J. Chem. Soc., Faraday Trans. 2, 1986, 82, 653–663

Diffusion of an Asymmetric-top Molecule in Three Dimensions

Langevin Equations and New, One-particle Cross-correlation Functions

Myron Wyn Evans

Department of Physics, University College of Swansea, Singleton Park, Swansea SA 2 8PP

Langevin equations are developed for an asymmetric-top molecule rotating and translating as a Brownian particle in three dimensions. The translational Langevin equation is written in a rotating frame of reference $(1, 2, 3)'$ whose origin remains fixed at the origin of the laboratory frame (x, y, z). On the other hand, the rotational Langevin equation is written, as usual, in a moving frame $(1, 2, 3)$, that of the molecular principal moments of inertia. There appears in both equations a common deterministic variable, ω, the molecular angular velocity, together with terms such as the molecular Coriolis and centripetal accelerations, which are shown to exist in the laboratory frame of reference (x, y, z). The structure of the two equations suggests the existence of numerous, hitherto unknown, single-molecule cross-correlation functions, both in frame (x, y, z) and frame $(1, 2, 3)$. This is confirmed in this paper by computer simulation of two new types of cross-correlation function involving v, the centre-of-mass linear velocity of the molecule (*i.e.* a Brownian particle) and its own angular velocity, ω. By constructing vector and tensor products, the symmetry properties of these cross-correlation functions are computed and tabulated, both in the absence and presence of intense external electric field of force.

The three-dimensional diffusion in condensed matter of a rigid asymmetric top molecule requires adequate consideration of the statistical correlation between its rotation and translation. It is necessary to develop an adequate analytical theory of rotation and translation at a single-molecule level before embarking on an N-molecule theory. The available analytical theories[1–9] of asymmetric-top diffusion frequently make use of friction cross-coefficients to link the rotational and translational Langevin equations. This is a method first used by Condiff and Dahler,[1] but seems to lead to the result

$$\langle v(t)\omega^{\mathrm{T}}(0)\rangle_{(x,y,z)} \neq 0 \tag{1}$$

in the laboratory frame of reference (x, y, z). Here v is the centre-of-mass linear velocity of the molecule at the instant t and ω the angular velocity at $t = 0$. The result, eqn (1), conflicts with the Berne–Pecora theorem:[2,10]

$$\langle v(t)\omega^{\mathrm{T}}(0)\rangle_{(x,y,z)} = 0 \quad \text{for all } t. \tag{2}$$

Recent computer simulations[11,12] have shown that off-diagonal elements of $\langle v(t)\omega^{\mathrm{T}}(0)\rangle$ exist only in the frame of reference $(1, 2, 3)$ defined by the principal molecular moments of inertia. This frame of reference both rotates and translates with the molecule, and there is a subsequent need to develop an analytical theory for $\langle v(t)\omega^{\mathrm{T}}(0)\rangle$ in this frame. This paper aims to develop Langevin equations[13–15] for this purpose and to use computer simulation to investigate the nature of new auto- and cross-correlation functions suggested by the structure of these equations. It is shown by simulation that numerous new correlation functions indeed exist both in frames (x, y, z) and $(1, 2, 3)$, and these can be used to investigate much more completely the nature of three-dimensional asymmetric-top diffusion in condensed molecular matter.

It is of considerable interest to examine some correlation functions of higher order. We choose initially some functions suggested by the important role of the Coriolis acceleration in rotational dynamics.

Analytical Theory

Consider a frame of reference $(1, 2, 3)'$ whose origin is the same as that of the laboratory frame (x, y, z), but which rotates[16] at an angular velocity ω. This is the same as the angular velocity of the diffusing molecule defined with respect to frame (x, y, z), so that:

$$[\omega]_{(x,y,z)} = [\omega]_{(1,2,3)} = [\omega]_{(1,2,3)'}. \tag{3}$$

We label $(1, 2, 3)'$ as the 'rotating' frame of reference to distinguish it from frame $(1, 2, 3)$, the 'moving' frame that both rotates and translates.[11,12] Frame $(1, 2, 3)$ is defined as rotating with respect to (x, y, z) with the molecular angular velocity ω. It follows immediately that the reverse is true, *i.e.* frame (x, y, z) is rotating with respect to $(1, 2, 3)'$ with the same angular velocity. The only difference between the frame $(1, 2, 3)$ is that the origin of the latter is fixed at the centre of mass of the diffusing molecule, and this origin therefore translates with respect to the origin of (x, y, z) or $(1, 2, 3)'$. The angular velocity in frame $(1, 2, 3)$ is also ω.

An observer rotating in frame $(1, 2, 3)'$ would see only the resultant translational motion of a molecule that is also rotating with angular velocity ω. The observer and the molecule are always rotating, however, at the same rate, and the observer cannot therefore be aware of the molecule's resultant rotation discernible in frame (x, y, z). To an observer in frame $(1, 2, 3)'$ the molecule's diffusion seems to be governed by a translational Langevin equation. The first step in the analysis therefore consists of writing this in frame $(1, 2, 3)'$, which is a 'non-inertial' frame of reference[17] with respect to (x, y, z), the static laboratory frame. From elementary dynamics[16] it follows that

$$[v]_{(x,y,z)} = [v + \omega \times r]_{[1,2,3)'} \tag{4}$$

$$[\dot{v}]_{(x,y,z)} = [\dot{v} + 2\omega \times v + \dot{\omega} \times r + \omega \times (\omega \times r)]_{(1,2,3)'}. \tag{5}$$

On the right-hand side of these equations all the vectors are defined with reference to frame $(1, 2, 3)'$. On the left-hand side they are defined in frame (x, y, z). In eqn (4) and (5) r is the position vector of the molecular centre of mass. It is defined by

$$[\dot{r}]_{(1,2,3)'} = [v]_{(1,2,3)'}. \tag{6}$$

The translational Langevin equation in frame (x, y, z) is well known to be

$$[\dot{v} + \beta_v v]_{(x,y,z)} = [\dot{W}]_{(x,y,z)} \tag{7}$$

where β_v is the translational friction coefficient, a scalar invariant to any frame transformation, and $\dot{W}$ is a Wiener process.[8,14,15] Therefore, from eqn (4), (5) and (7) the translational Langevin equation in frame $(1, 2, 3)'$ is

$$[\dot{v} + 2\omega \times v + \dot{\omega} \times r + \omega \times (\omega \times r)]_{(1,2,3)'} + \beta_v [v + \omega \times r]_{(1,2,3)'} = [\dot{W}]_{(1,2,3)'}. \tag{8}$$

In eqn (8) $[\dot{W}]_{(1,2,3)'}$ is a statistical process generated from the Wiener process $[\dot{W}]_{(x,y,z)}$ by the frame transformation $(x, y, z) \rightarrow (1, 2, 3)'$.

Eqn (8) therefore governs the resultant translational motion of a diffusing molecule's centre of mass to an observer in frame $(1, 2, 3)'$. Note that eqn (8) involves[16,17] (i) the angular velocity $[\omega]_{(1,2,3)'} (= [\omega]_{(x,y,z)})$, (ii) the Coriolis acceleration $[2\omega \times v]_{(1,2,3)'}$, (iii) the centripetal acceleration $[\omega \times (\omega \times r)]_{(1,2,3)'}$, (iv) the 'non-uniform' acceleration $[\dot{\omega} \times r]_{(1,2,3)'}$ and (v) the velocity $[\omega \times r]_{(1,2,3)'}$. The appearance of these terms is basically the reason why there exist certain simple types of[11,12,15] statistical cross-correlation between v and ω in rotating (and moving) frames, but not in frame (x, y, z).

The molecular angular velocity $\boldsymbol{\omega}$, as noted already, is the same in frames (x, y, z), $(1, 2, 3)$ and $(1, 2, 3)'$. We know that the molecule is both translating and rotating, and therefore $\boldsymbol{\omega}$ is governed by both types of motion. A complete description of the diffusional motion of the asymmetric-top molecule must therefore involve eqn (8) supplemented by another Langevin equation describing the resultant rotational diffusion, invisible to an observer in frame $(1, 2, 3)'$.

This is well known[8,13–15] to be the Euler–Langevin equation, which is written in the moving frame $(1, 2, 3)$, and is

$$\begin{aligned} I_1\dot{\omega}_1 - (I_2 - I_3)\omega_2\omega_3 + I_1\beta_1\omega_1 &= I_1\dot{W}_1 \\ I_2\dot{\omega}_2 - (I_3 - I_1)\omega_3\omega_1 + I_2\beta_2\omega_2 &= I_2\dot{W}_2 \\ I_3\dot{\omega}_3 - (I_1 - I_2)\omega_1\omega_2 + I_3\beta_3\omega_3 &= I_3\dot{W}_3. \end{aligned} \tag{9}$$

Everything in eqn (9) is defined in frame $(1, 2, 3)$. I_1, I_2 and I_3 are the principal molecular moments of inertia; ω_1, ω_2 and ω_3 are the components of $[\boldsymbol{\omega}]_{(1,2,3)}$, and $\dot{W}_1$, $\dot{W}_2$ and $\dot{W}_3$ are components of the rotational Wiener process. The components β_1, β_2 and β_3 of the rotational friction tensor are assumed to be diagonal in the same frame $(1, 2, 3)$, as usual. Eqn (8) and (9) constitute a complete description of the diffusion of an asymmetric top that is simultaneously rotating and translating in three dimensions. They can be generalised to involve memory functions[18] in order to try to link them with the fundamental Liouville equation of motion.

By using the two frames $(1, 2, 3)'$ and $(1, 2, 3)$ it is possible to achieve this description without the use of friction cross-terms. Eqn (8) and (9) are also consistent with the Berne–Pecora theorem,[10] eqn (2), because in the laboratory frame (x, y, z) they become statistically independent. Eqn (8) and (9) as written, however, are not statistically independent because of the presence in both of the deterministic variable $\boldsymbol{\omega}$, which is the same in both frames, as noted already:

$$[\boldsymbol{\omega}]_{(1,2,3)} = [\boldsymbol{\omega}]_{(1,2,3)'}.$$

New Correlation Functions for Molecular Diffusion

The structure of eqn (8) and (9) suggests the development of many new methods of correlating statistically the net, three-dimensional, translational and rotational motions of a diffusing asymmetric top, and therefore of achieving a much more complete understanding of its molecular dynamics (m.d.) than hitherto. This can be illustrated by computer simulation,[19] and for this purpose we consider in this paper the motion of 108 CH_2Cl_2 molecules using a conventional m.d. algorithm. Before proceeding to this illustration, however, it is instructive to note that eqn (4) and (5) are fully reversible because of the relativity of frame transformation in elementary dynamics. This means that

$$[\boldsymbol{v}]_{(1,2,3)'} = [\boldsymbol{v} + \boldsymbol{\omega} \times \boldsymbol{r}]_{(x,y,z)} \tag{10}$$

$$[\dot{\boldsymbol{v}}]_{(1,2,3)'} = [\dot{\boldsymbol{v}} + 2\boldsymbol{\omega} \times \boldsymbol{v} + \dot{\boldsymbol{\omega}} \times \boldsymbol{r} + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \boldsymbol{r})]_{(x,y,z)}. \tag{11}$$

Eqn (10) and (11) imply the existence in the laboratory frame itself of new types of accelerations which are encountered in the available theory of molecular diffusion. These accelerations only appear when the inter-relations between $\boldsymbol{r}$, $\boldsymbol{v}$ and $\boldsymbol{\omega}$ are considered and include, for example, a new type of molecular Coriolis acceleration $(2\boldsymbol{\omega} \times \boldsymbol{v})_{(x,y,z)}$. (This should be distinguished carefully from the very well known Coriolis acceleration generated in the quantum theory of vibration–rotation, a purely intramolecular phenomenon.)

The autocorrelation functions of all the laboratory-frame terms of eqn (10) and (11) and of all the rotating-frame terms of eqn (4) and (5) exist, and we have confirmed this

by computer simulation.[20] Furthermore, any vector A that is defined in frame (x, y, z) also exists in frame $(1, 2, 3)$, the moving frame of the molecular principal moments of inertia. This can be shown using the general relations[15]

$$\begin{aligned} A_1 &= e_{1x}A_x + e_{1y}A_y + e_{1z}A_z \\ A_2 &= e_{2x}A_x + e_{2y}A_y + e_{2z}A_z \\ A_3 &= e_{3x}A_x + e_{3y}A_y + e_{3z}A_z . \end{aligned} \tag{12}$$

Here e_1, e_2 and e_3 are unit vectors in axes 1, 2 and 3 of the principal moments of inertia of the asymmetric top. The relations (12) enable us to use computer simulation to calculate any auto- or cross-correlation in frames (x, y, z) and $(1, 2, 3)$.

Vector Cross-correlation functions

Cross-correlation functions (c.c.f.) can be calculated among the various terms of eqn (8), in frame $(1, 2, 3)'$, and also in frames (x, y, z) and $(1, 2, 3)$. The latter two frames are amenable to our method of computer simulation and are used for convenience in this section. Of the very many possible new vector c.c.f. suggested[20,21] by the structures of eqn (8) and (9) we can choose for illustration the following two:

$$C_1(t) = \frac{\langle \omega(t) \times v(t) \cdot \omega(0) \rangle}{\langle \omega^2(0) \rangle \langle v^2(0) \rangle^{1/2}} \tag{13}$$

$$C_2(t) = \frac{\langle v(t) \times \omega(t) \cdot v(0) \rangle}{\langle \omega^2(0) \rangle^{1/2} \langle v^2(0) \rangle} . \tag{14}$$

These are the vector cross-correlation functions between the molecular Coriolis acceleration and, respectively, the same molecule's angular velocity and linear velocity. These two c.c.f. do not appear on the analytical theory of molecular diffusion, but it is shown later in this paper that $C_2(t)$ exists in frame $(1, 2, 3)$ and vanishes in frame (x, y, z). In contrast $C_1(t)$ vanishes in both frames. Further results of this nature are obtained in the presence of an externally applied z axis electric field E.

Tensor Cross-correlation functions[11,12,15]

A great amount of extra information can be obtained by computing tensor c.c.f., exemplified by

$$\mathbf{C}_3(t) = \langle [\omega(t) \times v(t)] \omega^{\mathrm{T}}(0) \rangle \tag{15}$$

$$\mathbf{C}_4(t) = \langle [v(t) \times \omega(t)] v^{\mathrm{T}}(0) \rangle . \tag{16}$$

Each element of the c.c.f. matrix $\mathbf{C}_3(t)$ or $\mathbf{C}_4(t)$ is normalised. In the laboratory frame (x, y, z) there are nine 'elemental' c.c.f.:

$$\begin{bmatrix} (x,x) & (x,y) & (x,z) \\ (y,x) & (y,y) & (y,z) \\ (z,x) & (z,y) & (z,z) \end{bmatrix}$$

and in the moving frame $(1, 2, 3)$ nine more:

$$\begin{bmatrix} (1,1) & (1,2) & (1,3) \\ (2,1) & (2,2) & (2,3) \\ (3,1) & (3,2) & (3,3) \end{bmatrix}$$

In this notation the (x, y) elemental c.c.f. of the matrix $C_3(t)$ would be, for example:

$$C_3^{(x,y)}(t) = \frac{\langle (\boldsymbol{\omega}(t) \times \boldsymbol{v}(t))_x \omega_y(0) \rangle}{\langle \omega_x^2(0) \rangle \langle v_x^2(0) \rangle^{1/2}} \tag{17}$$

and so on. Similarly convenient normalisations can be adopted in the moving frame $(1, 2, 3)$.

The tensors $C_3(t)$ and $C_4(t)$ can be investigated in this way by computer simulation both in the absence and presence of an external, symmetry breaking, electric field, using methods discussed in the following section.

The trace of each tensor c.c.f. is the equivalent vector c.c.f. mentioned in the preceding section. This result has been used in this paper as a check for the self-consistency of the various computations.

Computer-simulation Methods and Algorithms

The classical equations of motion of 108 CH_2Cl_2 molecules were solved numerically with the standard technique of computer simulation,[19] at an input molar volume of 8.0×10^{-5} m^3 mol^{-1} and at a temperature of 296 K. The intermolecular pair potential was modelled with the simplest possible 3×3 site–site potential,[22] consisting of atom–atom Lennard-Jones and charge–charge terms as follows.

$$\frac{\varepsilon}{k}(CH_2—CH_2) = 70.5 \text{ K}$$

$$\sigma(CH_2—CH_2) = 3.96 \text{ Å}$$

$$q_{CH_2} = 0.302|e|$$

$$\frac{\varepsilon}{k}(Cl—Cl) = 173.5 \text{ K}$$

$$\sigma(Cl—Cl) = 3.35 \text{ Å}$$

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

The correlation functions were computed with running time averaging over segments of *ca.* 1000 records (3000 time steps of 5×10^{-15} s each.) The noise level in the simulation can be gauged by the difference between the results from two consecutive segments.

In addition to these standard field-off simulations a static electric field was applied to the liquid sample[23] in the z axis of the laboratory frame (x, y, z). This was strong enough to align the 108-molecule sample so as almost to saturate the Langevin function, producing the result $\langle e_{\mu z} \rangle = 0.90 \pm 0.05$, where e_μ is a unit vector in the μ axis of the molecular principal moment of inertia frame. The μ axis is that of the resultant molecular dipole moment, $\boldsymbol{\mu}$. This alignment is produced by the torque $\boldsymbol{\mu} \times \boldsymbol{E}$ on each molecule, where $\boldsymbol{E}$ is the applied electric field.

After initial application of the electric field the system is allowed to equilibrate, and subsequent segments of *ca.* 1000 records used to compute field-on vector and tensor cross-correlation functions. The heating effects produced by the presence of an extra field of force are dissipated at equilibrium using the standard methods of temperature rescaling, with the temperature allowed to fluctuate by 25 K either side of the mean input temperature of 296 K. This ensures that the only effect of the electric field is to increase the potential energy,[24] *i.e.* to make it less negative. The kinetic energy remains the same[24] in the field-off and field-on cases because the sample is thermostatted by the temperature rescaling routine. The algorithm is TRI 2.

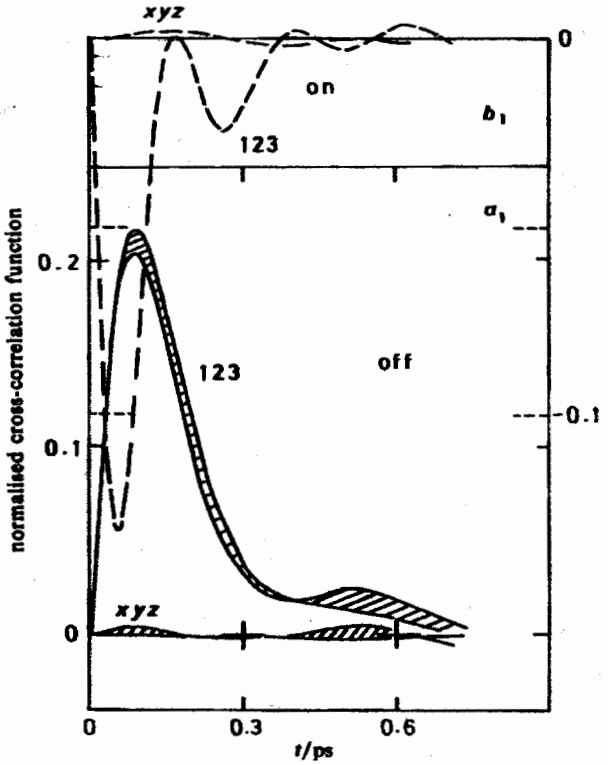


Fig. 1. (*a*) The vector cross-correlation function

$$\frac{\langle \omega(t) \times v(t) \cdot v(0) \rangle}{\langle v^2(0) \rangle \langle \omega^2(0) \rangle^{1/2}}$$

for $E = 0$ in frames (1, 2, 3) and (x, y, z) (left-hand ordinate scale). The hatched area denotes the difference between results from two consecutive segments of 3000 time steps each (see text). (*b*) (- - -) The vector cross-correlation function

$$\frac{\langle v(t) \times \omega(t) \cdot v(0) \rangle}{\langle v^2(0) \rangle \langle \omega^2(0) \rangle^{1/2}}$$

for $E > 0$ in frames (1, 2, 3) and (x, y, z) [right-hand (dotted) ordinate scale].

Illustrative Results

The results of this computer simulation show that the vector c.c.f. $C_1(t)$ vanishes for all t in both frames (x, y, z) and (1, 2, 3), both in the presence and absence of the electric field E. The trace of the corresponding tensor c.c.f. $C_3(t)$ is thus always zero, *i.e.* the three diagonal elements of this tensor c.c.f. are always zero. This has been checked by actually computing the diagonal elements of $C_3(t)$ separately.

In contrast, fig. 1 shows that the vector c.c.f. $C_2(t)$ exists in frame (1, 2, 3) but vanishes in the noise of the two segments used for this computation in frame (x, y, z). This result is true also in the presence of the electric field E. The field-on c.c.f. are also illustrated in fig. 1. The trace of the equivalent tensor c.c.f. $C_4(t)$ is therefore finite in frame (1, 2, 3) both in the presence and absence of an external electric field E.

Turning now to the off-diagonal c.c.f. of tensors $C_3(t)$ and $C_4(t)$ a considerable amount of new statistical information becomes available about the dynamical interrela-

Table 1. Symmetry patterns for single-molecule tensor c.c.f.

correlation matrix	frame of reference			
	(x, y, z)	$(x, y, z)+\boldsymbol{E}$	$(1, 2, 3)$	$(1, 2, 3)+\boldsymbol{E}$
$\langle[\boldsymbol{\omega}(t)\times\boldsymbol{\omega}(t)]\boldsymbol{v}^{\mathrm{T}}(0)\rangle$	$\begin{bmatrix}\delta&\delta&\delta\\ \delta&\delta&\delta\\ \delta&\delta&\delta\end{bmatrix}$	$\begin{bmatrix}\delta&\delta&\delta\\ \delta&\delta&\delta\\ \delta&\delta&\delta\end{bmatrix}$	$\begin{bmatrix}+&\delta&\delta\\ \delta&+&\delta\\ \delta&\delta&+\end{bmatrix}$	$\begin{bmatrix}+&\delta&\delta\\ \delta&+&\delta\\ \delta&\delta&+\end{bmatrix}$
$\langle[\boldsymbol{\omega}(t)\times\boldsymbol{v}(t)]\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$	$\begin{bmatrix}\delta&+&+\\ +&\delta&+\\ +&+&\delta\end{bmatrix}$	$\begin{bmatrix}\delta&+&\delta\\ +&\delta&\delta\\ +&+&\delta\end{bmatrix}$	$\begin{bmatrix}\delta&\delta&\delta\\ \delta&\delta&\delta\\ \delta&\delta&\delta\end{bmatrix}$	$\begin{bmatrix}\delta&\delta&\delta\\ \delta&\delta&+\\ \delta&+&\delta\end{bmatrix}$

tion between the vectors $\boldsymbol{v}$ and $\boldsymbol{\omega}$, in both frames of reference, both in the presence and absence of an external electric field. This information is summarised conveniently in table 1 in terms of eight 3×3 matrices, a total of 72 new cross-correlation functions. In table 1 the symbol δ means that that particular cross-correlation function vanishes in the noise for all t, and the symbol + means it exists above the noise for $0\leqslant t<\infty$. It is interesting to note the symmetry patterns of these matrices in the frames (x, y, z) and $(1, 2, 3)$.

The most significant result summarised in table 1 seems to be that off-diagonal elements of $C_3(t)$ and $C_4(t)$ exist in the laboratory frame, (x, y, z) in the absence of an electric field. (In the presence of the field two off-diagonal elements seem to vanish in the computer noise, but may exist and be very much smaller in magnitude in this case.)

This means that we immediately have a new result, to supplement the well known[10] Berne–Pecora theorem, eqn (2). This theorem is simply stated as

$$\langle[\boldsymbol{\omega}(t)\times\boldsymbol{v}(t)]\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle\neq\boldsymbol{0}\quad\text{for } 0\leqslant t<\infty \tag{18}$$

in the laboratory frame (x, y, z). Eqn (18) is a significant result because it is valid directly in frame (x, y, z) and therefore is a direct measure of the statistical correlation between $\boldsymbol{v}$ and $\boldsymbol{\omega}$. There seems to be no analytical theory in the literature to match these computed off-diagonal elements, summarised in table 1 and illustrated in fig. 2 both for $\boldsymbol{E}=\boldsymbol{0}$ and $\boldsymbol{E}>\boldsymbol{0}$. The analytical theory of molecular diffusion underpins the interpretation[8] of several types of spectra, and theorem (18) implies that these data must be reinterpreted to account for the interdependence of $\boldsymbol{v}$ and $\boldsymbol{\omega}$. Eqn (18) also invalidates Debye's theory of 'rotational' diffusion,[8] a historically popular approach to spectral interpretation in the investigation of molecular diffusion. Eqn (18) shows that there is in fact no such thing as 'purely rotational' or 'purely translational' diffusion. It shows that it is impossible to ignore the direct, mutual influence of $\boldsymbol{v}$ and $\boldsymbol{\omega}$ in frame (x, y, z) or in any frame of reference.

The matrix pattern (table 1) for $C_3(t)$ changes in frame $(1, 2, 3)$. For $\boldsymbol{E}=\boldsymbol{0}$ no elements seem to exist above the noise of two segments, but for $\boldsymbol{E}>\boldsymbol{0}$ off-diagonal elements appear in this frame. None of these results is explicable with contemporary theories of molecular diffusion. In this context one would have to develop analytical solutions for eqn (8) and (9), a very formidable problem[13–15] bypassed in this paper with standard computer simulation. Strictly speaking, therefore, any future interpretation of spectral data on molecular diffusion should be made with computer simulation in the continued absence of adequate analytical theory in this area of chemical physics.

The symmetry properties of $C_4(t)$ are wholly different from those of $C_3(t)$, as summarised in table 1. For $C_4(t)$ the matrices are slightly more sparse; the most significant feature is the existence of all three diagonal elements in frame $(1, 2, 3)$ both in the absence and presence of $\boldsymbol{E}$. This is implied, of course, by fig. 1, and the normalised

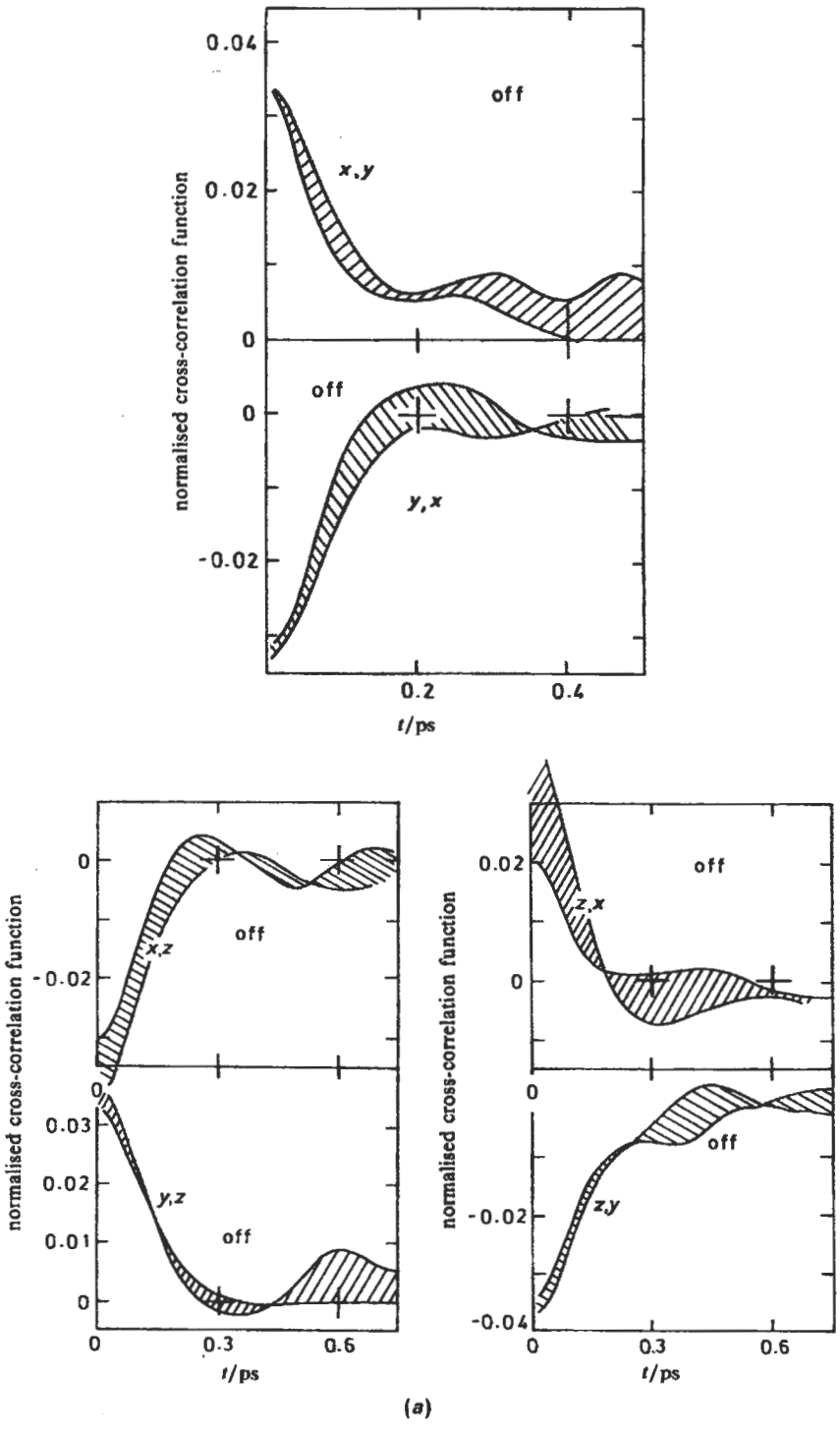
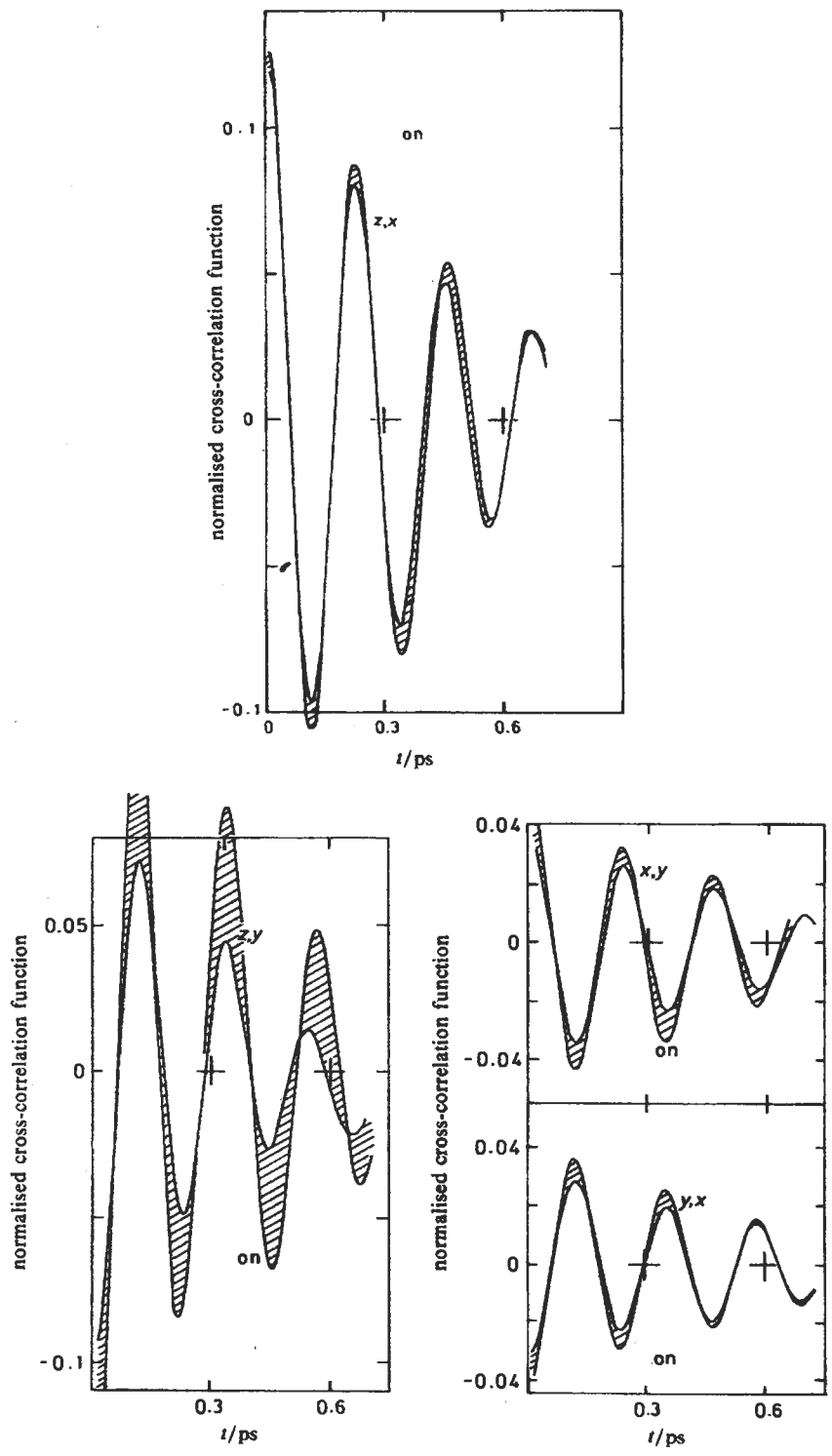
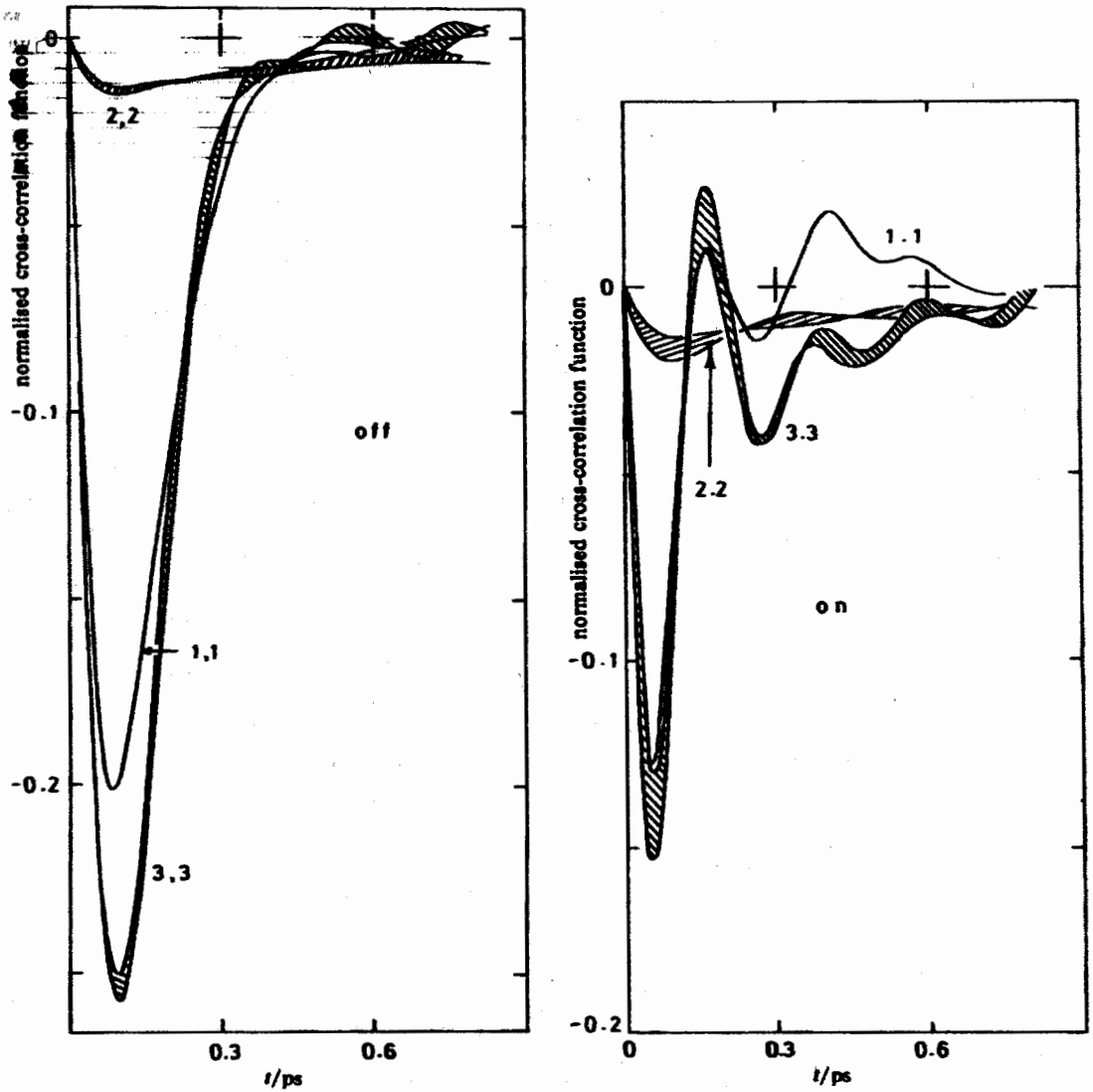


Fig. 2. (*a*) Illustration of the off-diagonal elements of $\langle[\boldsymbol{\omega}(t)\times\boldsymbol{v}(t)]\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ in laboratory frame (x, y, z) for $E \geq 0$. (*b*) As for (*a*), moving frame (1, 2, 3). (*c*) The diagonal elements of the cross-correlation function $\langle[\boldsymbol{v}(t)\times\boldsymbol{\omega}(t)]\boldsymbol{v}^{\mathrm{T}}(0)\rangle$ in the moving frame (1, 2, 3) for $E \geq 0$.


0.1
on
z,x
normalised cross-correlation function
0
-0.1
0
0.3
0.6
t/ps
0.05
z,y
0
on
-0.1
0.3
0.6
t/ps
0.04
x,y
0
-0.04
on
0.04
y,x
0
on
-0.04
0.3
0.6
t/ps

(*b*)

Fig. 2 (*cont.*)



(*c*)

Fig. 2 (*cont.*)

magnitude of these elements is greater than those of the off-diagonal elements, (fig. 2) of $C_3(t)$. The statistical correlation in this case seems to be 'concentrated', therefore, into these diagonal elements, thus giving rise to the vector c.c.f. $C_2(t)$. In contrast, the statistical correlation in $C_3(t)$ is 'spread out' over the off-diagonal elements of the complete tensor, and the diagonal elements vanish. Therefore the vector product $C_1(t)$ also vanishes (in both frames) for $E \geqslant 0$.

If one finally takes into consideration all the various new terms in eqn (8), together with the well known eqn (9), it is possible to generate many hundreds of new (*i.e.* previously unknown), but at the same time fundamental, single-molecule, cross-correlation functions of time involving the various accelerations and velocities in frames (x, y, z) and $(1, 2, 3)$. This simple exercise shows how much has been lost by the historical reliance on the mathematical convenience of 'rotational' diffusion,[8] where v is undefined

(and therefore r is also undefined). This is true in general for the various condensed states of molecular matter.

Parity Reversal Symmetry in Frame (x, y, z)

In an isotropic, achiral medium the hamiltonian is invariant to parity reversal. Ryckaert *et al.* have shown that this implies the relation

$$\langle X(t)X^{\mathrm{T}}(0)\rangle M = M\langle X(t)X^{\mathrm{T}}(0)\rangle \tag{19}$$

where

$$X(\Gamma') = MX(\Gamma).$$

Here $X(\Gamma')$ is dependent on the phase space variable Γ' generated from Γ by an operation such as parity inversion in frame (x, y, z). Eqn (19) implies that if the parity inversion symmetry of two variables is different in the laboratory frame, then they are incorrelated in that frame for all t. Therefore the results of table 1 can be explained only on the basis that the parity of $v(t)\times\omega(t)$ and that of $\omega(0)$ obey eqn (19) for the non-vanishing elements of the cross-correlation matrix. For $E \neq 0$ eqn (19) no longer applies.

The University of Wales is thanked for a Fellowship.

References

1 D. W. Condiff and J. S. Dahler, *J. Chem. Phys.*, 1966, **44**, 3988.
2 N. K. Ailawadi, B. J. Berne, and D. Forster, *Phys. Rev. A*, 1971, **3**, 1462.
3 L. P. Hwang and J. H. Freed, *J. Chem. Phys.*, 1975, **63**, 118; 4017.
4 P. G. Wolynes and J. M. Deutch, *J. Chem. Phys.*, 1977, **67**, 733.
5 G. T. Evans, *Mol. Phys.*, 1978, **36**, 1199.
6 U. Steiger and R. F. Fox, *J. Math. Phys.*, 1982, **23**, 296.
7 G. van der Zwan and J. T. Hynes, *Physica*, 1983, **121A**, 227.
8 For a review see: M. W. Evans, G. J. Evans, W. T. Coffey and P. Grigolini, *Molecular Dynamics* (Wiley Interscience, New York, 1982), chap. 5.
9 E. Dickinson, *Annu. Rep. Chem. Soc., Part C*, 1983, 3.
10 B. J. Berne and R. Pecora, *Dynamic Light Scattering With Reference to Physics, Chemistry and Biology* (Wiley Interscience, New York, 1976).
11 J. P. Ryckaert, A. Bellemans and G. Ciccotti, *Mol. Phys.*, 1981, **44**, 979.
12 M. W. Evans, *Phys. Rev. Lett.*, 1983, **50**, 371.
13 A. Morita, *J. Phys. D*, 1978, **11**, 1357.
14 J. T. Lewis, J. McConnell and B. K. P. Scaife, *Proc. R. Irish Acad., Part A*, 1976, **76**, 43.
15 W. T. Coffey, M. W. Evans and P. Grigolini, *Molecular Diffusion* (Wiley Interscience, New York, 1984).
16 M. R. Spiegel, *Theory and Problems of Vector Analysis* (Schaum Publishing Co., New York, 1959), p. 53.
17 L. D. Landau and E. M. Lifshitz, *Mechanics* (Pergamon Press, Oxford, 3rd edn, 1976), p. 5ff.
18 *Memory Function Approaches to Dynamical Problems in Condensed Matter*, vol. 62 and 63 of *Advances in Chemical Physics*, ed. M. W. Evans, P. Grigolini and G. Pastori-Parravicini, series ed. I. Prigogine and S. A. Rice (Wiley Interscience, New York, 1985).
19 For a review of contemporary computer simulation methods see D. Fincham and D. Heyes, in ref. (18), vol. 63, chap. 6.
20 M. W. Evans, *Phys. Rev. Lett.*, 1985, **55**, 1551.
21 M. W. Evans and G. J. Evans, *Phys. Rev. A*, submitted for publication; *Phys. Rev. Lett.*, 1985, **55**, 818.
22 Originally described in M. Ferrario and M. W. Evans, *Chem. Phys.*, 1982, **72**, 141.
23 Using a method originally described in M. W. Evans, *J. Chem. Phys.*, 1982, **76**, 5473; 5480; **77**, 108; 1983, **79**, 5403; **78**, 925, and developed considerably in ref. (18), vol. 62, chap. 5 and 6.
24 M. W. Evans, *Phys. Rev. A*, 1984, **30**, 2062; 1985, **31**, 3947.

Paper 5/1320; *Received* 31*st July*, 1985