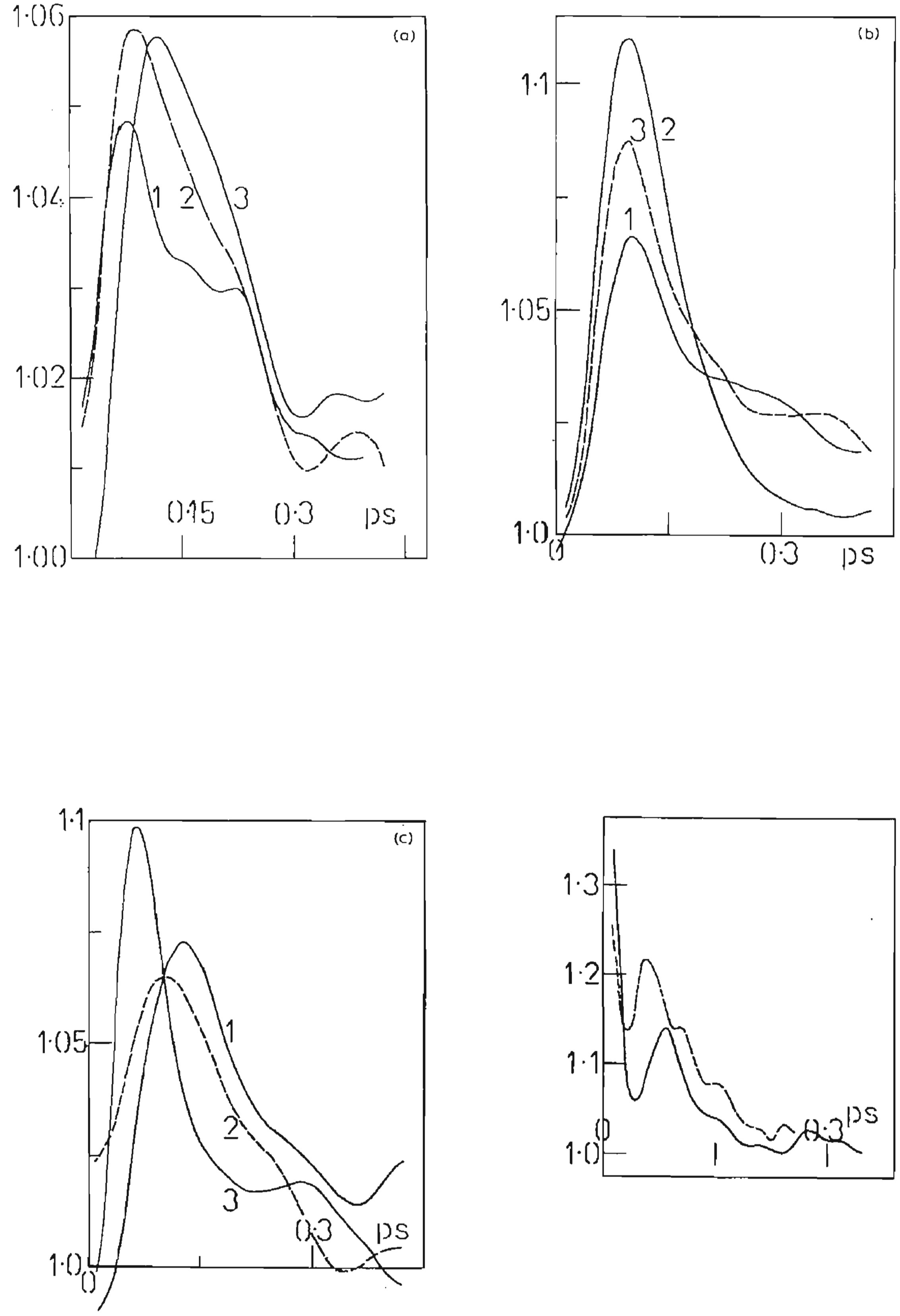
<u>Figure (1) (c)</u>

Illustration of the noise level in fig. (1) (a) and fig. (1) (b).

—— (3,2) element of the linear/angular momentum correlation matrix.

- - -(2,2) element.

Both of these a.c.f.'s should vanish by symmetry.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$$\frac{\partial P}{\partial t} = \sum_{i=1}^{3} - \frac{\partial}{\partial \omega_i} \frac{I_i - I_k}{I_i} \omega_j \omega_k P + \sum_{i=1}^{3} - \frac{\partial}{\partial V_i} (V_j \omega_k - V_k \omega_j) P$$

$$+ \sum_{\ell=1}^{3} \left[\frac{\partial}{\partial \omega_i} \left(\gamma_{i\ell}^{(r)} \omega_\ell + \gamma_{i\ell}^{(rt)} V_\ell \right) + \frac{\partial}{\partial V_i} \left(\gamma_{i\ell}^{(t)} V_\ell + \gamma_{i\ell}^{(tr)} \omega_\ell \right) \right] P$$

$$+ \sum_{\ell=1}^{3} \left[\frac{\partial}{\partial \omega_i} \gamma_{i\ell}^{(r)} \frac{kT}{I_i} \frac{\partial}{\partial \omega_\ell} + \frac{1}{2} \left(\gamma_{i\ell}^{(tr)} \frac{kT}{I_i} + \gamma_{i\ell}^{(rt)} \frac{kT}{m} \right) \frac{\partial}{\partial V_\ell} \right] P \qquad (5)$$

Eqn. (4) is the Langevin equation (written in the molecule fixed frame) for the rototranslation of asymmetric top molecules, and eqn. (5) is the equivalent Fokker-Planck equation. In both equations the subscripts i, j and k are taken in cyclic permutation. I_i, I_k and I_j are the principal moments of inertia, $\omega_{i,j,k}$ and $v_{i,j,k}$ are the angular and linear velocity components in the molecule frame, T_i and F_i are random torques and forces respectively, P is the joint conditional probability density function on the space spanned by $v_{i.j.k}$ and $\omega_{i.j.k}$, and γ are components of the rototranslational friction matrix. m is the molecular mass. We propose these equations as the least complicated ones needed to cope with the new indications of cybernetic spectroscopy. We have not yet involved memory or multiparticle effects in eqns. (4) and (5), but these are known to be important, for example in the far infra-red [11]. Numerical solution of eqns. (4) and (5) will lead to non-vanishing mixed autocorrelation functions, but these will not necessarily reproduce the features of figs. (1) to (5), for example, at

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Figure (2)

Second moment mixed a.c.f.'s of linear/angular momentum. These are invariant to frame transformation.

(a) (1) $[\langle p_3^2(o) J_2^2(t)\rangle + \langle p_3^2(t) J_2^2(o)\rangle] / [2 \langle p_3^2\rangle \langle J_2^2\rangle]$

(2) (2,2) element.

(3) (2,3) element.

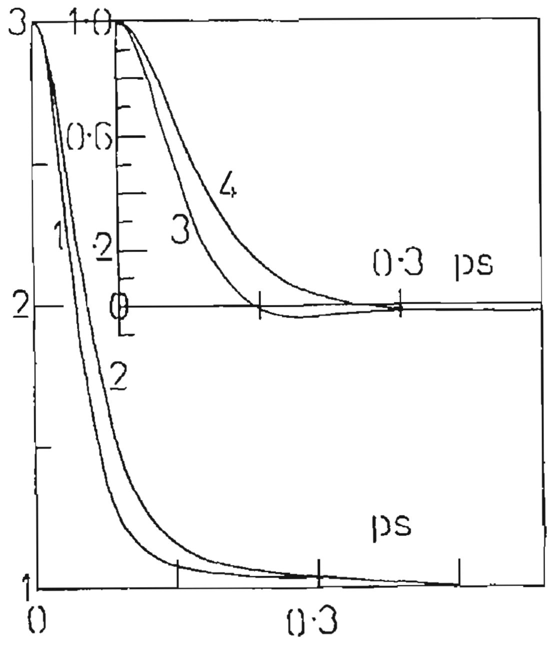
(b) (1) (2,1) element; (2) (1,3) element; (3) (3,1) element.

(c) (1) (1,1) element; (2) (3,3) element; (3) (1,2) element.

Figure (3)

Two elements of the mixed force/torque molecule frame a.c.f. matrix.

—— (1,1) element; – – – – (2,2) element.



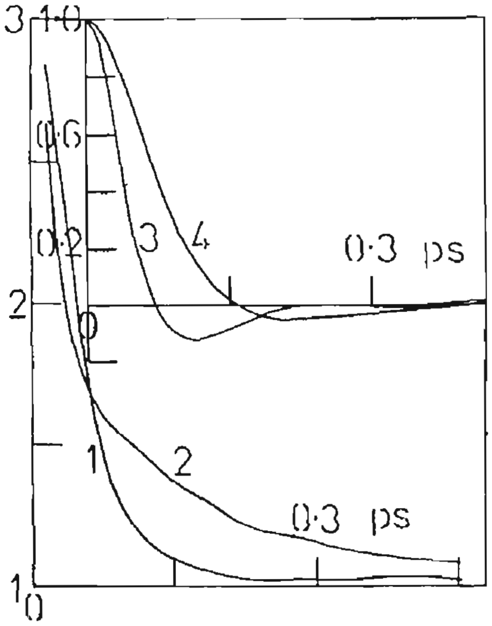


Figure (4)

Illustration of a.c.f.'s of linear, centre of mass, velocity in the molecule fixed frame.

(1) $[<V_1^2(t)V_1^2(o)> + <V_1^2(o)V_1^2(t)>] / [2<V_1^2>^2]$

(2) (2,2) element.

(3) $[<V_1(t)V_1(o)> + <V_1(o)V_1(t)>] / [2 <V_1^2>]$

(4) (2,2) element.

Figure (5)

As for fig. (4), angular momentum.

all accurately. We need hardly point out that eqns. (4) and (5) have no known analytical solution. All this merely underlines the fact that the phenomenological theory is not immediately useful when carried through to a stage further than that of Debye and his contemporaries [15]. In a purely mathematical sense, however, eqns. (4) and (5) seem to have many interesting properties.

Equations such as (4) and (5) should be used as a basis for the interpretation of incoherent neutron scattering spectroscopy [16], where rototranslation effects are very indirectly "detectible". However to classify mixed a.c.f.'s according to symmetry the molecular dynamics simulation is far more direct and informative. Such rototranslation effects are likely to become increasingly interesting when we start dealing with elongated molecules and liquid crystal mesophases. The techniques of picosecond-pulsed laser dephasing spectroscopy might possibly be useful for the indirect (lab. frame) study of rototranslation but it would be difficult to obtain information directly in the molecule frame without computer simulation. It is always the case however, that molecule frame effects carry through into the lab. frame and broad-band spectra of liquids are in a strict sense uninterpretable without molecular dynamics simulation as a guide. For this reason it is important to put every effort into improving our knowledge of the intermolecular pair potential [12] and into refining the molecular dynamics algorithms themselves [6].

In the fields of collision-induced spectroscopy [3,11] the translational induction of transient dipole moments (e.g. in pressurised rare-gas mixtures) is a well-known phenomenon, but interpretation is restricted to two or three molecule collisions. Induction and polarisation effects are non pair-additive, however, and computer simulation is not yet refined enough to cope with, for example, far infra-red collision-induced spectra such as observed in carbon tetrachloride liquid.

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