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CORRELATION FUNCTIONS FOR MOLECULAR ROTATION AND TRANSLATION

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ABSTRACT

By considering the Langevin equations governing the three-dimensional diffusion of a body that is simultaneously rotating and translating a number of new auto- and cross-correlation functions are established in both the laboratory and moving frames of reference. These provide a total of forty-four new ways of expressing the statistical correlation between rotation and translation.

Two examples are given, using a computer simulation of liquid CH_2Cl_2 at 296 K. The first is the auto-correlation function of the Coriolis acceleration, the second is a cross-correlation function of the type:

$$\frac{\langle 2\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t) \cdot \underset{\sim}{v}(o)\rangle}{2\langle\omega^2(o)\rangle^{\frac{1}{2}}\langle v^2(o)\rangle}$$

INTRODUCTION

The Langevin equations for the simultaneous rotational and translational motion of a diffusing molecule when written in frames of reference defined by that molecule's principal moment of inertia axes, lead to statistical cross-correlation between $\underline{v}$, the centre of mass linear velocity, and $\underline{\omega}$, the molecular angular velocity in the same frame [1-3]. Furthermore, consideration of the terms appearing in these equations leads to the conclusion that the correlation between $\underline{v}$ and $\underline{\omega}$ can take a variety of forms, both in the molecular frame of reference, and in the laboratory frame. To my knowledge, only one or two of these new correlation functions have been considered in the literature [3]. In this paper, they are demonstrated with reference to a computer simulation of liquid dichloromethane, examples being provided of some new types of correlation function.

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THEORETICAL BACKGROUND

It has been shown recently [1,2] that the Langevin equations that govern the diffusion of a molecule that is both rotating and translating must be written, to be useful, in frames of reference that move with the molecule. For convenience, these may be defined as the frame, (1,2,3), of the molecule principal moments of inertia and the frame (1,2,3)' rotating at the origin of the laboratory frame (x,y,z). In this frame, the equations involve Coriolis and centripetal accelerations, together with an acceleration term dependent on the non-uniformity of the rotational motion. They are:

$$\dot{\underset{\sim}{v}} + 2\underset{\sim}{\omega} \times \underset{\sim}{v} + \dot{\underset{\sim}{\omega}} \times \underset{\sim}{r} + \underset{\sim}{\omega} \times (\underset{\sim}{\omega} \times \underset{\sim}{r}) + \beta_v(\underset{\sim}{v} + \underset{\sim}{\omega} \times \underset{\sim}{r}) = \dot{W}_{vm} \tag{1}$$

$$\begin{aligned} I_1\dot{\omega}_1 - (I_2 - I_3)\omega_2\omega_3 + I_1\beta_1\omega_1 &= I_1\dot{W}_1 \\ I_2\dot{\omega}_2 - (I_3 - I_1)\omega_3\omega_1 + I_2\beta_2\omega_2 &= I_2\dot{W}_2 \\ I_3\dot{\omega}_3 - (I_1 - I_2)\omega_1\omega_2 + I_3\beta_3\omega_3 &= I_3\dot{W}_3 \end{aligned} \tag{2}$$

Eqns (1) and (2) are written with reference to the coordinate systems (1,2,3)' and (1,2,3) respectively. Eqn (1) is the translational Langevin equation in this frame and eqn (2) the rotational counterpart, sometimes known as the Euler/Langevin equation [4]. β_v is the scalar translational friction coefficient, and β_1, β_2 and β_3 the three scalar rotational friction coefficients. The position vector $\underline{r}$ is defined with respect to frame (1,2,3)' as:

$$[\dot{r}]_{(1,2,3)'} = [v]_{(1,2,3)'} \tag{3}$$

The quantities I_1, I_2 and I_3 are the three principal molecular moments of inertia; ω_1, ω_2 and ω_3 are the components in frame (1,2,3) of the molecular angular velocity, $\underline{\omega}$. These are identical in frame (1,2,3)'. Clearly, $\underline{v}$, the molecular centre of mass velocity, and $\underline{r}$ are both defined in frame (1,2,3)'. The random processes $\dot{\underline{W}}_{vm}$, $\dot{W}_1$, $\dot{W}_2$ and $\dot{W}_3$ are Wiener processes in these frames. The three components $\dot{W}_1$, $\dot{W}_2$ and $\dot{W}_3$ are defined as being statistically independent, but each is not statistically independent of the translational Wiener process $\dot{\underline{W}}_{vm}$ because of the presence of the deterministic variable $\underline{\omega}$ in both equations. Eqn (2) can be written more concisely as:

$$\underline{\underline{I}} \cdot \dot{\underset{\sim}{\omega}} + \underset{\sim}{\omega} \times \underline{\underline{I}} \cdot \underset{\sim}{\omega} + \underline{\underline{\beta}} \cdot \underset{\sim}{\omega} = \dot{\underset{\sim}{W}}_r \tag{4}$$

where $\underline{\underline{I}}$ is the principal molecular moment of inertia tensor, and $\underline{\underline{\beta}}$ the rotational friction tensor. It is assumed implicitly from eqn (4) that both $\underline{\underline{I}}$ and $\underline{\underline{\beta}}$ are diagonal in frame (1,2,3). These quantities are both dependent therefore, only on the molecular symmetry. In the same way that $\underline{\underline{I}}$ can be generated from m, the friction tensor $\underline{\underline{\beta}}$ can be generated from β_V by consideration of the molecular symmetry alone.

In eqn (1), the Coriolis acceleration is $2\underline{\omega} \times \underline{v}$, the centripetal acceleration is $\underline{\omega} \times (\underline{\omega} \times \underline{r})$, and the acceleration $\dot{\underline{\omega}} \times \underline{r}$ is non-zero if $\dot{\underline{\omega}} \neq \underline{0}$, which is always the case in the presence of inter-molecular torques. None of these terms appears in the conventional treatment of either rotational or translational molecular diffusion.

By inspection of eqns (1) and (4), the following eight terms are involved in the description of the molecular diffusion in frames (1,2,3) and (1,2,3)': i) $\dot{\underset{\sim}{v}}$; ii) $2\underset{\sim}{\omega} \times \underset{\sim}{v}$; (iii) $\underset{\sim}{\omega} \times (\underset{\sim}{\omega} \times \underset{\sim}{r})$; iv) $\beta_V \underset{\sim}{v}$; v) $\beta_V \underset{\sim}{\omega} \times \underset{\sim}{r}$; vi) $\underline{\underline{I}} \cdot \underset{\sim}{\omega}$; vii) $\underset{\sim}{\omega} \times \underline{\underline{I}} \cdot \underset{\sim}{\omega}$; viii) $\underline{\underline{\beta}} \cdot \underset{\sim}{\omega}$. Computer simulation has already revealed [2-4] that a statistical correlation exists between the tensor product of term iv) and term viii). This has been quantified [2] in frame (1,2,3) for many molecular symmetries with the cross-correlation matrix $\langle \underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)\rangle$. Results are also available on the statistical cross-correlation between terms i) and vi), essentially the molecular force and torque in frame (1,2,3).

This paper aims to show that similar cross-correlation functions in frames (1,2,3) and (1,2,3)' exist between all the eight terms listed above. Clearly, each of these vectors also generates its own time auto-correlation function in both these frames. For example, there exists in frame (1,2,3) the auto correlation function of the Coriolis acceleration:

$$C_{Cor} = \langle (2\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t)) \cdot (2\underset{\sim}{\omega}(o) \times \underset{\sim}{v}(o))\rangle_{(1,2,3)} \tag{5}$$

and so on. Therefore the correct description of the Langevin dynamics of a simultaneously rotating and translating body in frames (1,2,3) and (1,2,3)' suggests the existence of a number of new auto and cross-correlation functions. This suggestion is followed up in this paper with a computer simulation of these correlation functions for liquid dichloromethane at 296 K.

The nature of the new cross-correlation functions can be clarified if we write the laboratory frame equivalent of eqn (1) :

$$[\dot{\underset{\sim}{v}} + \beta_v \underset{\sim}{v}]_{(x,y,z)} = [\dot{\underset{\sim}{W}}_v]_{(x,y,z)} \qquad (6)$$

where (x,y,z) defines the static, laboratory frame of the observer. Eqn (6) is generated from eqn (1) with the frame transformations:

$$[v]_{(x,y,z)} \equiv [\underset{\sim}{v} + \underset{\sim}{\omega} \times \underset{\sim}{r}]_{(1,2,3)}, \qquad (7)$$

$$[\dot{v}]_{(x,y,z)} \equiv [\dot{\underset{\sim}{v}} + 2\underset{\sim}{\omega} \times \underset{\sim}{v} + \dot{\underset{\sim}{\omega}} \times \underset{\sim}{r} + \underset{\sim}{\omega} \times (\underset{\sim}{\omega} \times \underset{\sim}{r})]_{(1,2,3)} \qquad (8)$$

of elementary dynamics. The existence of the well-known laboratory frame correlation functions $\langle \underset{\sim}{v}(t) \cdot \underset{\sim}{v}(o)\rangle_{(x,y,z)}$; $\langle \dot{\underset{\sim}{v}}(t) \cdot \dot{\underset{\sim}{v}}(o)\rangle_{(x,y,z)}$ and $\langle \dot{\underset{\sim}{v}}(t) \cdot \underset{\sim}{v}(o)\rangle_{(x,y,z)}$ immediately implies, from identities (7) and (8) the existence in frame (1,2,3) of the following new auto and cross-correlation functions:

i) $\langle(\underset{\sim}{v}(t) + \underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t)) \cdot (\underset{\sim}{v}(o) + \underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o))\rangle_{(1,2,3)},$

$$= \langle \underset{\sim}{v}(t) \cdot \underset{\sim}{v}(o)\rangle_{(1,2,3)}, + \langle \underset{\sim}{v}(t) \cdot \underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o)\rangle_{(1,2,3)}, \qquad (9)$$

$$+ \langle \underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t) \cdot \underset{\sim}{v}(o)\rangle_{(1,2,3)}, + \langle \underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t) \cdot \underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o)\rangle_{(1,2,3)},$$

ii) $(\dot{\underset{\sim}{v}}(t) + 2\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t) + \dot{\underset{\sim}{\omega}}(t) \times \underset{\sim}{r}(t) + \underset{\sim}{\omega}(t) \times (\underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t)))$

$$\cdot(\dot{\underset{\sim}{v}}(o) + 2\underset{\sim}{\omega}(o) \times \underset{\sim}{v}(o) + \dot{\underset{\sim}{\omega}}(o) \times \underset{\sim}{r}(o) + \underset{\sim}{\omega}(o) \times (\underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o)))\rangle_{(1,2,3)},$$

$$= \langle \dot{\underset{\sim}{v}}(t) \cdot \dot{\underset{\sim}{v}}(o)\rangle_{(1,2,3)}, + \langle \dot{\underset{\sim}{v}}(t) \,.\, 2\underset{\sim}{\omega}(o) \times \underset{\sim}{v}(o)\rangle_{(1,2,3)},$$

$$+ \langle \dot{\underset{\sim}{v}}(t) \,.\, \dot{\underset{\sim}{\omega}}(o) \times \underset{\sim}{r}(o)\rangle_{(1,2,3)}, + \langle \dot{\underset{\sim}{v}}(t) \,.\, \underset{\sim}{\omega}(o) \times (\underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o))\rangle_{(1,2,3)},$$

$$+ \langle 2\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t) \,.\, \dot{\underset{\sim}{v}}(o)\rangle_{(1,2,3)}, + \langle 2\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t) \,.\, 2\underset{\sim}{\omega}(o) \times \underset{\sim}{v}(o)\rangle_{(1,2,3)},$$

$$+ \langle 2\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t) \,.\, \dot{\underset{\sim}{\omega}}(o) \times \underset{\sim}{r}(o)\rangle_{(1,2,3)}, + \langle 2\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t) \,.\, \underset{\sim}{\omega}(o) \times (\underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o))\rangle_{(1,2,3)},$$

$$+ \langle \dot{\underset{\sim}{\omega}}(t) \times \underset{\sim}{r}(t) . \dot{\underset{\sim}{v}}(o)\rangle_{(1,2,3)}, + \langle \dot{\underset{\sim}{\omega}}(t) \times \underset{\sim}{r}(t) . 2\underset{\sim}{\omega}(o) \times \underset{\sim}{v}(o)\rangle_{(1,2,3)},$$

$$+ \langle \dot{\underset{\sim}{\omega}}(t)\times\underset{\sim}{r}(t)\cdot\dot{\underset{\sim}{\omega}}(o)\times\underset{\sim}{r}(o)\rangle_{(1,2,3)'} + \langle\dot{\underset{\sim}{\omega}}(t)\times\underset{\sim}{r}(t)\cdot\underset{\sim}{\omega}(o)\times(\underset{\sim}{\omega}(o)\times\underset{\sim}{r}(o))\rangle_{(1,2,3)'}$$

$$+ \langle\underset{\sim}{\omega}(t)\times(\underset{\sim}{\omega}(t)\times\underset{\sim}{r}(t))\cdot\dot{\underset{\sim}{v}}(o)\rangle_{(1,2,3)'} + \langle\underset{\sim}{\omega}(t)\times(\underset{\sim}{\omega}(t)\times\underset{\sim}{r}(t))\cdot 2\underset{\sim}{\omega}(o)\times\underset{\sim}{v}(o)\rangle_{(1,2,3)'}$$

$$+ \langle\underset{\sim}{\omega}(t)\times(\underset{\sim}{\omega}(t)\times\underset{\sim}{r}(t))\cdot\dot{\underset{\sim}{\omega}}(o)\times r(o)\rangle_{(1,2,3)'} + \langle\underset{\sim}{\omega}(t)\times(\underset{\sim}{\omega}(t)\times\underset{\sim}{r}(t))\cdot\underset{\sim}{\omega}(o)\times(\underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o))\rangle_{(1,2,3)'} \quad (10)$$

iii) $$\langle(\dot{\underset{\sim}{v}}(t)+2\underset{\sim}{\omega}(t)\times\underset{\sim}{v}(t)+\dot{\underset{\sim}{\omega}}(t)\times\underset{\sim}{r}(t) + \underset{\sim}{\omega}(t)\times(\underset{\sim}{\omega}(t)\times\underset{\sim}{r}(t)))$$

$$\cdot\ (\underset{\sim}{v}(o) + \underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o))\rangle_{(1,2,3)'}$$

$$= \langle\dot{\underset{\sim}{v}}(t)\cdot\underset{\sim}{v}(o)\rangle_{(1,2,3)'} + \langle 2\underset{\sim}{\omega}(t)\times\underset{\sim}{v}(t)\cdot\underset{\sim}{v}(o)\rangle_{(1,2,3)'}$$

$$+ \langle\dot{\underset{\sim}{\omega}}(t)\times\underset{\sim}{r}(t)\cdot\underset{\sim}{v}(o)\rangle_{(1,2,3)'} + \langle\underset{\sim}{\omega}(t)\times(\underset{\sim}{\omega}(t)\times\underset{\sim}{r}(t))\cdot\underset{\sim}{v}(o)\rangle_{(1,2,3)'}$$

$$+ \langle\dot{\underset{\sim}{v}}(t)\cdot\underset{\sim}{\omega}(o)\times\underset{\sim}{r}(o)\rangle_{(1,2,3)'} + \langle 2\underset{\sim}{\omega}(t)\times\underset{\sim}{v}(t)\cdot\underset{\sim}{\omega}(o)\times\underset{\sim}{r}(o)\rangle_{(1,2,3)'}$$

$$+ \langle\dot{\underset{\sim}{\omega}}(t)\times\underset{\sim}{r}(t)\cdot\underset{\sim}{\omega}(o)\times\underset{\sim}{r}(o)\rangle_{(1,2,3)'}$$

$$+ \langle\underset{\sim}{\omega}(t) \times (\underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t)) \cdot \underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o)\rangle_{(1,2,3)'} \quad (11)$$

Therefore, there are at least twenty-four available moving frame correlation functions to describe the simultaneous rotation and translation of a diffusing asymmetric top molecule as governed by eqns (1) and (2). The function defined on the left hand side of eqns (9) and (10) exist at t = 0, because they are generated from auto-correlation functions. On the other hand, those on the right hand side of eqn (11) are generated from the laboratory frame cross-correlation function $\langle\underset{\sim}{v}(t)\cdot\underset{\sim}{v}(o)\ _{(x,y,z)}$ which vanishes at the origin (t = 0). Therefore, the six correlation functions on the r.h.s. of eqn (11) vanish separately at t = 0. (This is illustrated later in fig. 3).

Of these twenty-four moving frame correlation functions, only the simple auto-correlation functions $\langle\underset{\sim}{v}(t)\cdot\underset{\sim}{v}(o)\rangle_{(1,2,3)'}$ and $\langle\dot{\underset{\sim}{v}}(t)\cdot\underset{\sim}{v}(o)\rangle_{(1,2,3)'}$ seem to have appeared in the literature. The nature of the other twenty-two seems to be unknown, but can be investigated by computer simulation. Examples are provided in this paper.

If we now start to consider eqn (4), this is generated by frame transformations similar to eqns (7) and (8), viz:

$$[\underset{\sim}{\omega}]_{(x,y,z)} \equiv [\underset{\sim}{\omega}]_{(1,2,3)} \tag{12}$$

$$[\underline{\underline{I}}\cdot\dot{\underset{\sim}{\omega}}]_{(x,y,z)} \equiv [\underline{\underline{I}}\cdot\dot{\underset{\sim}{\omega}} + \underset{\sim}{\omega} \times \underline{\underline{I}} \cdot \underset{\sim}{\omega}]_{(1,2,3)} \tag{13}$$

Eqn (12) follows because the molecular angular velocity, $\underline{\omega}$, is also the angular velocity of one frame with respect to the other, which is the same to an observer in frame (1,2,3) or an observer in frame (x,y,z). Eqn (13) follows from the elementary theorem of frame transformation:

$$[\dot{\underset{\sim}{A}}]_{(x,y,z)} = [\dot{\underset{\sim}{A}} + \underset{\sim}{\omega} \times \underset{\sim}{A}]_{(1,2,3)} \tag{14}$$

where $\underline{A}$ is a vector quantity.

Now, it is known that in the laboratory frame of reference, (x,y,z):

$$\langle\underset{\sim}{v}(t)\ .\ \underset{\sim}{\omega}(o)\rangle_{(x,y,z)} = 0 \qquad \text{for all } t, \tag{15}$$

$$\langle\dot{\underset{\sim}{v}}(t)\ .\ (\underline{\underline{I}}\ .\ \underset{\sim}{\omega}(o))\rangle_{(x,y,z)} = 0 \text{ for all } t \tag{16}$$

These are the Berne/Pecora theorems [5] which are proved because the sign of $\underline{v}$ is reversed by parity reversal, and that of $\underline{\omega}$ remains the same.

From eqns (7), (12) and (15), it follows that

$$\langle(\underset{\sim}{v}(t) + \underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t))\ .\ \underset{\sim}{\omega}(o)\rangle_{(1,2,3)'} = 0 \tag{17}$$

Therefore, eqn (17) provides the results:

$$\langle\underset{\sim}{v}(t)\ .\ \underset{\sim}{\omega}(o)\rangle_{(1,2,3)} = 0, \qquad \text{for all } t \tag{18}$$

$$\langle\underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t)\ .\ \underset{\sim}{\omega}(o)\rangle_{(1,2,3)'} = 0, \quad \text{for all } t \tag{19}$$

Eqn (18) proves that the three diagonal elements of the moving frame tensor:

$$\langle\underset{\sim}{v}(t)\underset{\sim}{\omega}^{T}(o)\rangle_{(1,2,3)} \neq 0 \tag{20}$$

are all zero for all t. Computer simulation has shown, however, that the off-diagonal elements of eqn (20) are not necessarily zero for $t > 0$.

In the laboratory frame (x,y,z), we have the result, from computer simulation:

$$\langle \mathbf{v}(t)\boldsymbol{\omega}^T(o)\rangle_{(x,y,z)} = \mathbf{0} \qquad \text{for all } t \tag{21}$$

Eqn (21) seems to be true for all molecular symmetries provided the Hamiltonian is invariant to parity reversal [5]. From eqns (7), (12) and (21), it follows that:

$$\langle(\mathbf{v}(t) + \boldsymbol{\omega}(t) \times \mathbf{r}(t))\omega^T(o)\rangle_{(1,2,3)'} = \mathbf{0} \quad \text{for all } t \tag{22}$$

However, we know that:

$$\langle \mathbf{v}(t)\boldsymbol{\omega}^T(o)\rangle_{(1,2,3)'} \neq 0, \quad t > 0,$$

from eqn (20), and it follows from eqns (22) and (20) that:

$$\langle \mathbf{v}(t)\boldsymbol{\omega}^T(o)\rangle_{(1,2,3)'} = - \langle(\boldsymbol{\omega}(t) \times \mathbf{r}(t))\boldsymbol{\omega}^T(o)\rangle_{(1,2,3)'} \tag{23}$$

THEOREM

In the moving frame of reference (1,2,3)' the off-diagonal cross-correlation elements of the "Coriolis Correlation tensor" $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(o)\rangle_{(1,2,3)'}$ are equal and opposite to those of the "centripetal correlation tensor" $- \langle(\omega(t) \times \mathbf{r}(t))\omega^T(o)\rangle_{(1,2,3)'}$

If we note that, for each molecule in the ensemble:

$$\boldsymbol{\omega}(t) \times \mathbf{r}(t) = - \mathbf{r}(t) \times \boldsymbol{\omega}(t) \tag{24}$$

then it follows that:

$$\langle \mathbf{v}(t)\boldsymbol{\omega}^T(o)\rangle_{(1,2,3)'} = \langle(\mathbf{r}(t) \times \boldsymbol{\omega}(t))\boldsymbol{\omega}^T(o)\rangle_{(1,2,3)'} \tag{25}$$

$$<(\dot{\underset{\sim}{v}}(t) + 2\underset{\sim}{\omega}(t)\times\underset{\sim}{v}(t) + \dot{\underset{\sim}{\omega}}(t)\times\underset{\sim}{r}(t) + \underset{\sim}{\omega}(t)\times(\underset{\sim}{\omega}(t)\times\underset{\sim}{r}(t)))\cdot{}_{(1,2,3)'}\,,$$

$$(\underline{\underline{I}} \cdot \dot{\underset{\sim}{\omega}}(o) + \underset{\sim}{\omega}(o) \times \underline{\underline{I}} \cdot \underset{\sim}{\omega}(o))_{(1,2,3)}> \;= 0 \tag{26}$$

This result may be obtained if it is assumed that all the component correlation functions of the l.h.s. of eqn (26) vanish separately in the moving frame of reference. It is known already from computer simulation that

$$<\dot{\underset{\sim}{v}}(t) \cdot \underline{\underline{I}} \cdot \dot{\underset{\sim}{\omega}}(o)>_{(1,2,3)} = 0 \tag{27}$$

but the nature of the other terms from eqn (26) is not yet known.

Finally, note that:

$$<\dot{\underset{\sim}{v}}(t)\; (\underline{\underline{I}} \cdot \dot{\underset{\sim}{\omega}}(o))^T>_{(1,2,3)} \neq 0 \quad (t > 0) \tag{28}$$

which implies that the tensor product is analogous to the vector product, eqn (26) also generates symmetry theorems analogous to eqns (23) or (25).

NEW CORRELATION FUNCTIONS IN THE LABORATORY FRAME OF REFERENCE

The relativity of frame transformation implies that identities (7), (8), (12) and (13) can be reversed, i.e.:

$$[\underset{\sim}{v}]_{(1,2,3)'} \equiv [\underset{\sim}{v} + \underset{\sim}{\omega} \times \underset{\sim}{r}]_{(x,y,z)} \tag{29}$$

$$[\dot{\underset{\sim}{v}}]_{(1,2,3)'} \quad [\dot{\underset{\sim}{v}} + 2\underset{\sim}{\omega} \times \underset{\sim}{v} + \dot{\underset{\sim}{\omega}} \times \underset{\sim}{r} + \underset{\sim}{\omega} \times (\quad \times r)]_{(x,y,z)} \tag{30}$$

$$[\underset{\sim}{\omega}]_{(1,2,3)} \equiv [\underset{\sim}{\omega}]_{(x,y,z)} \equiv [\underset{\sim}{\omega}]_{(1,2,3)'} \tag{31}$$

$$[\underline{\underline{I}} \cdot \dot{\underset{\sim}{\omega}}]_{(1,2,3)} \equiv [\underline{\underline{I}} \cdot \dot{\underset{\sim}{\omega}} + \underset{\sim}{\omega} \times \underline{\underline{I}} \cdot \underset{\sim}{\omega}]_{(x,y,z)} \tag{32}$$

In elementary dynamics, it is well-known that some frame transformations are "inertial", and some are "non-inertial". ("Inertial" in this context should not be confused with "inertial", as in "moment of inertia"). A rotating frame of reference is "non-inertial" with respect to a static frame, and eqns (7), (8), (12) and (13) or (29)-(32) define this property for linear and angular velocity and acceleration. (These identities can be visualised by thinking, for example, of the horizon as seen from a turning aircraft. The horizon seems to be rotating to a passenger seated in the aircraft. The principle embodied in these identities is sometimes known as Galileo's relativity principle, although this is strictly applicable only to a frame (x', y', z') that translates uniformly with respect to frame (x,y,z), and does not rotate relative to the latter. This is an "inertial frame").

I have risked labouring this point because identities (29)-(30) immediately provide us with a large number of new laboratory frame correlation functions which describe the statistical correlation between a molecule's rotational movement and its own centre of mass translation directly in the laboratory frame of reference (x,y,z).

These are generated simply by taking the various possible moving frame correlation functions from among the vectors on the l.h.s.'s of eqns (29) to (32). (These moving frame correlation functions exist, of course, for $t \geq 0$.). For example:

$$\begin{aligned}
&\langle \underset{\sim}{v}(t).\underset{\sim}{v}(o)\rangle_{(1,2,3)'} = \langle(\underset{\sim}{v}(t)+\underset{\sim}{\omega}(t)\mathrm{x}\underset{\sim}{r}(t)).(\underset{\sim}{v}(o)+\underset{\sim}{\omega}(o)\mathrm{x}\underset{\sim}{r}(o))\rangle_{(x,y,z)} \\
&= \langle \underset{\sim}{v}(t).\underset{\sim}{v}(o)\rangle_{(x,y,z)} + \langle \underset{\sim}{\omega}(t)\mathrm{x}\underset{\sim}{r}(t).\underset{\sim}{v}(o)\rangle_{(x,y,z)} \qquad (33) \\
&+ \langle \underset{\sim}{v}(t).\underset{\sim}{\omega}(o)\mathrm{x}\underset{\sim}{r}(o)\rangle_{(x,y,z)} + \langle \underset{\sim}{\omega}(t)\mathrm{x}\underset{\sim}{r}(t).\underset{\sim}{\omega}(o)\mathrm{x}\underset{\sim}{r}(o)\rangle_{(x,y,z)}
\end{aligned}$$

The group of correlation functions on the r.h.s. of eqn (33) is the laboratory frame equivalent of eqn (9). It follows therefore that all the twenty-four moving frame correlating functions in eqns (9), (10) and (11) also exist in the laboratory frame. This brings the total of available correlation functions to forty-eight. The existence of all forty-eight of these functions has been deduced in this paper from first principles; and they are generated once we start to consider the Langevin dynamics of a molecule that is simultaneously rotating and translating. As far as I am aware, none of these appears in the literature on molecular diffusion, with the exception of the simple auto-correlation functions of $\underline{v}$ and $\underline{\dot{v}}$. These simple autocorrelation functions can, of course, be calculated from the 'traditional' approach to Langevin dynamics, involving 'decoupled' translation. It becomes clear, therefore, that the traditional approach misses no less than forty-four out of the forty-eight correlation functions considered so far in this paper.

Some of the auto-correlation functions missed in this way are those of fundamental molecular dynamical quantities such as the Coriolis acceleration, the centripetal acceleration and so forth. The existence of these correlation functions in both frames: (x,y,z) and (1,2,3) is illustrated later in this paper by computer simulation. These a.c.f.'s are as important (both in magnitude and time dependence) to a full description of the molecular dynamics as those of $\underline{v}$ (or $\underline{\omega}$) themselves. To leave them out of consideration is simply not a valid approximation.

Finally in this section we point out that the result [2,3]:

$$<\underset{\sim}{v}(t)\underset{\sim}{\omega}^{T}(o)>_{(1,2,3)} \neq 0 \qquad (t > 0)$$

implies the existence, from identities (29) and (31), of yet more laboratory frame tensor cross-correlation functions, whose off-diagonal elements may be non-zero for t > 0. Similarly, another group of laboratory frame tensor correlation functions can be generated from the result:

$$<\dot{\underset{\sim}{v}}(t)\ (\underline{\underline{I}} \cdot \dot{\underset{\sim}{\omega}}(o))^{T}>_{(1,2,3)} \neq 0 \qquad (t > 0).$$

These two last groups are subject, however, to the general constraints imposed by laboratory frame parity reversal symmetry, mentioned already, and first discussed [5] by Berne and co-workers.

COMPUTER SIMULATION ALGORITHMS

One of the simplest types of asymmetric top has been chosen to illustrate some of the new correlation functions described analytically already. This is CH_2Cl_2 modelled in a 3 x 3 Lennard Jones and charges site-site representation of the intermolecular potential. The group was considered as a moiety. The parameters were: $\varepsilon/k(Cl-Cl) = 173.5$ K; $\varepsilon/k(CH_2-CH_2) = 70.5$ K; $\sigma(CH_2-CH_2) = 3.96$ Å; $\sigma(Cl-Cl) = 3.35$ Å; $q_{Cl} = -0.15\ |e|$; $q_{CH_2} = 0.30\ |e|$. The input temperature was 296 K, the input molar volume was $8.0 \times 10^{-5}\ m^{-3}$ for 108 molecules. The algorithm was TRI2, which has been modified by Ferrario and Evans [6] and is described in the literature. Approximately 1000 records (one segment of 3000 time steps of 5×10^{-15} sec) were used to build up an individual correlation function, either in the laboratory or moving frame.

A given vector $\underset{\sim}{A}$ could be defined either in frame (x, y, z) or in frame

$$A_1 = A_x e_{1x} + A_y e_{1y} + A_z e_{1z}$$

$$A_2 = A_x e_{2x} + A_y e_{2y} + A_z e_{2z} \qquad (34)$$

$$A_3 = A_x e_{3x} + A_y e_{3y} + A_z e_{3z}$$

where $\underline{e}_1$, $\underline{e}_2$ and $\underline{e}_3$ are unit vectors in the axes 1, 2 and 3 of frame (1,2,3). Using this method, any correlation function can be constructed in either frame. The correlation functions were computed by standard running-time averaging [4] of data generated in the computer simulation runs, and stored on disk or tape. Many examples of vector and tensor correlation functions generated in this way are now available in the literature. [2-4].

RESULTS AND DISCUSSION

Given enough computer power, it is perfectly possible to illustrate all forty-four new correlation functions mentioned already. However, it is sufficient to illustrate them and confirm their existence with two examples: one of an auto-correlation function and the other a vector cross-correlation function.

Fig 1(a) illustrates the autocorrelation functions of the molecular Coriolis acceleration in frame (x, y, z) (curve 1), and frame (1,2,3) (curve 2). These auto-correlation functions are normalised to unity at the origin, but clearly, their magnitude depends on the cross product of $\underline{\omega}$ and $\underline{v}$, and this is therefore fully comparable with those of the simple a.c.f.'s $<\underset{\sim}{v}(t).\underset{\sim}{v}(o))>$ and $<\underset{\sim}{\omega}(t).\underset{\sim}{\omega}(o)>$. The latter are illustrated for convenience in figs 1(b) and 1(c). A good check of self-consistency is the expected result:

$$\left| \frac{<\underset{\sim}{\omega}(t).\underset{\sim}{\omega}(o)>}{<\omega^2(o)>} \right|_{(x,y,z)} = \left| \frac{<\underset{\sim}{\omega}(t).\underset{\sim}{\omega}(o)>}{<\omega^2(o)>} \right|_{(1,2,3)} \qquad (35)$$

These normalised a.c.f.'s from the computer simulation are indeed almost indistinguishable on the scale of fig 1(b). This is the result expected from identify (12). The same is not true, however, of the linear, centre of mass, velocity a.c.f.'s in fig 1(b), as expected from identity (7). This means that the Coriolis acceleration a.c.f.'s in fig 1(a) have different time dependencies in frames (x,y,z) and (1,2,3). In the latter frame, there is a negative overshoot, which is not there in frame (x, y, z).

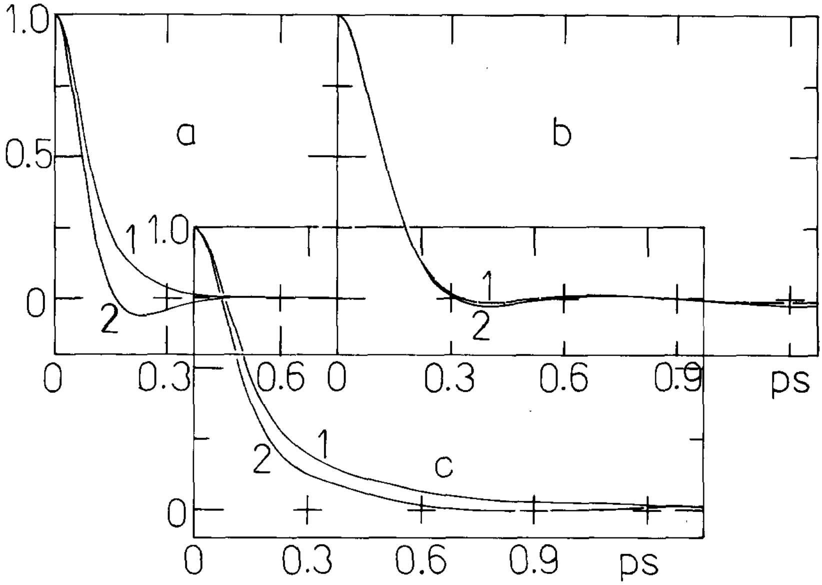

Figure 1(a)

Coriolis autocorrelation functions in (1) the laboratory frame;
(2) the moving frame

Figure 1(b)

Angular velocity autocorrelation function (1) Laboratory frame;
(2) moving frame. The two correlation functions are identical within the noise.

Figure 1(c)

Linear centre of mass velocity autocorrelation function (1) Laboratory frame; (2) moving frame. The two correlation functions are distinctly different in time dependence.

Fig (1) therefore illustrates the distinct identities taken by this particular auto-correlation function in frames (x, y, z) and (1, 2, 3). This result confirms the analysis based on eqns (1) and (2), which are therefore valid descriptions of the diffusion of a molecule that is simultaneously rotating and translating. The existence of the functions illustrated in fig 1(a) was deduced directly from eqns (1) and (2) without further assumptions of any kind. Therefore it is no longer acceptable in the light of these results to base the description of molecular diffusion on tranditional "decoupled" translational or rotational Langevin equations. It is necessary to solve eqns (1) and (2) as simultaneous equations - a formidable but far from impossible task.

Note that the use of elementary vector analysis produces the result:

$$<(\underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t)).(\underset{\sim}{v}(o) \times \underset{\sim}{\omega}(o))> = <\underset{\sim}{v}(t).\underset{\sim}{v}(o)\underset{\sim}{\omega}(t).\underset{\sim}{\omega}(o)> - <\underset{\sim}{v}(t).\underset{\sim}{\omega}(o)\underset{\sim}{\omega}(t).\underset{\sim}{v}(o)> \tag{36}$$

in <u>both</u> frames of reference. I have checked by computer simulation that the "straight" and "mixed" components on the r.h.s. of eqn (36) both exist, in both frames, and have similar, but distinct, time dependencies. Both components, being second order in $\underline{v}$ and $\underline{\omega}$, exist at t = 0 in both frames.

Similarly, elementary analyses of this kind can be carried out on all the forty-four new correlation functions defined in this paper, thus generating some hundreds of new and distinct correlation functions with which to characterise simultaneously rotating and translating molecules in an ensemble at thermodynamic equilibrium. An analytical solution of eqns (1) and (2) must be capable of describing these results self-consistently in both frames if it is to be acceptable. A fuller description, involving memory functions, must use generalisations of eqns (1) and (2). The most powerful theory at the moment seems to be the Reduced Model Theory of Grigolini and co-workers [7].

Finally in this section on the molecular Coriolis acceleration it is instructive to consider the effect on its auto-correlation function of a strong z-axis electric field. This can be achieved using the new technique of "field-effect computer simulation" of molecular liquids [2] . An electric field strong enough to saturate the Langevin function, and to align the molecules in the field direction produces the results illustrated in fig (2).

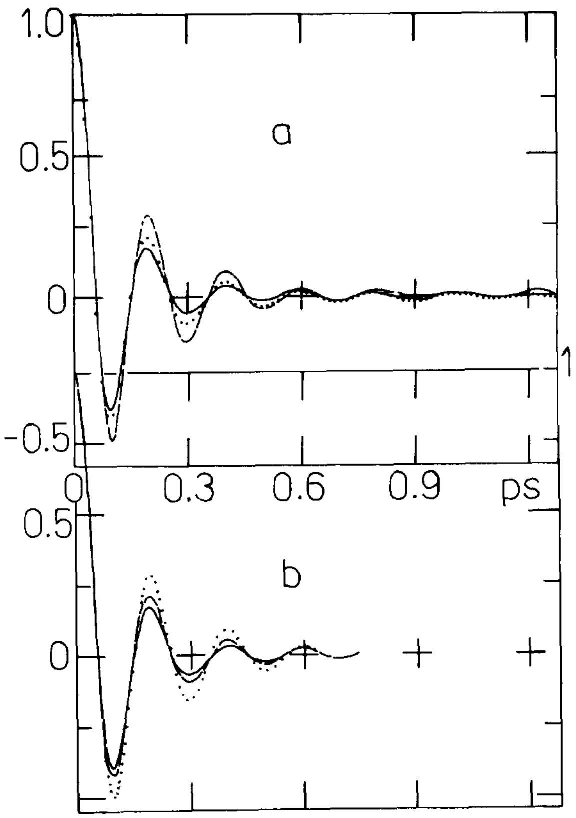

Figure (2)

a) Laboratory frame Coriolis functions in liquid dichloromethane subjected to an intense z axis electric field.

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

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

.... $$\frac{\langle \underset{\sim}{v}(t)\cdot\underset{\sim}{v}(t)\underset{\sim}{\omega}(o)\cdot\underset{\sim}{\omega}(o)\rangle}{\langle \underset{\sim}{v}(o)\cdot\underset{\sim}{v}(o)\underset{\sim}{\omega}(o)\cdot\underset{\sim}{\omega}(o)\rangle}$$

b) As for fig 2(a), moving frame.

The a.c.f. of the complete Coriolis a.c.f. (the l.h.s. of eqn (36) is now highly oscillatory and shows the Grigolini decoupling effect [7], i.e. is longer lived than its field-off counterpart in fig (1). The a.c.f.'s both in frames (x,y,z) and (1,2,3) are now virtually identical, because the molecular Coriolis acceleration is dominated by the oscillatory nature of the molecular angular $\underline{\omega}$. However, it is now easy to see in both frames the distinctly different time dependencies of the components on the r.h.s. of eqn (36). Again, these two components are identical on the scale of fig (2), in both frames.

A NEW CROSS-CORRELATION FUNCTION

I have chosen for illustration from among the new cross-correlation functions of group (11) the simple type:

$$C_{\mathrm{Cross}}(t) = \frac{\langle 2\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t) \cdot \underset{\sim}{v}(o)\rangle}{2\langle\omega^2(o)\rangle^{\frac{1}{2}} \langle v^2(o)\rangle} \qquad (37)$$

conveniently normalised by the denominator. This function has an existence in the moving frame of reference, as illustrated in fig (3). It vanishes in both frames at t = 0, but in marked contrast to the a.c.f. of the Coriolis acceleration the moving frame function (1,2,3) exists (fig 3(a)), but the laboratory frame function (x,y,z) does not (fig 3(b)). The laboratory frame function therefore vanishes by symmetry restrictions akin to the Berne-Pecora Theorem.

An interesting and suggestive result of the computations in the moving frame (fig 3(a)) becomes clear if the roles of $\underline{v}$ and $\underline{\omega}$ are interchanged, thus generating the function:

$$C_1(t) = \langle\underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t) \cdot \underset{\sim}{\omega}(o)\rangle / (\langle v^2(o)\rangle^{\frac{1}{2}} \langle\omega^2(o)\rangle). \qquad (38)$$

This function vanishes in <u>both</u> frames ((1,2,3) and (x,y,z)). The Coriolis acceleration $\underline{v}(t) \times \underline{\omega}(t)$ is unchanged (except for sign) in eqns (37) and (38), but the cross-correlation function $\langle\underset{\sim}{v}(t)\times\underset{\sim}{\omega}(t)\cdot\underset{\sim}{\omega}(o)\rangle$ does not appear in group (11) and the basic equations of motion ((1) and (2)) do not predict its existence, in contrast to function (37). This is strong corroborative evidence therefore for the validity of the initial equations (1) and (2).

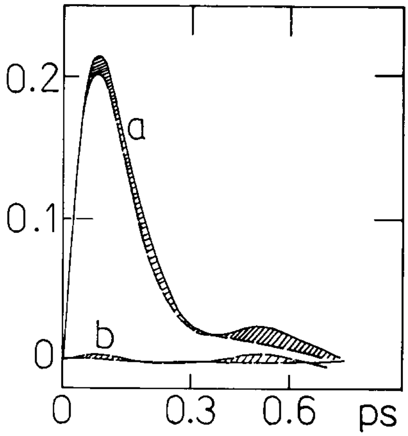

Figure 3

(a)———————— The cross-correlation function:

$$\frac{\langle \underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t) \,.\, \underset{\sim}{v}(o)\rangle}{\langle |\underset{\sim}{\omega}(o)|\; v^2(o)\rangle}$$

in the moving frame.

--------- In contrast, the cross-correlation function

$$\frac{\langle \underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t) \,.\, \underset{\sim}{\omega}(o)\rangle}{\langle |\underset{\sim}{v}(o)|\,\omega^2(o)\rangle}$$

does not exist in the moving frame, because this does not appear in group (11).

(b) The cross-correlation function:

$$\frac{\langle \underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t) \,.\, \underset{\sim}{v}(o)\rangle}{\langle |\underset{\sim}{\omega}(o)|\; v^2(o)\rangle}$$

in the laboratory frame of reference. The Hatched area denotes the difference between two successive segments.

These functions are unknown in the conventional approach to molecular diffusion, using "decoupled" rotational and translational Langevin equations but provide us with subtle new insights to the ensemble statistical correlation between molecular rotation and translation.

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