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THE STATISTICAL CORRELATION OF INTERMOLECULAR CORIOLIS AND CENTRIFUGAL FORCES

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ABSTRACT

Correlation functions are computed in the laboratory frame for the molecular coriolis and centrifugal forces with respect to a frame of reference static in the laboratory. The molecular Coriolis and centrifugal forces in this laboratory frame result from a combination of the molecule's rotational and translational motion, and correlate statistically these two types of motion. They are not usually considered in the theory of decoupled rotational or translational diffusion. Correlation functions are computed for the enantiomers and racemic mixture of liquid bromochlorofluoromethane, and for dichloromethane liquid subjected to a strong, uniaxial, electric field of force in the z axis of the laboratory frame.

INTRODUCTION

This paper describes a computer simulation of correlation functions of inter-molecular Coriolis and centrifugal forces in the laboratory frame of reference. The Coriolis force [1,2] is proportional to $\mathbf{v}(t) \times \boldsymbol{\omega}(t)$, where $\mathbf{v}(t)$ is the molecular centre of mass velocity and $\boldsymbol{\omega}$ the angular velocity of the same molecule. Therefore it is a natural measure of the statistically interdependent nature of molecular rotation and translation. The time-correlation function of the Coriolis force is:

$$C_{\mathrm{Cor}}(t) = \langle \mathbf{v}(t) \times \boldsymbol{\omega}(t) \cdot \mathbf{v}(o) \times \boldsymbol{\omega}(o) \rangle$$

and also exists in the laboratory frame of reference for all molecular symmetries. C_{Cor} is therefore a natural method of expressing, directly in the laboratory frame, the statistical correlation between molecular rotation and translation, because it correlates in this frame a real force, the molecular Coriolis force at t = 0 and a time t later. Coriolis forces have a

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real effect on measurable spectra, and this is well known in the quantum theory of vibration-rotation coupling. In this case they arise from the quantised vibrational movement of atoms in a molecule superimposed on the quantised rotational movement of the complete molecule. However, there are also classical intermolecular Coriolis forces of the type $\underset{\sim}{v} \times \underset{\sim}{\omega}$, due to the resultant centre of mass translation of the complete molecule superimposed on its own rotation, and these do not seem to have been treated in anything like as much detail in the context of molecular diffusion. It is difficult to treat these forces quantum mechanically because they involve the centre of mass translation of the whole molecule. Their computation in this paper is therefore restricted to classical mechanics, using computer simulation to solve the classical equations of motion for an assembly of 108 molecules.

The paper is arranged as follows.

Section 1 is a discussion of the nature of the Coriolis and centrifugal forces in the context of molecular rotation and translation. The correlation function $C_{\mathrm{Cor}}(t)$ is analysed in terms of its component correlation functions. In this context the treatment is extended to the statistical time-correlation function of molecular centrifugal forces in the laboratory frame of reference.

Section 2 is a discussion of the algorithms used and the conditions under which the computer simulations were pursued.

Section 3 is a discussion of some results, in terms of the time-correlation functions and their spectra. Results are provided for the (R) enantiomer and racemic mixture of bromochlorofluoromethane and for liquid dichloromethane subjected to an intense z-axis electric field, which removes the isotropy of the molecular ensemble with respect to parity inversion in the laboratory frame of reference. [3] The statistical cross-correlation between molecular rotation and translation is not usually considered in the theory of linear response and the Onsager reciprocal relations. It is pointed out, de facto, that the theory of 'rotational' diffusion does not describe the molecular Coriolis and centrifugal forces correlated statistically in this paper.

Section 1: The Origin of the Molecular Coriolis Force, $2m\underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t)$ and Centrifugal Force $m\underset{\sim}{\omega}(t) \times (\underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t))$.

Consider an inertial frame of reference defined by the frame of the three principal molecular moments of inertia. A laboratory frame of reference then rotates and translates with respect to this molecule-fixed frame, and is therefore a non-inertial frame of reference, with respect to the molecule-fixed frame. It follows that Newton's equation of motion for the molecule in this non-inertial frame, the laboratory frame, is: [4]

$$m\frac{d\underset{\sim}{v}}{dt} = -\frac{\partial U}{\partial \underset{\sim}{r}} + 2m\underset{\sim}{v} \times \underset{\sim}{\omega} + m\underset{\sim}{\omega} \times (\underset{\sim}{r} \times \underset{\sim}{\omega}) - m\underset{\sim}{W} + m\underset{\sim}{r} \times \dot{\underset{\sim}{\omega}} \qquad (2)$$

where $\underset{\sim}{W}$ is the translational acceleration of the one frame with respect to the other; the energy U is defined by the Lagrangian:

$$L_o = \frac{1}{2} mv_o^{\,2} - U \qquad (3)$$

expressed in the original inertial molecule fixed frame; m is the molecular mass, $\underset{\sim}{v}$ is the molecular centre of mass velocity in the laboratory frame, $\underset{\sim}{\omega}$ is the angular velocity of the one frame with respect to the other, and according to the definition adapted above for the molecule fixed frame, is also the molecular angular velocity in the laboratory frame; and $\underset{\sim}{r}$ is the position vector of the molecular centre of mass with respect to the origin of the laboratory frame. In eqn. 3 $\underset{\sim}{v}$ is the centre of mass linear velocity defined with respect to the original inertial frame of reference, i.e. the molecule fixed frame, and L_o is the Lagrangian in this same frame.

Note that theories of decoupled translational diffusion simply write eqn (2) in the laboratory frame as the equivalent of :

$$m\frac{d\underset{\sim}{v}}{dt} = \underset{\sim}{F} \qquad (4)$$

with no account taken of the terms involving molecular angular velocity, $\underset{\sim}{\omega}$ in the laboratory frame.

The molecular Coriolis force in the laboratory frame of reference is an example of a real force neglected in theories both of decoupled rotation and of decoupled translational diffusion [5]. It is the term $2m\underset{\sim}{v} \times \underset{\sim}{\omega}$ in eqn (2). In so far as the theory of rotational diffusion does not involve the vector $\underset{\sim}{v}$, this theory neglects the real force defined by $m\underset{\sim}{\omega} \times (\underset{\sim}{r} \times \underset{\sim}{\omega})$, which is the molecular centrifugal force in the laboratory frame of reference. This is also absent in theories of translational diffusion which do not involve $\underset{\sim}{\omega}$. In this paper, we use the technique of "molecular dynamics" computer simulation to construct laboratory frame time-correlation functions of each force. It follows that these c.f.'s measure the natural statistical correlation between molecular rotation and centre of mass translation and position in the laboratory frame of reference. The Fourier transforms of these c.f.'s are spectra, and molecular Coriolis and centrifugal forces therefore have an effect on far infrared and dielectric spectra [7] and indeed on all the spectra dependent on molecular diffusion. Conversely, these spectra all contain information on the natural statistical correlation in the lab frame, between molecular rotation and centre of mass translation. The theory of decoupled rotational (or translational) diffusion is therefore an incomplete description of these spectra.

Component Correlation Functions of the Coriolis and Centrifugal Forces

1) The vector identify

$$(\underset{\sim}{A} \times \underset{\sim}{B}) \cdot (\underset{\sim}{C} \times \underset{\sim}{D}) = (\underset{\sim}{A}.\underset{\sim}{C})(\underset{\sim}{B}.\underset{\sim}{D}) - (\underset{\sim}{A}.\underset{\sim}{D})(\underset{\sim}{B}.\underset{\sim}{C}) \tag{5}$$

immediately provides the result:

$$\begin{aligned}&<(\underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t)) \cdot (\underset{\sim}{v}(o) \times \underset{\sim}{\omega}(o))> \\ &\quad = <(\underset{\sim}{v}(t).\underset{\sim}{v}(o))(\underset{\sim}{\omega}(t) \cdot \underset{\sim}{\omega}(o))> - <(\underset{\sim}{v}(t) \cdot \underset{\sim}{\omega}(o))(\underset{\sim}{\omega}(t) \cdot \underset{\sim}{v}(o))>\end{aligned} \tag{6}$$

The Coriolis force $2m(\underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t))$ exists in the laboratory frame, and therefore by eqn (6)

$$<(\underset{\sim}{v}(t).\underset{\sim}{v}(o))(\underset{\sim}{\omega}(t).\underset{\sim}{\omega}(o))> \neq <(\underset{\sim}{v}(t).\underset{\sim}{\omega}(o))(\underset{\sim}{\omega}(t).\underset{\sim}{v}(o))> \tag{7}$$

and all three types of natural mixed rotation/translation correlation functions therefore exist in the laboratory frame and have a different time dependence in this frame. At $t = 0$, the inequality in eqn (7) becomes clearer, i.e.:

$$<(v_x\omega_x + v_y\omega_y + v_z\omega_z)^2> \neq <(v_x^2 + v_y^2 + v_z^2)(\omega_x^2 + \omega_y^2 + \omega_z^2)> \quad . \tag{8}$$

The time correlations in eqn (6) are, therefore natural measures of rotation-translation coupling in the laboratory frame of reference.

2) the time-correlation of the molecular centrifugal force in the laboratory frame is:

$$C_{\text{cent.}} = \langle \boldsymbol{\omega}(t) \times (\boldsymbol{\omega}(t) \times \boldsymbol{r}(t)) \cdot \boldsymbol{\omega}(o) \times (\boldsymbol{\omega}(o) \times \boldsymbol{r}(o))\rangle \tag{9}$$

This is the natural way of expressing the correlation between the laboratory frame molecular angular velocity, $\boldsymbol{\omega}$, and the position of the centre of mass of the same molecule in the laboratory frame, expressed by the vector $\boldsymbol{r}$, linking this point in the 3-D space of the laboratory frame to the origin of this frame. In order to analyse the time-correlation function (a), the following two vector identities are useful:

$$\begin{aligned} \boldsymbol{A} \times (\boldsymbol{B} \times \boldsymbol{C}) = {} & (A_2B_1C_2 - A_2B_2C_1 - A_3B_3C_1 + A_3B_1C_3)\boldsymbol{i} \\ & + (A_3B_2C_3 - A_3B_3C_2 - A_1B_1C_2 + A_1B_2C_1)\boldsymbol{j} \\ & + (A_1B_3C_1 - A_1B_1C_3 - A_2B_2C_3 + A_2B_3C_2)\boldsymbol{k} \end{aligned} \tag{10}$$

$$\begin{aligned} & \boldsymbol{A} \times (\boldsymbol{A} \times \boldsymbol{B}) \cdot \boldsymbol{C} \times (\boldsymbol{C} \times \boldsymbol{D}) \\ & \quad = (\boldsymbol{A} \cdot \boldsymbol{C})(\boldsymbol{A} \cdot \boldsymbol{B})(\boldsymbol{C} \cdot \boldsymbol{D}) - (\boldsymbol{B} \cdot \boldsymbol{C})(\boldsymbol{A} \cdot \boldsymbol{A})\ (\boldsymbol{C} \cdot \boldsymbol{D}) \\ & \quad - (\boldsymbol{A} \cdot \boldsymbol{D})(\boldsymbol{A} \cdot \boldsymbol{B})(\boldsymbol{C} \cdot \boldsymbol{C}) + (\boldsymbol{B} \cdot \boldsymbol{D})(\boldsymbol{A} \cdot \boldsymbol{A})(\boldsymbol{C} \cdot \boldsymbol{C}) \end{aligned} \tag{11}$$

Using eqn (11) gives

$$\begin{aligned} C_{\text{cent}} = {} & \langle(\boldsymbol{\omega}(t).\boldsymbol{\omega}(o))(\boldsymbol{\omega}(t).r(t))(\boldsymbol{\omega}(o).\boldsymbol{r}(o))\rangle \\ & - \langle(\boldsymbol{r}(t).\boldsymbol{\omega}(o))(\boldsymbol{\omega}(t).\boldsymbol{\omega}(t))(\boldsymbol{\omega}(o).\boldsymbol{r}(o))\rangle \\ & - \langle(\boldsymbol{\omega}(t).\boldsymbol{r}(o))(\boldsymbol{\omega}(t).\boldsymbol{r}(t))(\boldsymbol{\omega}(o).\boldsymbol{\omega}(o))\rangle \\ & + \langle(\boldsymbol{r}(t).\boldsymbol{r}(o))(\boldsymbol{\omega}(t).\boldsymbol{\omega}(t))(\boldsymbol{\omega}(o).\boldsymbol{\omega}(o)\rangle \end{aligned} \tag{12}$$

which therefore exist in the laboratory frame.

It is interesting to point out that the force proportional to $\boldsymbol{\omega} \times \dot{\boldsymbol{\mu}}$, where $\dot{\boldsymbol{\mu}}$ is the time derivative of the molecular dipole moment [7], is <u>both</u> a Coriolis <u>and</u> a centrifugal force. This follows immediately from the kinematic relation:

$$\dot{\boldsymbol{\mu}} = \boldsymbol{\omega} \times \boldsymbol{\mu} \tag{13}$$

In this context the vector $\dot{\boldsymbol{\mu}}$, whose time-correlation function in the laboratory frame is the Fourier transform of the far infra-red power absorption coefficient, can always be written as:

$$\dot{\boldsymbol{\mu}}(t) = \dot{\boldsymbol{r}}_x(t) - \dot{\boldsymbol{r}}_y(t) \tag{14}$$

where $\boldsymbol{r}_x$ and $\boldsymbol{r}_y$ are the position vectors in the laboratory frame. The rotational velocity described by the molecular vector $\boldsymbol{\mu}(t)$ is therefore the difference of two translational velocities at the same instant t. It follows that the Coriolis force $\boldsymbol{\omega}(t) \times \dot{\boldsymbol{\mu}}(t)$ exists in the laboratory frame, and that is also a centrifugal force, as mentioned already, because, evidently:

$$\boldsymbol{\mu}(t) = \boldsymbol{r}_x(t) - \boldsymbol{r}_y(t) \tag{15}$$

The equality:

$$\boldsymbol{\mu} \times \dot{\boldsymbol{\mu}} = \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \boldsymbol{\mu}) \tag{16}$$

provides the following relations between laboratory frame correlation functions involving the vectors $\boldsymbol{\omega}, \dot{\boldsymbol{\mu}}$ and $\boldsymbol{\mu}$ which, again, do not seem to have been considered in the literature on the theory of molecular diffusion:

$$\begin{aligned}
&<(\boldsymbol{\omega}(t) \times \dot{\boldsymbol{\mu}}(t)) \cdot (\boldsymbol{\omega}(o) \times \dot{\boldsymbol{\mu}}(o)) \\
&\qquad = <(\boldsymbol{\omega}(t) \times (\boldsymbol{\omega}(t) \times \boldsymbol{\mu}(t))) \cdot (\boldsymbol{\omega}(o) \times (\boldsymbol{\omega}(o) \times \boldsymbol{\mu}(o)))> \\
&\qquad = <(\dot{\boldsymbol{\mu}}(t) \cdot \dot{\boldsymbol{\mu}}(o))(\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(o))> \\
&\qquad - <(\boldsymbol{\omega}(t) \cdot \dot{\boldsymbol{\mu}}(o))(\dot{\boldsymbol{\mu}}(t) \cdot \boldsymbol{\omega}(o))> \\
&\qquad = <(\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(o))(\boldsymbol{\omega}(t) \cdot \boldsymbol{\mu}(t))(\boldsymbol{\omega}(o) \cdot \boldsymbol{\mu}(o))> \\
&\qquad - <(\boldsymbol{\mu}(t) \cdot \boldsymbol{\omega}(o))(\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(t))(\boldsymbol{\omega}(o) \cdot \boldsymbol{\mu}(o))> \\
&\qquad - <(\boldsymbol{\omega}(t) \cdot \boldsymbol{\mu}(o))(\boldsymbol{\omega}(t) \cdot \boldsymbol{\mu}(t))(\boldsymbol{\omega}(o) \cdot \boldsymbol{\omega}(o))> \\
&\qquad + <(\boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(o))(\boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(t))(\boldsymbol{\omega}(o) \cdot \boldsymbol{\omega}(o))>
\end{aligned} \tag{17}$$

The existence of all these correlation functions is a natural consequence of the fact that a molecule must rotate and translate in the laboratory frame.

If this rotational motion is non-uniform, i.e. if intermolecular torques are present, then we must also take into account the term $m\underset{\sim}{r}(t) \times \dot{\underset{\sim}{\omega}}(t)$ in eqn (2). This means that the following relation between *time correlation functions of this force exists naturally in the* laboratory frame:

$$\begin{aligned} &\langle \underset{\sim}{r}(t) \times \dot{\underset{\sim}{\omega}}(t) \,.\, \underset{\sim}{r}(o) \times \dot{\underset{\sim}{\omega}}(o) \rangle \\ &= \langle \underset{\sim}{r}(t) \,.\, \underset{\sim}{r}(o)\, \dot{\underset{\sim}{\omega}}(t) \,.\, \dot{\underset{\sim}{\omega}}(o) \rangle \\ &- \langle \underset{\sim}{r}(t) \,.\, \dot{\underset{\sim}{\omega}}(o)\, \dot{\underset{\sim}{\omega}}(t) \,.\, \underset{\sim}{r}(o) \rangle \end{aligned} \qquad (18)$$

It becomes clear now that eqns (6) to (17) are valid for a translating and uniformly rotating molecule, and eqn (18) for a translating and non-uniformly rotating molecule in the laboratory frame. This leads us to the conclusion that there are correlations of this type, involving the vectors $\underset{\sim}{v}$ and $\underset{\sim}{\omega}$, in dilute gases, as well as liquids and solids. Furthermore, correlations of the type (18) disappear only in the abstract case of the infinitely dilute gas where the intermolecular torque is infinitely small.

These correlations are therefore present in all spectra as a natural outcome of rotation and translation.

Eqn (15) implies the natural existence in the laboratory frame of the correlation functions:

$$\begin{aligned} &\langle \underset{\sim}{\mu}(t) \times \dot{\underset{\sim}{\omega}}(t) \,.\, \underset{\sim}{\mu}(o) \times \dot{\underset{\sim}{\omega}}(o) \rangle \\ &= \langle \underset{\sim}{\mu}(t) \,.\, \underset{\sim}{\mu}(o)\, \dot{\underset{\sim}{\omega}}(t) \,.\, \dot{\underset{\sim}{\omega}}(o) \rangle \\ &- \langle \underset{\sim}{\mu}(t) \,.\, \dot{\underset{\sim}{\omega}}(o)\, \dot{\underset{\sim}{\omega}}(t) \,.\, \underset{\sim}{\mu}(o) \rangle \end{aligned} \qquad (19)$$

Furthermore, we have the kinematic relation (by differentiation of eqn 13).

$$\dot{\underset{\sim}{\omega}} \times \underset{\sim}{\mu} = \ddot{\underset{\sim}{\mu}} - \underset{\sim}{\omega} \times \dot{\underset{\sim}{\mu}} \qquad (20)$$

Eqn (20) leads directly to the following result, important from an experimental point of view:

$$\begin{aligned}<\ddot{\underset{\sim}{\mu}}(t)\ .\ \ddot{\underset{\sim}{\mu}}(o)> = {} & <\dot{\underset{\sim}{\omega}}(t) \times \underset{\sim}{\mu}(t)\ .\ \dot{\underset{\sim}{\omega}}(o) \times \underset{\sim}{\mu}(o)> \\ & + <\underset{\sim}{\omega}(t) \times \dot{\underset{\sim}{\mu}}(t)\ .\ \underset{\sim}{\omega}(o) \times \dot{\underset{\sim}{\mu}}(o)> \\ & + <\dot{\underset{\sim}{\omega}}(t) \times \underset{\sim}{\mu}(t)\ .\ \underset{\sim}{\omega}(o) \times \dot{\underset{\sim}{\mu}}(o)> \\ & + <\underset{\sim}{\omega}(t) \times \dot{\underset{\sim}{\mu}}(t)\ .\ \dot{\underset{\sim}{\omega}}(o) \times \underset{\sim}{\mu}(o)> \end{aligned} \qquad (21)$$

A we--known theorem on spectral moments [7] provides the result:

$$\mathcal{L}<\ddot{\mu}(t)\ .\ \ddot{\mu}(o)> \propto \omega^2\alpha(\omega) \qquad (22)$$

where $\mathcal{L}$ stands for Fourier transform and $\alpha(\omega)$ is the far infrared power absorption coefficient. The higher spectral moment $\omega^2\alpha(\omega)$ is directly observable in favourable cases by careful interferometric spectroscopy, and eqn 21 therefore shows that its time Fourier transform is a combination of correlations between forces such as $\dot{\underset{\sim}{\omega}}(t) \times \underset{\sim}{\mu}(t)$, dependent on the non-uniformity of the relation of the molecule-fixed frame with respect to the laboratory frame (or vice-versa) and terms such as $\underset{\sim}{\omega}(t) \times \dot{\underset{\sim}{\mu}}(t)$, which, as we have seen, are both Coriolis and centrifugal in nature.

For uniform rotation ($\dot{\underset{\sim}{\omega}} = \underset{\sim}{o}$) eqn 21 reduces to:

$$<\ddot{\underset{\sim}{\mu}}(t)\ .\ \ddot{\underset{\sim}{\mu}}(o)>_{\dot{\underset{\sim}{\omega}}=\underset{\sim}{o}} \ = \ <\underset{\sim}{\omega}(t) \times \dot{\underset{\sim}{\mu}}(t)\ .\ \underset{\sim}{\omega}(o) \times \dot{\underset{\sim}{\mu}}(o)>$$

Therefore, for uniform rotation the Fourier transform of the second moment $\omega^2\alpha(\omega)$ is the time correlation function of the Coriolis force $\underset{\sim}{\omega}(t) \times \dot{\underset{\sim}{\mu}}(t)$.

Note that this result is also true in the so-called [8] 'inertial approximation' in the theory of molecular diffusion, where angular accelerations are ignored, but paradoxically in this case $\omega^2\alpha(\omega)$ (and indeed $\alpha(\omega)$) has no Fourier transform because the area beneath $\alpha(\omega)$ is the so-called limit of the 'Debye plateau', is infinite. (The meaning of $\dot{\underset{\sim}{\mu}}(t)$ in the 'inertial approximation' is obscure).

Eqn 23 would be valid for an ensemble of 'free rotors'.

The Spectral Observations of Direct Coriolis Forces

By 'direct' Coriolis forces, we mean terms of the type $\mathbf{v} \times \boldsymbol{\omega}$ dependent on the centre of mass linear velocity $\mathbf{v}$ of a molecule in the laboratory frame. In this respect, terms such as $\dot{\boldsymbol{\mu}} \times \boldsymbol{\omega}$, etc, involving a vector (the dipole moment vector for example) fixed in the molecule are indirect Coriolis forces).

It is impossible to construct a theory for direct Coriolis forces in a diffusing molecule without taking into account explicitly both rotational and translational diffusion [9-19]. However, it is possible to treat forces such as $\dot{\boldsymbol{\mu}} \times \boldsymbol{\omega}$ in a purely 'rotational' context, although no satisfactory treatment exists at present apart from the subject of this paper, computer simulation.

It is possible to observe direct Coriolis forces of the type $\mathbf{v} \times \boldsymbol{\omega}$ in at least two ways.

1) In Anisotropic Materials

The application of an electric field ($\mathbf{E}$) to a non-polarizable dipolar molecular liquid imparts the extra laboratory frame torque $-\boldsymbol{\mu} \times \mathbf{E}$ to each molecule [20] . If $\mathbf{E}$ is uniform and uniaxial the liquid becomes anisotropic in the laboratory frame, and its refractive index in the axis of $\mathbf{E}$ (eg, the z axis of the laboratory frame) differs from that in the x axis. This is the well-known Kerr effect [21]. Similarly, birefringence can be induced by a magnetic field (the Faraday effect) and an electromagnetic field.

Note in this context that birefringence of this type occurs across the whole range of frequencies from static to the visible through the infrared. It therefore follows from the Kramers-Kronig relations that the power absorption coefficient $\alpha(\omega)$ must also be different in the z and x axes in the presence of $\mathbf{E}$.

It has been shown recently [3] (by computer simulation) that two elements of the matrix $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(o)\rangle$ exist in the laboratory frame in a birefringent liquid subjected to a uniform electric field $\mathbf{E}$ in the laboratory frame z axis. There are the (x,y) and (y,x) elements, one being the other's exact mirror image, i.e.

$$<v_x(t)\omega_y(o) \quad = - \quad <v_y(t)\omega_x(o)> \qquad (24)$$

It follows from eqn 24 that the 'time-offset' direct Coriolis force $\mathbf{v}(t) \times \boldsymbol{\omega}(o)$ does not average to zero in the laboratory frame in the presence of E_z.
In other words:

$$<\mathbf{v}(t) \times \boldsymbol{\omega}(o)> \;\neq\; \mathbf{o} \qquad (E_z \neq o)$$

$$= 2\mathbf{k} \;< v_x(t)\omega_y(o)> \qquad (25)$$

$$(= \mathbf{k}[<(v_x(t)\omega_y(o)> - <v_y(t)\omega_x(o)>])$$

In eqn. 25 $\mathbf{k}$ is a unit vector in the z axis; of the laboratory frame and <> denote the usual ensemble averaging used to construct a correlation function (equivalent in a statistically stationary sample to running-time averaging [5]).

The presence of the vector $\mathbf{k}$ on the r.h.s. of eqn 25 implies that the existence of the correlation function $<\mathbf{v}(t) \times \boldsymbol{\omega}(o)>$ in the laboratory frame is always, dependent on <u>anisotropy</u>. A diffusional theory for $<v_x(t)\omega_y(o)>$ can be developed from the generalised Langevin equation governing the complete column vector $\begin{matrix}\mathbf{v}(t)\\ \boldsymbol{\omega}(t)\end{matrix}$ and is described elsewhere [21]. This theory shows that the 'time-offset' Coriolis force correlation $<v_x(t)\omega_y(o)>$ is observable approximately from the correlation of the far infra-red power absorption coefficient $\alpha(\omega)$ perpendicular and parallel to E_z.

Note that $<\mathbf{v}(t) \times \boldsymbol{\omega}(t) \;= \mathbf{0}$ for all t and $\mathbf{E}$, so that computer simulation seems to be the only means at present of calculating correlations between the natural direct Coriolis force proportional to $\mathbf{v}(t) \times \boldsymbol{\omega}(t)$. Results of this type are given for the first time in this paper.

2) <u>Far Infra-red Collision Induced Absorption [23]</u>

Collision induced absorption is dependent on the molecular polarisability and <u>intramolecular separation</u>. The induced dipole moment is therefore directly dependent on centrifugal terms such as $\boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}_{ij})$, where $\mathbf{r}_{ij}$ is the inter-centre of mass distance. If the relative velocity of two molecules in the laboratory frame is $\mathbf{v}_{ij}$, then the Coriolis forces $\mathbf{v}_{ij} \times \boldsymbol{\omega}$ also play a part in the dynamics of the induction process. The translation part of the far infra-red spectrum of simple linear molecules such as N_2 and CO_2 has been identified [23] as the low frequency component of a broad infra-red band.

Section 2: Computer Simulation Method

The Chiral Bromochlorofluoromethanes

Standard constant volume molecular dynamics computer simulation methods [6] were employed for 108 molecules of the R enantiomer of CHBrClF and for the racemic mixture of 54 R and S molecules. The input temperature and molar volume were, respectively, 296 K and 1.2×10^{26} A^3. Atom-atom Lennard-Jones parameters were used as follows:

$\sigma(\mathrm{Br{-}Br}) = 3.9$ Å; $\sigma(\mathrm{Cl{-}Cl}) = 3.6$ Å; $\sigma(\mathrm{F{-}F}) = 2.7$ Å; $\sigma(\mathrm{H{-}H}) = 2.8$ Å;

$\sigma(\mathrm{C{-}C}) = 3.4$ Å; $\varepsilon/k(\mathrm{Br{-}Br}) = 218.0$K; ε/k $(\mathrm{Cl{-}Cl}) = 158.0$ K;

$\varepsilon/k(\mathrm{F{-}F}) = 54.9$K; $\varepsilon/k(\mathrm{H{-}H}) = 10.0$ K; $\varepsilon/k(\mathrm{C{-}C}) = 35.8$ K.

The electrostatic part of the force field was simulated with partial charges on each atom as follows:

$q_{Br} = -0.16\ |e|$; $q_{Cl} = -0.18\ |e|$;

$q_F = -0.22\ |e|$; $q_H = 0.225\ |e|$; $q_C = 0.335\ |e|$.

The complete pair-potential between two molecules therefore consisted of 25 (5x5) site-site terms with the above parameters. This was assumed to be the same for R-R and R-S interactions because of the mirror-image symmetry of the R and S enantiomers.

The system was equilibrated over about 2000 time-steps of 0.005 ps each and time correlation functions then computed with about 1000 time steps (500 records, each separated by 0.01 ps). Running time averages were used in building up the correlation functions in the laboratory frame of reference.

Liquid Dichloromethane in the presence of a Strong, z-Axis External Electric Field [20]

This is the same algorithm as used in the first description [3,22] of the functions $\langle v_x(t)\omega_y(o)\rangle$ and $\langle v_y(t)\omega_x(o)\rangle$ referred to already. The external torque $-\underset{\sim}{\mu}\times\underset{\sim}{E}$ is applied as described in the literature [20a]. The external field used in this algorithm can be strong enough almost to saturate the Langevin function, the sample remaining as a liquid and in anisotropic equilibrium. At present, this is possibly only with computer simulation. (However, experimentally available Kerr effect apparatus can be adopted to measure $<v_x(t)\omega_y(o)>$ using far infra-red data and this is an experiment that remains to be done).

The intermolecular potential is a 3 x 3 Lennard-Jones atom-atom with point charges representing the electrostatic part of the complete potential. The $-CH_2$ group (of mass 14) is represented by

$\sigma(CH_2 - CH_2)/k = 70.5K;$

or $\sigma(CH_2 - CH_2) = 3.96$ A,

$q_{CH_2} = 0.302|e|$

The Cl group is represented by a mass of 35.5 and Lennard-Jones and partial-charge parameters:

$\varepsilon(Cl - Cl) / k = 173.5K;$

$\sigma(Cl - Cl) = 3.35$ Å ;

$q_{Cl} = - 0.151 |e|$

The input temperature was 296K and the input molar volume 8.0×10^{-5} m^3/mole. Autocorrelation functions were evaluated with 900 records (2700 time steps) of 0.015 ps each after field-on equilibration. An electric field strength equivalent to about 14.0 kT was used to investigate the effect of pronounced liquid anisotropy on the direct Coriolis forces.

RESULTS AND DISCUSSION

(R) - Bromochlorofluoro Methane and the Racemic Mixture

Figure (1) illustrates the (normalised) correlation functions defined in Eqn (6); a) for the R enantiomer, and b) for the racemic mixture. All three correlation functions of Eqn (6) exist in the laboratory frame with similar but not identical time dependencies.

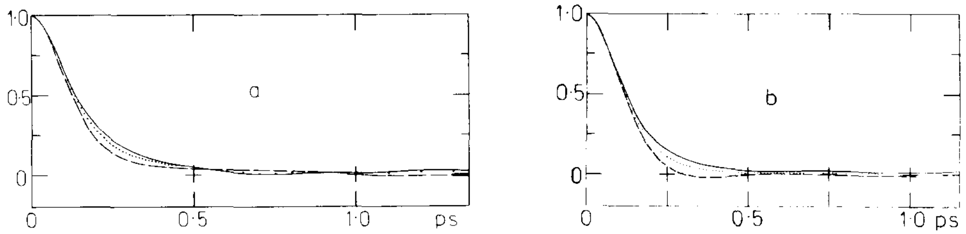

Figure (1)

(a) Auto-correlation functions of the Coriolis force in (R)-CHBrClF.

———— $\langle \underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t) \cdot \underset{\sim}{v}(o) \times \underset{\sim}{\omega}(o)\rangle / \langle(\underset{\sim}{v}(o) \cdot \underset{\sim}{\omega}(o)) \cdot (\underset{\sim}{v}(o) \cdot \underset{\sim}{\omega}(o))\rangle$

-------- $\langle(\underset{\sim}{v}(t) \cdot \underset{\sim}{\omega}(o)) (\underset{\sim}{\omega}(t) \cdot \underset{\sim}{v}(o))\rangle / \langle(\underset{\sim}{v}(o) \cdot \underset{\sim}{\omega}(o))^2\rangle$

.... $\langle(\underset{\sim}{v}(t) \cdot \underset{\sim}{v}(o)) (\underset{\sim}{\omega}(t) \cdot \underset{\sim}{\omega}(o))\rangle / \langle v^2(o)\, \omega^2(o)\rangle$

(b) As for (a), racemic mixture.

The three correlation functions seem to be different for the racemic mixture, so that comparison of spectra for an enantiomer and racemic mixture is a useful lead into the nature of the statistical dependence of $\underset{\sim}{v}$ upon $\underset{\sim}{\omega}$ and vice-versa. This has been pointed out in the literature [20b] for elements of the matrix $\langle\underset{\sim}{v}(t)\omega^T(o)\rangle$ in enantiomers and racemic mixtures.

Some Fourier transforms of these correlation functions are compared for the R enantiomer in fig (2), together with Fourier transforms of the velocity a.c.f. $\langle\underset{\sim}{v}(t).\underset{\sim}{v}(o)\rangle/\langle v^2\rangle$ and angular velocity a.c.f. $\langle\underset{\sim}{\omega}(t).\underset{\sim}{\omega}(o)\ /\langle\omega^2\rangle$. It can be seen from fig. 2(a) that the frequency dependence of the Coriolis correlation function is similar to those of the above two auto correlation functions. This fits in with the general finding from computer simulation that rotational and translational motion in isotropic molecular ensembles evolve on a similar time scale. (However, this is not the case in anisotropic liquids (see fig 5(b)) or in liquid crystals [21]).

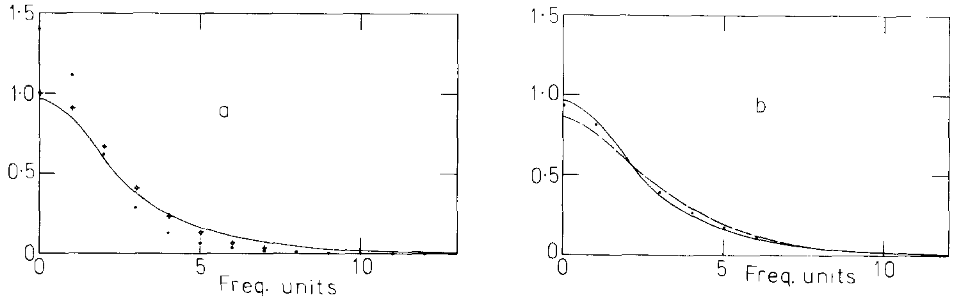

Figure (2)

(a) Fourier transform of the a.c.f. of $\mathbf{v}(t) \times \boldsymbol{\omega}(t)$ for (R) - CHBrClF.

◇ Fourier transform of $< \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(o)> / <\omega^2>$.

● Fourier transform of $< \mathbf{v}(t) \cdot \mathbf{v}(o)> / <v^2>$.

(b) Fourier transforms of the curves in Fig 1(a).

Therefore, to a first approximation, the Coriolis a.c.f. may be estimated experimentally to being roughly similar to the angular velocity a.c.f., which in turn is approximately the same as the rotational velocity a.c.f. (fig. (3)). The rotational velocity a.c.f. $<\dot{\boldsymbol{\mu}}(t) . \dot{\boldsymbol{\mu}}(o)>$ is related to the Fourier transform of the far infra-red power absorption coefficient. Therefore the Coriolis a.c.f. can be estimated approximately from the far infra-red power absorption of isotropic liquids.

The correlation function of the centrifugal force (C_{cent} of Eqn (9)) is illustrated in fig (4) for the R enantiomer and racemic mixture. It is clear that this correlation function reaches a constant level as t → ∞, and is again different for enantiomer and racemic mixture.

This property is echoed in fig (3), for the correlation function:

$$C_A = <(\dot{\mathbf{e}}_A(t) \times \boldsymbol{\omega}(t)) \cdot (\dot{\mathbf{e}}_A(o) \times \boldsymbol{\omega}(o))><(\dot{\mathbf{e}}_A(o) \times \boldsymbol{\omega}(o) \cdot \dot{\mathbf{e}}_A(o) \times \boldsymbol{\omega}(o))>$$

where $\dot{\underset{\sim}{e}}_A$ is a unit vector in the A axis of the molecular principal moment of inertia frame. As discussed already this is both a centrifugal force correlation function and a Coriolis force correlation function; and is amenable to calculation with a theory of 'purely rotational' diffusion. No satisfactory theoretical description exists, however, at present.

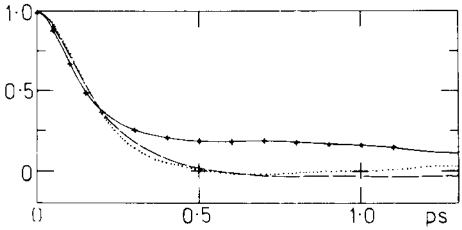

Figure 3

——— (R) CHBrClF, the a.c.f.:

$$\frac{\langle \dot{\underset{\sim}{e}}_A(t) \times \underset{\sim}{\omega}(t) \cdot \dot{\underset{\sim}{e}}_A(o) \times \underset{\sim}{\omega}(o)\rangle}{\langle(\dot{\underset{\sim}{e}}_A(o) \times \underset{\sim}{\omega}(o))^2\rangle}$$

where $\underset{\sim}{e}_A$ is a unit vector in the principal moment of inertia frame of the molecule. The dipole moment vector, μ, is a combination of $\underset{\sim}{e}_A$, $\underset{\sim}{e}_B$ and $\underset{\sim}{e}_C$.
◇ , the same c.f. computed with $\underset{\sim}{\omega} \times \underset{\sim}{e}_A$ for $\dot{\underset{\sim}{e}}_A$ as a check of the computational accuracy and overall self-consistency in the correlation function.

-------- $\langle\dot{\underset{\sim}{e}}_A(t) \cdot \dot{\underset{\sim}{e}}_A(o)\rangle / \langle\dot{e}_A^2\rangle$, the rotational velocity autocorrelation function of $\dot{\underset{\sim}{e}}_A$.

.... $\langle \underset{\sim}{\omega}(t) \cdot \underset{\sim}{\omega}(o)\rangle / \langle\omega^2\rangle$, the angular velocity autocorrelation function.

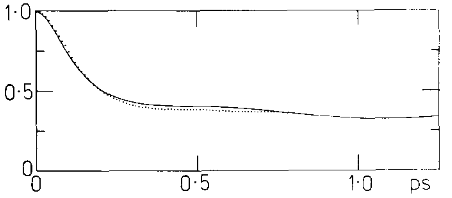

Figure (4)

The a.c.f. of the molecular centrifugal force: $m\underset{\sim}{\omega} \times (\underset{\sim}{\omega} \times \underset{\sim}{r})$, for:

(1) ——— (R) CHBrClF;

(2) ------ the racemic mixture.

Dichloromethane in the Presence of a z Axis Electric Field

Fig (5a) illustrates the correlation functions of eqn (6) computer simulated for dichloromethane in the presence of an intense z axis electric field. The Coriolis function is oscillatory, and the component a.c.f.'s (eqn (6) are likewise oscillatory, but clearly different in time dependence. Fig 5(b) illustrates the angular velocity a.c.f. $<\underset{\sim}{\omega}(t) \cdot \underset{\sim}{\omega}(o)>$ and linear velocity a.c.f. $<\underset{\sim}{v}(t) \cdot \underset{\sim}{v}(o)>$ under the same conditions as those of fig 5(a). A complete theory of molecular diffusion should be able to describe figs 5(a) and 5(b) self-consistently from the basic equations of motion. The most promising line of approach at present seems to be the Reduced Model Theory (R.M.T.) of Grigolini [24].

Fig (6) illustrates the correlation function of the vector $\underset{\sim}{r} \times \dot{\underset{\sim}{\omega}}$ (l.h.s. of eqn (18)) for the R enantiomer and racemic mixture of bromochlorofluoromethane. This autocorrelation function is not usually considered in theories of molecular diffusion but clearly exists in the laboratory frame of reference in both enantiomer and racemic mixture due to the presence of inter-molecular torques, and the subsequent non-uniformity of the molecular rotation in the laboratory frame.

Finally, fig (7) illustrates the a.c.f. of the Coriolis cum centrifugal vector $\underset{\sim}{\omega}(t) \times \dot{\underset{\sim}{e}}_A(t)$ for the anisotropic CH_2Cl_2 liquid. Here $\dot{\underset{\sim}{e}}_A(t)$ is the time derivative of a unit vector $\underset{\sim}{e}_A$, in the principal moment of inertia

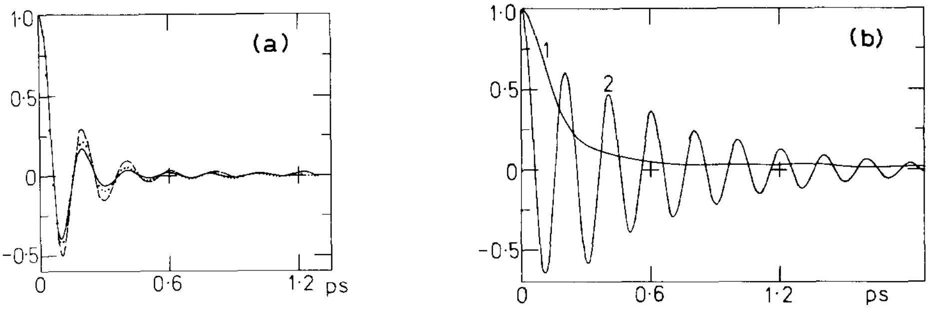

Figure (5)

(a) As for Fig. (1), liquid CH_2Cl_2 subjected to an intense uniaxial electric field of force in the lab frame z axis.

(b) ——— (1) $\langle \mathbf{v}(t) \cdot \mathbf{v}(o) \rangle / \langle v^2 \rangle$
(2) $\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(o) \rangle / \langle \omega^2 \rangle$

Note that the time-dependence of these two functions is very different. The time dependence of the Coriolis functions of Fig. 5(a) is intermediate.

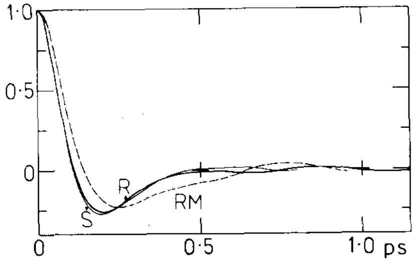

Figure (6)

▬ (R) ——— CHBrClF and -------, the racemic mixture: the normalised a.c.f. of the vector $\mathbf{r} \times \dot{\boldsymbol{\omega}}$, due to the non-uniformity of the angular motion of one frame of references (the molecule fixed frame) with respect to the other (the laboratory frame).

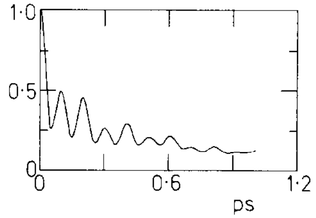

Figure (7)

CH_2Cl_2 + field, the auto-correlation function of the force vector

$\underset{\sim}{\omega}(t) \times \dot{\underset{\sim}{e}}_A(t)$

frame of the CH_2Cl_2 molecule. This function is oscillatory and reaches a constant level at $t \to \infty$. The Coriolis and centrifugal force a.c.f.'s computed in this paper will show the Grigolini decoupling effect [25], and fall-transient acceleration effect [26] with varying field-strength E_z.

CONCLUSIONS

Autocorrelation functions have been shown to exist in the laboratory frame of reference which are not usually fully considered in theories of molecular diffusion. These include autocorrelation functions of the Coriolis force, $2m\underset{\sim}{v} \times \underset{\sim}{\omega}$; centrifugal force $m\underset{\sim}{\omega} \times (\underset{\sim}{\omega} \times \underset{\sim}{r})$ and the vector $\underset{\sim}{r} \times \dot{\underset{\sim}{\omega}}$ generated by the non-uniformity of molecular motion due to intermolecular torques in the laboratory frame. It is appropriate to consider these vectors as natural measures of the inter-relation between the centre of mass translation or position of a molecule and its own rotational motion. It follows that a theory of collisional broadening of spectra must take these basic non-inertial forces into account whenever the molecular frame rotates and translates with respect to the laboratory frame.

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REFERENCES

1 E.F. Taylor, 'Introductory Mechanics', Wiley, (1963), pp 258

2 E.A. Desloge, 'Classical Mechanics', Vol. 1, p. 138 (Wiley/Interscience, N.Y., 1982).

3 M.W. Evans, Phys. Rev. A, 31 (1985) 3947

4 L.D. Landau and E.M. Lifshitz, 'Mechanics', 3rd Ed., Pergamon, Oxford, 1976), p. 128.

5 M.W. Evans, G.J. Evans, W.T. Coffey and P. Grigolini, "Molecular, Dynamics", (Wiley/Interscience, N.Y., 1982), Chapter 5.

6 D. Fincham and D.M. Heyes, A review in Vol 63 of "Advances in Chemical Physics", ed. M.W. Evans, ser. ed. Prigogine and Rice, (Wiley/Interscience, N.Y., 1985), in press.

7 Ref (5) chapters 1,4, and 6.

8 W.T. Coffey, M.W. Evans, and P. Grigolini, "Molecular Diffusion", (Wiley) Interscience, N.Y. 1984)

9 D.W. Condiff and J.S. Dahler, J. Chem. Phys., 44 (1966) 3988

10 G.D. Harpe and B.J. Berne, Phys. Rev. A, 2 (1970) 975

11 N.K. Ailawadi, B.J. Berne, and D. Forster, Phys. Rev. A, 3 (1971) 1462; 3 (1971) 1472

12 D. Chandler, J. Chem. Phys., 60 (1974) 3508

13 L.P. Hwang and J.H. Freed, J. Chem. Phys., 63 (1975) 118, 4017

14 P.G. Wolynes and J.M. Deutch, J. Chem. Phys., 67 (1977) 733

15 G.T. Evans, Mol. Phys., 36 (1978) 1199

16 U. Steiger and R.F. Fox, J. Math. Phys., 23 (1982) 296

17 B.J. Berne and R. Pecora, "Dynamic Light Scattering with Reference to Physics, Chemistry and Biology (Wiley, New York, 1976).

18 J.P. Ryckaert, A. Bellemans and G. Ciccotti, Mol. Phys., 44 (1981) 979

19 G. van der Zwan and J.T. Hynes, Physica, 121A (1983) 227

20a M.W. Evans, J. Chem. Phys. 76 (1982) 5473, 76 (1982) 5480; 77 (1982) 4632; 78 (1983) 925; 78 (1983) 5403; J. Mol. Liq., 26 (1983) 49

20b M.W. Evans, Phys. Rev. Letters, 50 (1983) 371

21 J.K. Moscicki, review in ref. (6).

22 M.W. Evans, Phys. Scripta, in press, 1985, Physica B, in press, 1985.

23 Ref. (5), Chapter 11.

24 "Memory Function Approaches to Stochastic Problems in Condensed Matter", Vol. 62 of "Advances in Chemical Physics", ed. M.W. Evans, P. Grigolini and G. Pastori-Parravicini, series ed. Progogine and Rice, (Wiley/Interscience, N.Y., 1985, in press), Chapter 1, by P. Grigolini.

25 Ref. (24), Chapter 6.

26 Ref. (24), Chapter 5.