112

Vol. A62 (1982) *ACTA PHYSICA POLONICA* No 1–2

OPERATOR THEORY OF ANGULAR MOMENTUM AND ORIENTATIONAL AUTO-CORRELATION FUNCTIONS

BY M. W. EVANS

Chemistry Department, University College, Aberystwyth, Wales*

(Received July 24, 1981; final version received November 19, 1981)

The rigorous relation between the orientational auto-correlation function and the angular momentum autocorrelation function is described in two cases of interest. Firstly when a description of the complete zero–THz spectrum is required from the Mori continued fraction expansion for the angular momentum autocorrelation function and secondly when rotation/translation effects are important. (*i*) The Mori–Evans theory of 1976, relying on the simple Shimizu relation is found to be essentially unaffected by the higher order corrections recently worked out by Ford and co-workers in the Markov limit. (*ii*) The mutual interaction of rotation and translation is important in determining the details of both the orientational and angular momentum a.c.f.'s in the presence of sample anisotropy or a symmetry breaking field. In this case it is essential to regard the angular momentum a.c.f. as non-Markovian and methods are developed to relate this to the orientational a.c.f. in the presence of rotation/ /translation coupling.

PACS numbers: 05.20.Dd

1. *Introduction*

In this paper we consider the rigorous mathematical relation between the orientational autocorrelation function $\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0)\rangle$ and angular velocity a.c.f. $\langle \omega(t) \cdot \omega(0)\rangle$ of a diffusing molecule. We consider two special cases in detail. The first is when $\langle \omega(t) \cdot \omega(0)\rangle$ is governed by a Mori–Evans type continued fraction expansion [1], the second when rotation/translation effects [2] are included in the equations of motion for $\langle \omega(t) \cdot \omega(0)\rangle$.

The first order and subsequent order corrections to $\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0)\rangle$ of Mori–Evans theory are evaluated and found to be small in cases of experimental interest hitherto considered [3]. It may be the case, of course, that these corrections are important in zero-THz spectra yet to be discovered. However, for practical purposes it seems that the formulation [1] by Evans in 1976 is a good enough approximation (i.e. the correction is two orders of magnitude within the experimental uncertainty in far infra-red power absorption coefficient).

---

* Address: Edward Davies Chemical Laboratory, University College of Wales, Aberystwyth SY23 1NE, Wales, UK.

Rotation/translation is a factor for direct consideration, secondly, whenever the symmetry of the sample is broken by an external field. For example, when a dipolar molecular liquid is treated with an intense electric field the resulting torque on each dipole breaks the parity invariance of the total hamiltonian. This means that mixed autocorrelation functions such as $\langle \boldsymbol{J}(t) \cdot \boldsymbol{T}_q(0) \rangle$ no longer vanish for $t > 0$. This has been demonstrated recently by Evans [4] using computer simulation. We have denoted by $\boldsymbol{J}$ the resultant angular momentum vector of the molecule in the laboratory frame at any instant $t \cdot \boldsymbol{T}_q$ is the molecular torque at the arbitrary initial $t = 0$ of the equilibrium running time average $\langle\ \rangle$. At thermodynamic equilibrium this is equal to the phase space average over the relevant probability density function [2]. The implications of this hitherto unsuspected result are widespread, not only for the theories of birefringence transients [5] (induced by electric, magnetic or laser fields) but also for the molecular dynamics of liquid crystals [6]. The alignment of the nematic by low intensity electric or magnetic fields is an obvious case where $\langle \boldsymbol{J}(t) \cdot \boldsymbol{T}_q(0) \rangle$ exists for $t > 0$, but has been neglected theoretically. Even in the isotropic phase considered by Evans in his computer simulation [4] $\langle \boldsymbol{J}(t) \cdot \boldsymbol{T}_q(0) \rangle$ is comparable in order of magnitude with $\langle \boldsymbol{J}(t) \cdot \boldsymbol{J}(0) \rangle$ or $\langle \boldsymbol{T}_q(t) \cdot \boldsymbol{T}_q(0) \rangle$ in normalised units. In the nematic phase, where the external symmetry breaking torque is "amplified" by intermolecular interaction, mixed autocorrelation functions such as $\langle \boldsymbol{J}(t) \cdot \boldsymbol{T}_q(0) \rangle$ must surely assume a primary importance.

The paper is organised as follows. In Section 1 we develop the rigorous operator theory of Ford et al. [7], to deal with the Mori–Evans continued fraction approximation to $\langle \omega(t) \cdot \omega(0) \rangle$ and with continued fractions in a Laplace space of the general type first suggested by Mori [8]. In Section 2 we develop some arguments for the consideration of rotation/translation as opposed to just rotation in the theory of molecular diffusion in the presence of symmetry breaking fields. Section 3 deals with the numerical results and discussion.

2. *Theory*

Recently Ford et al. [7] have considered the solution of a stochastic differentiale quation of the form:

$$\dot{x}(t) = \varepsilon \Omega(t) x(t), \tag{1}$$

where ε is a parameter and $\Omega(t)$ a stochastic operator, as defined by van Kampen [9]. The solution of Eq. (1) is dictated by the equation:

$$\frac{d}{dt}\langle x(t) \rangle = (\varepsilon^2 \Omega^{(2)}(t) + \varepsilon^4 \Omega^{(4)}(t) + \ldots) \langle x(t) \rangle, \tag{2}$$

where $\Omega^{(n)}(t)$ is a non-stochastic operator. This is provided

(*i*) the stochastic operator $\Omega(t)$ is a centred, Gaussian, random variable.

(*ii*) $\Omega(t)$ refers to a stationary state and obeys a relation

$$\langle \Omega(t_k) \Omega(t_e) \rangle = f(t_k - t_e) 1 \tag{3}$$

with **1** the identity operator.

(iii)
$$\langle \Omega(t_{i_1})\Omega(t_{i_2}) \ldots \Omega(t_{i_{2n-1}})\rangle = 0 \tag{4}$$

(iv)
$$\langle \Omega(t_{i_1})\Omega(t_{i_2}) \ldots \Omega(t_{i_{2n}})\rangle$$

is equal to the sum of the mean values when pairs of the Ω's are linked in all possible different ways, mean values being taken for linked pairs.

In Eq. (2) the $\Omega^{(2)}(t)$ and $\Omega^{(4)}(t)$ operators are defined respectively as:

$$\begin{aligned}\Omega^{(2)}(t) &= \int_0^t [\langle \Omega(t)\Omega(t_1)\rangle - \langle \Omega(t)\rangle \langle \Omega(t_1)\rangle]\, dt_1 \\ &\equiv \int_0^t [\langle 12\rangle - \langle 1\rangle \langle 2\rangle]\, dt_1 = \int_0^t \langle 12\rangle\, dt_1\end{aligned} \tag{5}$$

and

$$\Omega^{(4)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 [\langle 1234\rangle - \langle 12\rangle \langle 34\rangle - \langle 13\rangle \langle 24\rangle - \langle 14\rangle \langle 23\rangle]. \tag{6}$$

Eqs. (1) to (6) may be used to solve for the orientational autocorrelation function $\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0)\rangle$ of an asymmetric molecule undergoing isotropic rotational diffusion. In this case Evans ([1, 2], 1976) the relevant equation of motion is the generalised Langevin equation (or Liouville equation);

$$I_r \dot{\omega}(t) = -I_r \int_0^t K(t-\tau)\omega(\tau)\, d\tau + I_r \frac{dW}{dt}, \tag{7}$$

where I_r is a reduced moment of inertia and $\boldsymbol{\omega}$ the angular velocity vector of the molecule regarded as an equivalent rotating sphere with an embedded dipole vector along one of its diameters. $I_r dW/dt$ is a random driving torque. The use of Eq. (7) simplifies the algebra associated with the rotational Brownian motion of an asymmetric top to that associated with the spherical top whilst retaining the physical picture associated with the diffusion of a dipolar molecule. This is essentially the device used by Debye [10], to whose equation of motion Eq. (7) reduces when the memory function K is a delta function in time.

Mori [8] has shown that the solution of Eq. (7) may be expressed in Laplace space (p) as an infinite continued fraction:

$$C(p) = L\langle \omega(t) \cdot \omega(0)\rangle = \cfrac{\langle \omega(0)^2\rangle}{p + \cfrac{K_0(0)}{p + \cfrac{K_1(0)}{\vdots}}} \tag{8}$$

This may be inverted, or back transformed, using the Heaviside expansion theorem [11] to produce:

$$C(t) = \langle \omega(t) \cdot \omega(0) \rangle = \langle \omega^2(0) \rangle \sum_{n=1}^{m} \frac{A(a_n)}{B^1(a_n)} e^{a_n t}; \; m \to \infty \tag{9}$$

Here a_n are the roots (in general complex) of the polynomial which makes up the denominator of Eq. (8) when expressed as the fraction $A(p)/B(p)$. If B is a polynomial of order m, then it follows from Eq. (8) that A is a polynomial of order $m-1$. These finite polynomials can be produced by truncating the continued fraction assuming that:

$$K_{m-2}(t) = K_{m-2}(0) \exp(-\gamma t). \tag{10}$$

With $m = 3$ Reid et al. have shown [3] that the resulting expression for $C(t)$ is a useful representation of the absorption of dipolar molecules from static frequencies to far infra-red. In that work an approximate relation was used to link $C(t)$ to the orientational autocorrelation function $\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0) \rangle$:

$$\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0) \rangle = \exp\left[-\frac{2kT}{I} \int_0^t dt_1 \int_0^t dt_2 C(t_1 - t_2) \right], \tag{11}$$

where $I = I_r/2$ is the moment of inertia of the rotating dipolar molecule when regarded as a Debye isotropic diffuser [10]. If the molecule has $\boldsymbol{u}$ along the $\boldsymbol{a}$ (least axis of inertia, then $1/I_r = 1/I_b + 1/I_c$. In general:

$$\mu^2 I_r^{-1} = (\mu_b^2 + \mu_c^2) I_a^{-1} + (\mu_a^2 + \mu_c^2) I_b^{-1} + (\mu_a^2 + \mu_b^2) I_c^{-1}$$

for the asymmetric top where a, b, and c denote the principal moment of inertia axes. Eq. (11) was, however, derived on the basis of the Shimizu expansion [12] for linear molecules, in turn based on an expansion in terms of cumulant averages. Lewis et al. [7b] and Ford et al. [7a] have produced a rigorous relation based on Eq. (1), and part of the purpose of this section is to generalise this to deal with Eq. (7) where K is in general not a delta function. We shall be concerned with solutions of the continued fraction of the form taken by Eq. (9).

Ford et al. have shown that Eq. (11) is an approximate form of the rigorous relation between $\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0) \rangle$ and $\langle \omega(t) \cdot \omega(0) \rangle$ based on the generally valid kinematical equation:

$$\dot{\boldsymbol{u}}(t) = \omega(t) \times \boldsymbol{u}(t), \tag{12}$$

or in operator form of Eq. (1)):

$$\dot{\boldsymbol{u}}(t) = (\omega(t) \cdot \boldsymbol{\sigma}) \boldsymbol{u}(t), \tag{13}$$

with:

$$\sigma_1 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}; \quad \sigma_2 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}; \quad \sigma_3 = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

Eqs. (1) to (6) then imply:

$$\langle \boldsymbol{u}(t)\cdot \boldsymbol{u}(0)\rangle = \exp\left\{-2\left[\frac{kT}{I}I^{(2)}(t)+\left(\frac{kT}{I}\right)^2 I_2^{(4)}(t)\right.\right.$$
$$+\left(\frac{kT}{I}\right)^3 (I_3^{(6)}(t)+4I_4^{(6)}(t))+\left(\frac{kT}{I}\right)^4 (I_4^{(8)}(t)+8I_5^{(8)}(t)$$
$$\left.\left.+8I_7^{(8)}(t)+18I_8^{(8)}(t))+\ldots\right]\right\}, \tag{14}$$

where the $I^{(n)}$ factors are repeated integrals defined in the original paper by Ford et al. [7a] in their case $\langle \omega(t)\cdot\omega(0)\rangle = \frac{2kT}{I}\exp(-\beta t)$. Here β is the friction coefficient of the rotational Langevin equation 2:

$$I\dot{\omega} = -I\beta\omega + I\dot{W} \tag{15}$$

We note that solutions of the form of Eq. (9) for $\langle \omega(t)\cdot\omega(0)\rangle$ are sums of complex exponentials. In this case $\langle \boldsymbol{u}(t)\cdot \boldsymbol{u}(0)\rangle$ will take the form of Eq. (14). In this notation the approximate expression [1] by Evans (1976) can be written as:

$$\langle \boldsymbol{u}(t)\cdot \boldsymbol{u}(0)\rangle = \exp\left[-\frac{2kT}{I}I^{(2)}(t)\right], \tag{16}$$

where

$$I^{(2)}(t) = \int_0^t dt_1 \int_0^t dt_2 \sum_{n=1}^{3} \frac{A(a_n)}{B^1(a_n)}\, e^{a_n(t_1-t_2)}, \tag{17}$$

$$B(a_3) = p^3+\gamma p^2+p(K_0+K_1)+\gamma K_0$$
$$\equiv (p-a_1)(p-a_2)(p-a_3),$$
$$A(a_3) = p^2+p\gamma+K_1,$$

with γ defined by the truncation:

$$K_1(t) = K_1(0)\exp(-\gamma t). \tag{18}$$

Reid and Evans [3] have evaluated this result with microwave and for infra-red data for thirty-nine dipolar solutes in decalin solution. After considerable algebra the approximate solution, Eq. (16), can be extended to the result (14) with the $I^{(n)}$ integrals defined in the appendix.

Using these results and expanding the exponential in Eq. (14) we have the series:

$$\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle = 1-2\left(\frac{kT}{I}\right)I^{(2)}(t)+\left(\frac{kT}{I}\right)^2[4I_1^{(4)}(t)+6I_2^{(4)}(t)]$$

$$-\left(\frac{kT}{I}\right)^3[8I_1^{(6)}(t)+24I_2^{(6)}(t)+18I_3^{(6)}(t)+20I_4^{(6)}(t)]$$

$$+\left(\frac{kT}{I}\right)^4[16I_1^{(8)}(t)+72I_2^{(8)}(t)+108I_3^{(8)}(t)+54I_4^{(8)}(t)$$

$$+120I_5^{(8)}(t)+80I_6^{(8)}(t)+80I_7^{(8)}(t)+100I_8^{(8)}(t)]-\ldots. \tag{19}$$

From this asymptotic expansion and the further relation:

$$\langle \dot{\boldsymbol{u}}(t)\cdot\dot{\boldsymbol{u}}(0)\rangle \frac{-d^2}{dt^2}\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle \tag{20}$$

we may obtain an expression for the far infra-red power absorption coefficient $\alpha(\omega)$ which is the Fourier transform of the rotational velocity correlation function of Eq. (20). Using

$$L\left(-\frac{d^2}{dt^2}F(t)\right) = -p^2\tilde{F}(p)+pF(0)+F'(0)$$

we have:

$$L(\langle\dot{\boldsymbol{u}}(t)\cdot\dot{\boldsymbol{u}}(0)\rangle) = p(1-p^2\tilde{F}(p)) = p(1-pL\langle\boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle)$$

$$= p^2\left\{\frac{2kT}{I}L(I^{(2)}(t))-\left(\frac{kT}{I}\right)^2[4L(I_1^{(4)}(t))+6L(I_2^{(4)}(t))]\right.$$

$$+\left(\frac{kT}{I}\right)^3[8LI_1^{(6)}(t)+24LI_2^{(6)}(t)+18LI_3^{(6)}(t)+20LI_4^{(6)}(t)]$$

$$-\left(\frac{kT}{I}\right)^4[16LI_1^{(8)}(t)+72LI_2^{(8)}(t)+108LI_3^{(8)}(t)$$

$$+54LI_4^{(8)}(t)+120LI_5^{(8)}(t)+80LI_6^{(8)}(t)+80LI_7^{(8)}(t)$$

$$\left.+100LI_8^{(8)}(t)]+\ldots\right\}. \tag{21}$$

This is however a slowly convergent series which would need several terms before a realistic spectrum is obtained. Rather than consider this series we will use a more direct method of computing the far infra-red spectrum from the first order correction term only, i.e.

$$\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle = \exp\left[-2\left(\frac{kT}{I}I^{(2)}(t)+\left(\frac{kT}{I}\right)^2 I_2^{(4)}(t)\right)\right] \tag{22}$$

and compare this with the simple Mori–Evans–Shimizu equation (16). We aim to see what is the effect of terms non-linear in kT/I on the far infra-red spectrum.

The most convenient expression for $I^{(2)}(t)$ to extract a far infra-red spectrum is:

$$\begin{gathered} I^{(2)}(t) = C_1 t + A_0 e^{-(\alpha_1 - i\beta)t} + B_0 e^{-(\alpha_1+i\beta)t} + C_0 e^{-\alpha_2 t} + D_0 \\ A_0 = \tfrac{1}{2}(A_x - iB_x); \quad B_0 = \tfrac{1}{2}(A_x + iB_x); \end{gathered} \tag{23}$$

with

$$C_0 = \frac{\Gamma(1+\Gamma)^{-1}}{\alpha_2^2}; \quad D_0 = -A_0 - B_0 - C_0.$$

These are related to the coefficients γ, K_0 and K_1 of Eqs. (8) and (10) by:

$$\begin{aligned} \gamma &= 2\alpha_1 + \alpha_2; \\ K_0 + K_1 &= 2\alpha_1\alpha_2 + \beta^2 + \alpha_1^2; \\ \gamma K_0 &= (\alpha_1^2 + \beta^2)\alpha_2; \\ \Gamma &= \frac{2\alpha_1(\alpha_1^2+\beta^2)}{\alpha_2(\beta^2+\alpha_2^2-3\alpha_1^2)}. \end{aligned} \tag{24}$$

These relations further imply that:

$$\begin{aligned} a_1 &= \alpha_2; \\ a_2 &= \alpha_1 + i\beta; \\ a_3 &= \alpha_1 - i\beta; \\ A_1 &= \alpha_2^2 - \gamma\alpha_2 + K_1; \\ A_2 &= (\alpha_1+i\beta)^2 - \gamma(\alpha_1+i\beta) + K_1; \\ A_3 &= (\alpha_1-i\beta)^2 - \gamma(\alpha_1-i\beta) + K_1; \\ B_1' &= 3\alpha_2^2 - 2\alpha_2\gamma + K_0 + K_1; \\ B_2' &= 3(\alpha_1+i\beta)^2 - 2\gamma(\alpha_1+i\beta) + K_0 + K_1; \\ B_3' &= 3(\alpha_1-i\beta)^2 - 2\gamma(\alpha_1-i\beta) + K_0 + K_1; \end{aligned}$$

$$A_x = \frac{3\alpha_1^2+2\alpha_1\alpha_2\Gamma-\beta^2}{(1+\Gamma)(\alpha_1^2+\beta^2)^2};$$

$$B_x = \frac{3\beta^2\alpha_1+\Gamma\alpha_2\beta^2-\alpha_1^3-\Gamma\alpha_1^2\alpha_2}{\beta(1+\Gamma)(\alpha_1^2+\beta^2)^2};$$

$$C_1 = \frac{2\alpha_1\alpha_2+\Gamma(\alpha_1^2+\alpha_2^2+\beta^2)}{\alpha_2(1+\Gamma)(\alpha_1^2+\beta^2)}. \tag{25}$$

In view of the complexity of these equations it is easier to proceed by evaluating Eq. (22) and comparing directly with Eq. (16) for different values of γ, K_0 and K_1. An expression for $I_2^{(4)}(t)$ analogous with Eq. (23) for $I^{(2)}(t)$ is prepared in Appendix B. This is purely real, as it should be. This supports the validity of our generalisation for use with Mori theory the operator methods of Ford et al. To complete our chain of relations we have [1, 2]:

$$\alpha_1 = \tfrac{1}{2}(S_1+S_2)+\frac{\gamma}{3}; \quad \alpha_2 = -S_1-S_2+\frac{\gamma}{3};$$

$$\beta = \frac{\sqrt{3}}{2}(S_1-S_2);$$

$$S_1^3 = \frac{-B}{2}+\left(\frac{A^3}{27}+\frac{B^2}{4}\right)^{1/2}; \quad S_2^3 = \frac{-B}{2}-\left(\frac{A^3}{27}+\frac{B^2}{4}\right)^{1/2};$$

$$A = K_0+K_1-\gamma^2/3;$$

$$B = \frac{\gamma}{3}\left(\frac{2\gamma^2}{9}+2K_0-K_1\right). \tag{26}$$

from Cardan's solution of a cubic with negative discriminant. The latter is always the case experimentally in zero-THz spectroscopy [2]. The Eqs. (24), (25) and (26) allow us to compute $\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle$ from K_0, K_1 and γ using firstly Eq. (16) and then Eq. (22).

Note that $I_2^{(4)}(t)$ or any higher correction does not affect the thermodynamic definitions [2, 8] of K_0 and K_1, i.e.

$$K_0 = \frac{\langle\dot{\omega}^2(0)\rangle}{\langle\omega^2(0)\rangle}; \quad K_1 = \frac{\langle\ddot{\omega}^2(0)\rangle}{\langle\dot{\omega}^2(0)\rangle}-\frac{\langle\dot{\omega}^2(0)\rangle}{\langle\omega^2(0)\rangle}.$$

A discussion of the effect of $I_2^{(4)}(t)$ on the orientational autocorrelation function is given later in the paper using a range of sets of values of (K_0, K_1 and γ).

3. *Rotation translation coupling*

In the classical theory of molecular diffusion [2, 10, 13] it is assumed universally that the angular momentum vector $\boldsymbol{J}(0)$ is not correlated with the linear centre of mass momentum vector $\boldsymbol{p}(t)$. In other words the mixed auto-correlation functions $\langle \boldsymbol{p}(t)\cdot\boldsymbol{J}(0)\rangle$ or

$\langle \boldsymbol{J}(t) \cdot \boldsymbol{p}(0) \rangle$ are assumed to vanish. In this section we explain why this is not necessarily the case in the presence of symmetry breaking fields, and use the theory described above to link $\langle \boldsymbol{J}(t) \cdot \boldsymbol{J}(0) \rangle$ to $\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0) \rangle$ when translation/rotation coupling is fully accounted for. Here $\boldsymbol{\mu}$ is the dipole vector.

The general theorem which prohibits the existence of mixed autocorrelation functions of the type $\langle A(t)B(0) \rangle$ have been set out by Berne and Pecora [13]. In particular:

(*i*) If the total hamiltonian H is invariant to time reversal then $\langle A(0)B(0) \rangle$ vanishes if A and B have different time reversal symmetry. There are no reasons, based on time reversal alone, why $\langle A(t)B(0) \rangle$ should vanish for $t > 0$ even when A and B have different time reversal symmetry. If this were the case then $\langle A(t)B(0) \rangle$ would be an odd function of time in the classical limit. These considerations do not apply if, for any reason, $H \rightarrow -H$ when $t \rightarrow -t$.

(*ii*) If $H \rightarrow H$ under parity transformation then the correlation function $\langle A(t)B(0) \rangle$ vanishes for all t if A and B behave differently under parity transformation. However, if for some reason $H \rightarrow -H$ under parity transformation then the theorem does not apply. The parity invariance H is broken by mechanical, electric, magnetic, gravitational or any other type of field which breaks the directional symmetry of the system under consideration. For example, if we direct an electric field at an isotropic liquid the hamiltonian may take the form:

$$H = \tfrac{1}{2}\,\boldsymbol{\omega} \cdot \boldsymbol{I} \cdot \boldsymbol{\omega} + \tfrac{1}{2}\, m v^2 + V - \boldsymbol{\mu} \cdot \boldsymbol{E} \tag{27}$$

for every molecule in the system. Here $\boldsymbol{\omega}$ is the angular velocity, $\boldsymbol{I}$ the moment of inertia tensor, m the molecular mass, $\boldsymbol{v}$ the centre of mass velocity, V the potential energy from all sources, $\boldsymbol{\mu}$ the molecular dipole and $\boldsymbol{E}$ the external electric field. It is clear that H of Eq. (27) $\rightarrow -H$ under parity transformation, and we no longer have a general theorem which prohibits the existence of $\langle \boldsymbol{J}(t) \cdot \boldsymbol{p}(0) \rangle$ or $\langle \boldsymbol{p}(t) \cdot \boldsymbol{J}(0) \rangle$ on the grounds of parity symmetry. We note in passing that the correlation functions $\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{p}(0) \rangle$ or $\langle \boldsymbol{p}(t) \cdot \boldsymbol{\mu}(0) \rangle$ are not prohibited by parity symmetry or time reversal symmetry even in the absence of a symmetry breaking field. This is because $\boldsymbol{\mu}$ and $\boldsymbol{p}$ have the same parity. However, they have a different time reversal symmetry and $\langle \boldsymbol{\mu}(0) \cdot \boldsymbol{p}(0) \rangle$ vanishes. $\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{p}(0) \rangle$ is an odd function of time.

(*iii*) If H is invariant to reflection of positions and momenta then the system is said to have definite reflection symmetry. (a) If we take the autocorrelation function $\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{p}(0) \rangle$ then reflections such as

$$(x_j, y_j, z_j) \rightarrow (x_j, y_j, z_j)$$

$$(p_{jx}, p_{jy}, p_{jz}) \rightarrow (p_{jx}, -p_{jy}, p_{jz})$$

will obviously have the same effect on $\boldsymbol{\mu}$ (which is a difference of position vectors in the lab. frame) and $\boldsymbol{p}$. In the case $H \rightarrow H$ under reflection there is no reason why $\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{p}(0) \rangle$ or $\langle \boldsymbol{p}(t) \cdot \boldsymbol{\mu}(0) \rangle$ may not exist for $t > 0$.

(b) In the absence of a symmetry breaking field $\boldsymbol{J}$ and $\boldsymbol{p}$ transform differently under reflection symmetry so that $\langle \boldsymbol{p}(t) \cdot \boldsymbol{J}(0) \rangle$ and $\langle \boldsymbol{J}(t) \cdot \boldsymbol{p}(0) \rangle$ must vanish for all t provided $H \rightarrow H$ under reflection of all positions and momenta. However the introduction of a term such as $-\boldsymbol{\mu} \cdot \boldsymbol{E}$ means that $H \to -H$ under any reflection of the projection $\boldsymbol{\mu} \cdot \boldsymbol{E}$ (a difference of position vectors in the lab. frame). The theorems of reflection symmetry no longer prohibit the existence of $\langle \boldsymbol{p}(t) \cdot \boldsymbol{J}(0) \rangle$ or $\langle \boldsymbol{J}(t) \cdot \boldsymbol{p}(0) \rangle$.

(*iv*) Rotation symmetry is also broken by an unidirectional external field. At this stage we consider the experimental evidence for rototranslation as embodied in the phenomena associated with dielectrophoresis [14], the translation of a liquid dielectric under the influence of an electric field gradient. If we consider a parallel plate capacitor partially filled with an isotropic non-conducting liquid the bulk will translate in one direction when the field is switched on. If the conductors have equal and opposite charges Q, the energy $U = Q^2/2C$ where C is their capacitance. Using the principle of virtual work [14], any component of the force is given by a differentiation; for example, the force parallel to the plates in the direction x of translation of the bulk of the liquid is

$$F_x = -\frac{\partial U}{\partial x} = -\frac{Q^2}{2}\frac{\partial}{\partial x}\left(\frac{1}{C}\right). \tag{28}$$

However, though this may explain superficially the observable translation it leaves open the mechanism by which electric field gradient is transformed on a molecular scale into cooperative translation, and therefore uniaxial translation of an individual molecule in a preferred direction.

Conventionally it is assumed that the electric field interacts with the molecular field via terms such as $\boldsymbol{\mu} \cdot \boldsymbol{E}$; $\boldsymbol{E} \cdot \boldsymbol{\alpha} \cdot \boldsymbol{E}$ etc. where $\boldsymbol{\alpha}$ is the polarisability tensor. The presence of an electric field gradient (which is generally taken to be the least requirement for dielectrophoresis) means that the quadrupolar terms in the molecular frame will interact in the manner of field-gradient induced birefringence (Buckingham et al. [15]). However, in the absence of autocorrelation functions such as $\langle \boldsymbol{p}(t) \cdot \boldsymbol{J}(0) \rangle$ or $\langle \boldsymbol{p}(t) \cdot \boldsymbol{\mu}(0) \rangle$ these torque terms (e.g. $\boldsymbol{\mu} \times \boldsymbol{E}$) will not be transformed into bulk translation.

In a liquid crystal phase such as a nematic [2, 6] birefringence is induced by a small field $\boldsymbol{E}$. The dielectrophoresis movement in a nematic is therefore likely to be pronounced for small applied $\boldsymbol{E}$. In general, a sample of liquid dielectric always translates when an electric torque is applied via an inhomogeneous field. If a large enough homogeneous field is applied the dielectric sample develops birefringence, it is easier for a molecule to translate in one direction than in another as a direct result of the fact that the rotational motion is also anisotropic on both a microscopic and macroscopic level.

Illustration of orientation/translation coupling

A good example of rotation/translation coupling is of course the propeller [16]. Examples of orientation/translation coupling could be the Badminton shuttlecock, an arrow or dart. The faster the centre of mass translates the narrower the solid angle open to reorientation of the object when travelling under the influence of a field such as gravity. The axis $\boldsymbol{\mu}$ and the velocity $\boldsymbol{v}$ are therefore correlated. The vector $\boldsymbol{\mu}(t)$ will depend in magnitude and direction on $\boldsymbol{v}(0)$. The factor which causes the orientation /translation coupling is the air-friction on the flight of the shuttlecock.

However, on the molecular scale we always have to consider the flight of more than one "arrow". The angular brackets $\langle\ \rangle$ would mean that for each t we have to average the product $\boldsymbol{\mu}(0) \cdot \boldsymbol{v}(t)$ for all the molecules in the system. After several collisions $\boldsymbol{v}(t)$ will be dependent on $\boldsymbol{\mu}(0)$ if $\langle \boldsymbol{\mu}(0) \cdot \boldsymbol{v}(t) \rangle$ exists. As we have seen, the symmetry theorems really tell us nothing about $\langle \boldsymbol{\mu}(0) \cdot \boldsymbol{v}(t) \rangle$ except that this *may* exist. The mixed autocorrelation function of momenta *may* exist in the presence of a symmetry-breaking field (an electric field or field gradient). Therefore if this is the case then it behoves us to look at the effect this will have on the Debye theory as extended by Ford et al. [7] to include inertia.

The general case of three-dimensional asymmetric top motion is complicated by the fact that the angular components cannot be related to the orientation vector in a linear fashion. This means that the Langevin equation for the purely rotational diffusion motion of the asymmetric top is non-linear in the components (J_x, J_y, J_z) of $\boldsymbol{J}$, the angular momentum, or alternatively the angular velocity $\boldsymbol{\omega}(\equiv \boldsymbol{J} \cdot \boldsymbol{I}^{-1})$.

The rototranslational Langevin equations [17] are for components (i, j, k) of the angular velocity vector $\boldsymbol{\omega}$, or velocity vector $\boldsymbol{v}$:

$$\dot{\omega}_i = \frac{(I_j - I_k)}{I_i}\,\omega_j \omega_k - \sum_{l=1}^{3} (\gamma_{il}^{(r)}\omega_l + \gamma_{il}^{(rt)} v_l) + \Gamma_i(t) \tag{29}$$

$$\dot{v}_i = -\sum_{l=1}^{3} (\gamma_{il}^{(t)} v_l - \gamma_{il}^{(tr)}\omega_l) + F_i(t) \tag{30}$$

where i, j and k are cyclic permutations of 1, 2 and 3. In the isotropic phase the off-diagonal terms $\gamma_{il}^{(tr)}$ and $\gamma_{il}^{(rt)}$ of the friction tensor vanish and the equations decouple into separate rotational and translational parts. The corresponding Fokker–Planck equations for the joint probability density function p_2 may be written as

$$\begin{aligned}
\frac{\partial p_2}{\partial t}(v, \omega, t | v_0, \omega_0, t_0) = \sum_{l=1}^{3} \Bigg\{ &-\left[\frac{\partial}{\partial \omega_i}\left(\frac{I_j - I_k}{I_i}\right)\omega_j \omega_k P_2\right] \\
&+ \sum_{l=1}^{3}\left[\frac{\partial}{\partial \omega_i}(\gamma_{il}^{(r)}\omega_l + \gamma_{il}^{(rt)} v_l) + \frac{\partial}{\partial v_i}(\gamma_{il}^{(t)} v_l + \gamma_{il}^{(tr)}\omega)_l\right] P_2 \\
&+ \sum_{l=1}^{3} \frac{\partial}{\partial \omega_i}\left[\gamma_{il}^{(r)} \frac{kT}{I_l}\frac{\partial}{\partial \omega_l} + \tfrac{1}{2}\left(\gamma_{il}^{(tr)}\frac{kT}{I_l} + \gamma_{il}^{(rt)}\frac{kT}{m}\right)\frac{\partial}{\partial v_l}\right] P_2 \\
&+ \sum_{l=1}^{3} \frac{\partial}{\partial v_i}\left[\gamma_{il}^{(t)} \frac{kT}{m}\frac{\partial}{\partial v_l} + \tfrac{1}{2}\left(\gamma_{il}^{(rt)}\frac{kT}{m} + \gamma_{il}^{(tr)}\frac{kT}{I_l}\right)\frac{\partial}{\partial \omega_l}\right] P_2 \Bigg\},
\end{aligned} \tag{31}$$

where again i, j and k permute 1, 2 and 3 cyclically. In these equations the elements are those of the friction grand matrix:

$$\gamma = \begin{bmatrix} \gamma^{(r)} & \gamma^{(rt)} \\ \gamma^{(tr)} & \gamma^{(t)} \end{bmatrix}$$

whose elements are themselves matrices. I_i, I_j and I_k are components of the moment of inertia tensor and m is the molecular mass.

The solution of these equations is not known analytically and they are over-elaborate in that there are too many elements of γ. However there are simplifications which can be made to extract auto-correlation functions of interest such as $\langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0) \rangle$ where $\boldsymbol{u}$ is the dipole unit vector. The simplest method is to make the assumption that the matrices $\gamma^{(r)}$, $\gamma^{(rt)}$, $\gamma^{(tr)}$ and $\gamma^{(t)}$ are each diagonal with equal elements, and to take $I_i \sim I_j \sim I_k$ as a first approximation. The equations then reduce to:

$$I\dot{\omega} = -I\gamma^{(r)}\omega - \gamma^{(rt)}mv + \boldsymbol{\Gamma} \tag{32}$$

$$m\dot{v} = -m\gamma^{(t)}v - \gamma^{(tr)}I\omega + \boldsymbol{F} \tag{33}$$

which are linearised and soluble by Laplace transformation to give, for the normalised angular velocity autocorrelation function:

$$\frac{\langle \omega(t) \cdot \omega(0) \rangle}{\langle \omega(0) \cdot \omega(0) \rangle} = L^{-1} \left[\frac{p+\gamma^{(t)}}{(p+\gamma^{(r)})\,(p+\gamma^{(t)}) - \gamma^{(rt)}\gamma^{(tr)}} \right] \tag{34}$$

$$\rightarrow L^{-1}(p+\gamma^{(r)})^{-1} \tag{35}$$

when $\gamma^{(rt)} = \gamma^{(tr)} = 0$. Eq. (35) is, of course, the classical Debye result, valid for isotropic rotational diffusion. The inverse Laplace transform of this equation is:

$$\begin{aligned} \frac{\langle \omega(t) \cdot \omega(0) \rangle}{\langle \omega(0) \cdot \omega(0) \rangle} &= e^{-bt} \left\{ \cos\,[(c-b^2)^{1/2}t] + \frac{(\gamma^{(t)}-b)}{(c-b^2)^{1/2}} \sin\,[(c-b^2)^{1/2}t] \right\} \\ &= e^{-bt} \left\{ \cosh\,[(b^2-c)^{1/2}t] + \frac{(\gamma^{(t)}-b)}{(c-b^2)^{1/2}} \sinh\,[(b^2-c)^{1/2}t] \right\} \end{aligned}$$

where $b = 2(\gamma^{(t)}+\gamma^{(r)})$; $c = \gamma^{(t)}\gamma^{(r)} - \gamma^{(tr)}\gamma^{(rt)}$.

We are now faced with the problem of calculating $\langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0) \rangle$ from $\langle \omega(t) \cdot \omega(0) \rangle$, and this is tackled in the Appendix.

4. Results and discussion

Correction to Mori–Evans theory (1976)

Reid and Evans [3] have recently considered the evaluation of a range of microwave and far infra-red data with Eqs. (7), (10) and (11). The results have been tabulated for twenty-three solutes in decalin solution in terms of the parameters K_0, K_1 and γ. Using

TABLE I

Effect of first order correction on Mori/Evans theory

Ang. vel. a.c.f.	Corrected $C_u(t)$	Original $C_u(t)$	Torque a.c.f.	Time in reduced units
1,000000& 00	1,000000& 00	1,000000& 00	1,000000& 00	0,000000& 00
9,989756&–01	9,999709&–01	9,999750&–01	9,989257&–01	5,000000&–03
9,959101&–01	9,998913&–01	9,999001&–01	9,957109&–01	1,000000&–02
9,837560&–01	9,995814&–01	9,996012&–01	9,829681&–01	2,000000&–02
9,747918&–01	9,993521&–01	9,993778&–01	9,735286&–01	2,500000&–02
9,638620&–01	9,990738&–01	9,991059&–01	9,621228&–01	3,000000&–02
9,511616&–01	9,987472&–01	9,987859&–01	9,488232&–01	3,500000&–02
9,367229&–01	9,983731&–01	9,984185&–01	9,337116&–01	4,000000&–02
9,206286&–01	9,979524&–01	9,980045&–01	9,168779&–01	4,500000&–02
9,029673&–01	9,974858&–01	9,975448&–01	8,984185&–01	5,000000&–02
8,838331&–01	9,969745&–01	9,970402&–01	8,784359&–01	5,500000&–02
8,633245&–01	9,964195&–01	9,964919&–01	8,570374&–01	6,000000&–02
8,415434&–01	9,958220&–01	9,959009&–01	8,343336&–01	6,500000&–02
8,185944&–01	9,951830&–01	9,952684&–01	8,104385&–01	7,000000&–02
7,945840&–01	9,945040&–01	9,945956&–01	7,854675&–01	7,500000&–02
7,696200&–01	9,937861&–01	9,938838&–01	7,595376&–01	8,000000&–02
7,438106&–01	9,930308&–01	9,931342&–01	7,327656&–01	8,500000&–02
7,172639&–01	9,922395&–01	9,923483&–01	7,052682&–01	9,000000&–02
6,900871&–01	9,914135&–01	9,915275&–01	6,771611&–01	9,500000&–02
6,623866&–01	9,905542&–01	9,906732&–01	6,485580&–01	1,000000&–01
6,342664&–01	9,896633&–01	9,897868&–01	6,195704&–01	1,050000&–01
6,058290&–01	9,887421&–01	9,888699&–01	5,903073&–01	1,100000&–01
5,771737&–01	9,877922&–01	9,879239&–01	5,608741&–01	1,150000&–01
5,483972&–01	9,868150&–01	9,869503&–01	5,313728&–01	1,200000&–01
5,195927&–01	9,858121&–01	9,859506&–01	5,019013&–01	1,250000&–01
4,908499&–01	9,847849&–01	9,849264&–01	4,725532&–01	1,300000&–01
4,622545&–01	9,838350&–01	9,838791&–01	4,434175&–01	1,350000&–01
4,338883&–01	9,826638&–01	9,828101&–01	4,145786&–01	1,400000&–01
4,058289&–01	9,815728&–01	9,817211&–01	3,861157&–01	1,450000&–01
3,781492&–01	9,804634&–01	9,806133&–01	3,581031&–01	1,500000&–01
3,509179&–01	9,793370&–01	9.794883&–01	3,306098&–01	1,550000&–01
3,241990&–01	9,781951&–01	9,783474&–01	3,036995&–01	1,600000&–01
2,980518&–01	9,770389&–01	9,771920&–01	2,774308&–01	1,650000&–01
2,725310&–01	9,758697&–01	9,760234&–01	2,518570&–01	1,700000&–01
2,476864&–01	9,746890&–01	9,748429&–01	2,270259&–01	1,750000&–01
2,235631&–01	9,734978&–01	9,736518&–01	2,029805&–01	1,800000&–01
2,002018&–01	9,722975&–01	9,724512&–01	1,797585&–01	1,850000&–01
1,776386&–01	9,710891&–01	9,712424&–01	1,573925&–01	1,900000&–01
1,559047&–01	9,698738&–01	9,700265&–01	1,359105&–01	1,950000&–01
1,350273&–01	9,686526&–01	9,688046&–01	1,153356&–01	2,000000&–01
1,150289&–01	9,674266&–01	9,675776&–01	9,568628&–02	2,050000&–01
9,592793&–02	9,661967&–01	9,663467&–01	7,697678&–02	2,100000&–01
7,77388&–02	9,649639&–01	9,651127&–01	5,921701&–02	2,150000&–01
6,047212&–02	9,637290&–01	9,638765&–01	4,241287&–02	2,200000&–01
4,413429&–02	9,624929&–01	9,626390&–01	2,656640&–02	2,240000&–01

TABLE I (continued)

Ang. vel. a.c.f.	Corrected $C_u(t)$	Original $C_u(t)$	Torque a.c.f.	Time in reduced units
2,872843&-02	9,612563&-01	9,614009&-01	1,167605&-02	2,300000&-01
1,425409&-02	9,600200&-01	9,601631&-01	-2,263200&-03	2,350000&-01
7,075670&-04	9,587847&-01	9,589262&-01	-1,525955&-02	2,400000&-01
-1,191796&-02	9,575509&-01	9,576908&-01	-2,732423&-02	2,450000&-01
-2,353222&-02	9,563193&-01	9,543476&-01	-3,847124&-02	2,500000&-01
-3,444767&-02	9,550905&-01	9,552271&-01	-4,871716&-02	2,550000&-01
-4,437933&-02	9,538648&-01	9,539998&-01	-5,808094&-02	2,600000&-01
-5,344456&-02	9,526328&-01	9,527762&-01	-6,658368&-02	2,650000&-01
-6,166290&-02	9,514249&-01	9,515567&-01	-7,424845&-02	2,700000&-01

Eq. (22) we have recalculated the microwave and far infrared spectra for these solutes. The results are typified in Table 1, for 10% v/v bromobenzene in decalin at 293 K.

As the Table shows, the correction is very small, two orders of magnitude inside the experimental uncertainty. This means that the Mori–Evans theory of 1976 is adequate for use in the great majority of cases without the corrections of Ford et al. These may be more important as the limit of free rotation is approached. Higher order corrections have an even smaller effect.

Mixed autocorrelation functions

It is important to note that Eqs. (29) and (31), although extremely difficult to solve analytically are simple in concept because they carry no memory in the friction matrix. That is to say the random torque and force terms are statistically Markovian in nature. Such concepts carry no weight in the far infra-red (THz) region [2] of the complete zero--THz frequency range over which the molecular dynamical evolution takes place. A numerical method of dealing with rotation/translation is computer simulation [2, 18] where the equations of motion of the asymmetric top are solved (numerically) with model potentials for some hundreds of molecules at a time. Finally in this paper we present direct evidence for the existence of the analogous mixed a.c.f.'s: $\langle J(t) \cdot T_q(0)\rangle$ and $\langle T_q(t) \cdot J(0)\rangle$ from a simulation [4] using 108 triatomic asymmetric tops of C_{2v} symmetry subjected to an external torque near the thermal level, i.e. comparable in magnitude with kT. Here T_q is the resultant molecular torque.

The a.c.f.'s $\langle J(t) \cdot T_q(0)\rangle/\langle J(0) \cdot J(0)\rangle$ and $\langle T_q(t) \cdot J(0)\rangle/\langle J(0) \cdot J(0)\rangle$ (in normalised units) are mirror images of each other (Fig. 1) and are comparable in absolute terms with the individual a.c.f.'s $\langle J(t) \cdot J(0)\rangle$ and $\langle T_q(t) \cdot T_q(0)\rangle$. The algorithm used is called TRI2 and was written initially by Renaud and Singer. The sample was thermostatted to 220 K at a molar volume of 10^{-4}m^3. The molecules interact with a 3×3 atom-atom, Lennard–Jones potential with no electrodynamic (multipole-multipole) terms. A constant steady torque was applied along the laboratory Z axis in order to tilt the e_B axis of the molecule into the Z direction. This simulates the interaction of an external electric field E_Z with a "dipole" along e_B. This simulation is not designed to reproduce the real interaction of an electric field with a real system, but rather to get at the essence of what happens when a dipolar sample is subjected to an intense electric field. The work could easily be extended to real systems using, for example, the water algorithms now available. In the alignment of a nematic with an electric field this kind of torque is presumably amplified millions of times as discussed by van Vleck [19]. A greater amplification must be effective when a nematogen is aligned with a magnetic field because the magnetic dipole is so much weaker than the electric in a diamagnetic, dipolar molecule.

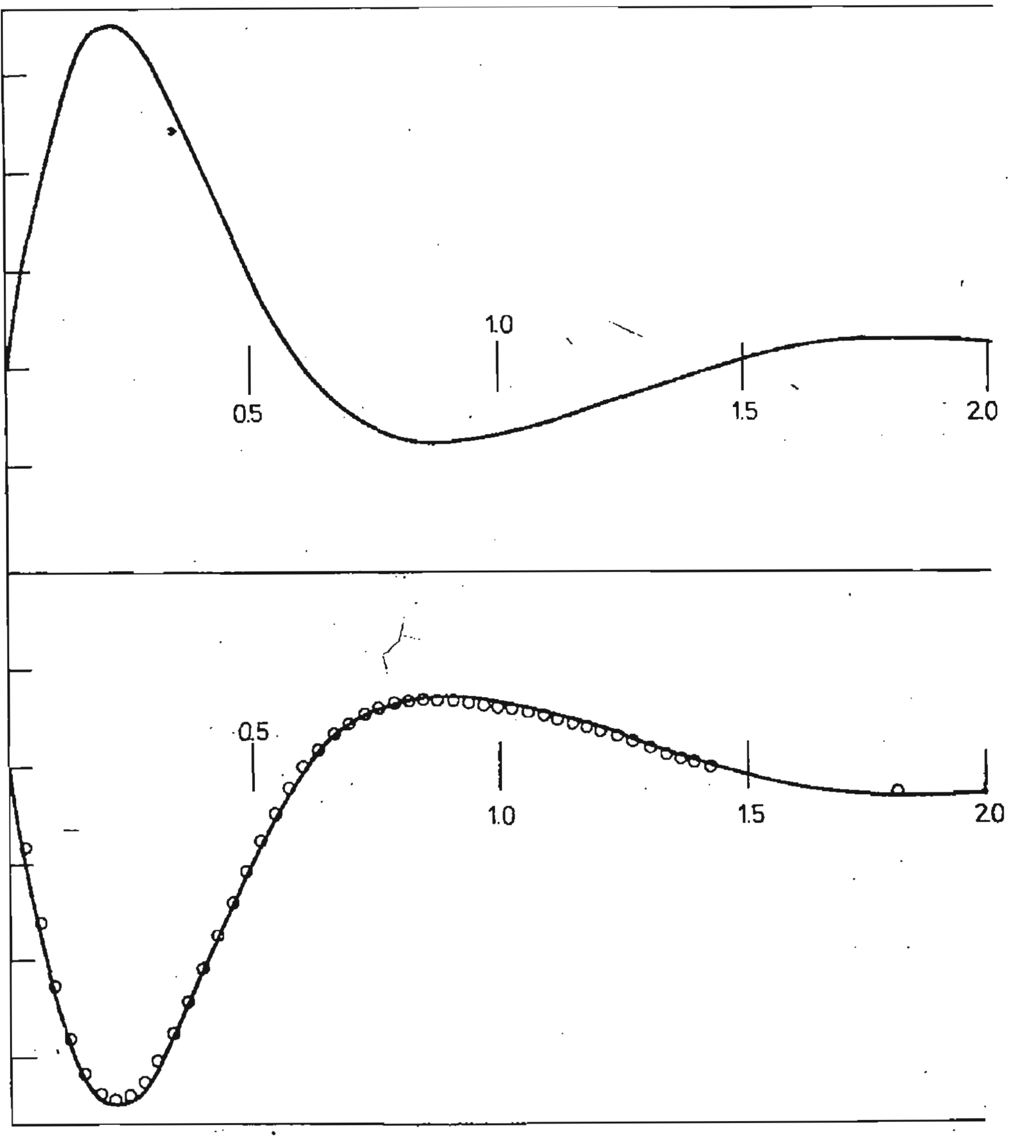

Fig. 1. Mixed autocorrelation functions (1) $\langle J(t) \cdot T_q(0) \rangle$ and (2) $\langle T_q(t) \cdot J(0) \rangle$ in a computer simulation. Here J is the angular momentum and T_q the torque

The torque applied along the Z direction does not disturb equilibrium properties such as the total energy. The mean square angular momentum in the torque off case is (in reduced units) 3.57×10^{-30}; and in the torque on case 3.51×10^{-30}. The application of a torque does however have the effect on the time dependence of angular momentum autocorrelation function illustrated in Fig. 2, and causes this function to become anisotropic e.g. $\langle J_x(t) J_x(0) \rangle$ and $\langle J_y(t) J_y(0) \rangle$ now behave dissimilarly, and each is different from $\langle J(t) \cdot J(0) \rangle$. We have $\langle J_y^2(0) \rangle = 2.24 \times 10^{-32}$; $\langle J_x^2(0) \rangle = 3.40 \times 10^{-33}$; $\langle J_z^2(0) \rangle = 3.5$

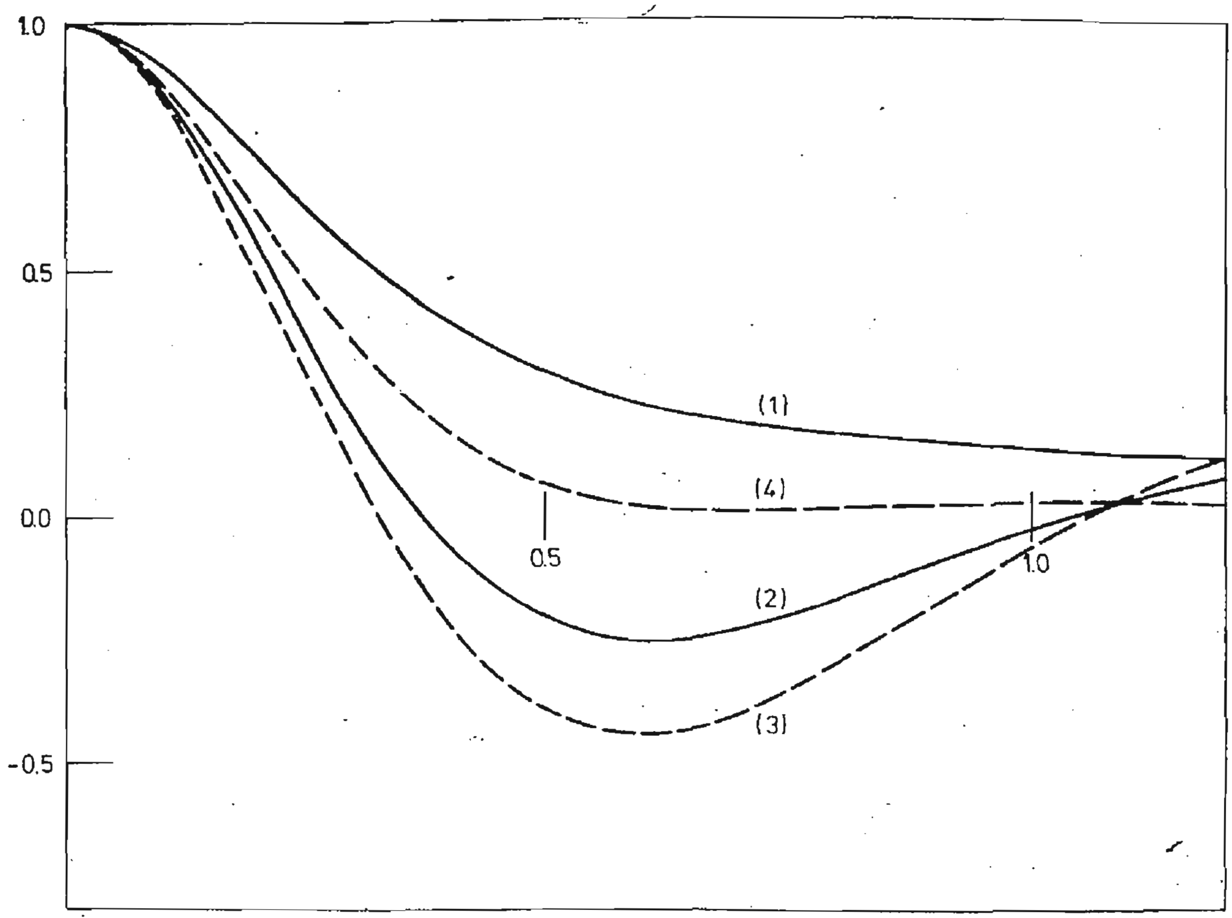

Fig. 2. Angular momentum a.c.f. $\langle J(t) \cdot J(0) \rangle$ in the presence and absence of external torque. (1) Torque on; (2) torque off

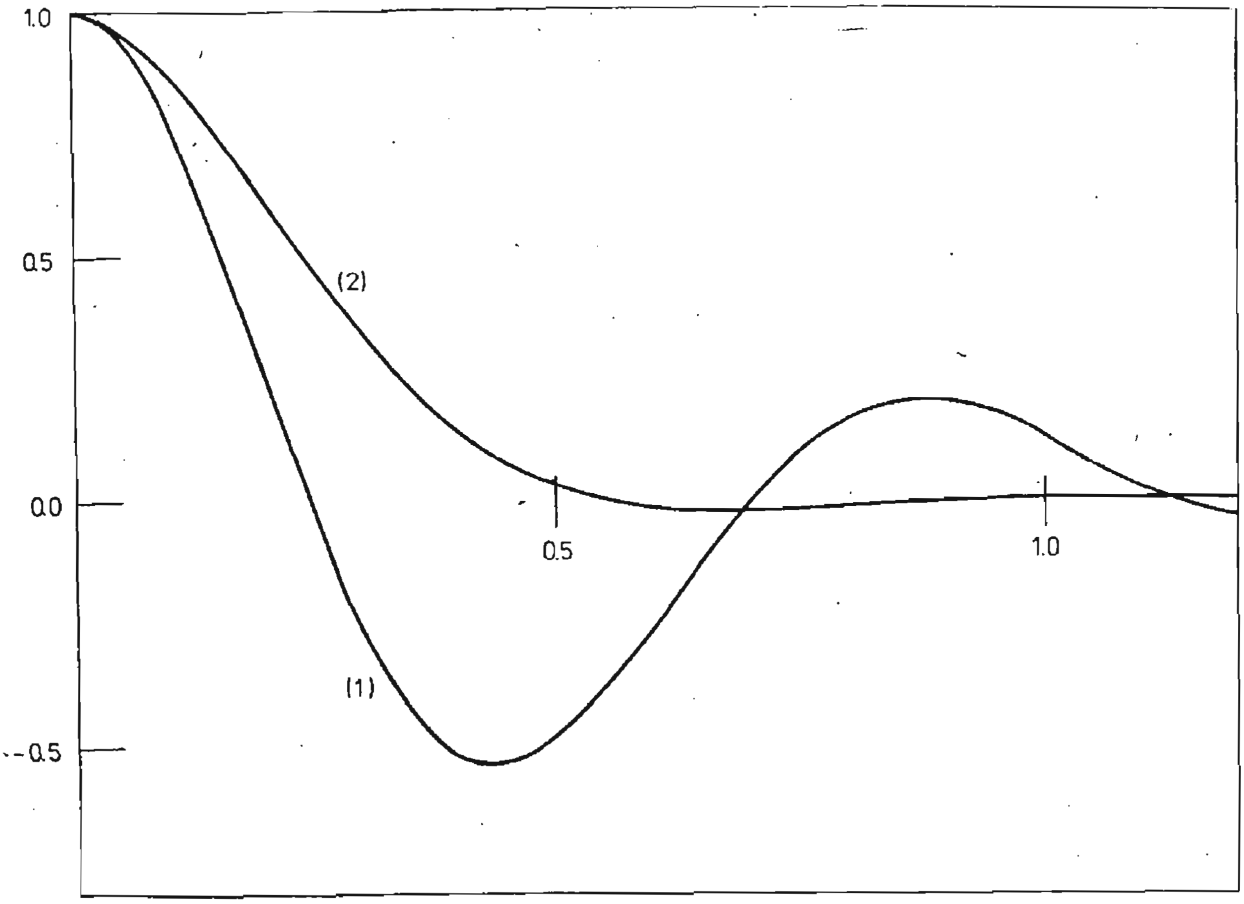

Fig. 3. Linear momentum a.c.f. in the presence (1) and absence (2) of external torque

$\times 10^{-30}$ over the 20 ps of our simulation. The external torque also has this effect on the *linear* momentum autocorrelation function (Fig. 3). If we define an angle θ between e_B of each molecule and a laboratory fixed axis, then we have $\langle P_2 \cos \theta(0)\rangle = 0.585$. These vanish in the absence of an external perturbation. Here P_n denotes Legendre polynomial in the usual way. The anisotropy in the orientation may be quantified by $\langle e_{Bx}^2(0)\rangle = 2.51 \times 10^{-4}$; $\langle e_{By}^2(0) = 2.55 \times 10^{-3}$; $\langle e_{Bz}^2(0)\rangle = 1.38 \times 10^{-3}$.

The Science Research Council is thanked for financial support.

APPENDIX A

For convenience we write:

$$A_n = A(a_n) = A(-a_n); \quad B_n = B(a_n) = B(-a_n). \tag{A1}$$

The integrals in Eq. (14) can now be written as follows:

$$I^{(2)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \sum_{n=1}^{m} \frac{A_n}{B_n'} \exp(-a_n(t_1 - t_2)) \tag{A2}$$

$$LI^{(2)}(t) = \sum_{n=1}^{m} \frac{A_n}{B_n'} [p^2(p+a_n)]^{-1} \tag{A3}$$

$$L^{-1}I^{(2)}(t) = \sum_{n=1}^{m} \frac{A_n}{B_n'} \frac{(a_n t - 1 + e^{a_n t})}{a_n^2} \tag{A4}$$

$$I_1^{(4)}(t) = \int_0^t dt_1 \ldots \int_0^{t_3} dt_4 \sum_{n=1}^{m} \frac{A_n}{B_n'} \exp(-a_n(t_1 - t_2 + t_3 - t_4)) \tag{A5}$$

$$I_2^{(4)}(t) = \int_0^t dt_1 \ldots \int_0^{t_3} dt_4 \sum_{n=1}^{m} \frac{A_n}{B_n'} \exp(-a_n(t_1 + t_2 - t_3 - t_4)) \tag{A6}$$

$$LI_1^{(4)}(t) = \sum_{n=1}^{m} \frac{A_n}{B_n'} [p^3(p+a_n)^2]^{-1} \tag{A7}$$

$$L^{-1}I_1^{(4)}(t) = \sum_{n=1}^{m} \frac{A_n}{B_n'} \left[\frac{\frac{1}{2}(a_n t)^2 - 2a_n t + 3 - (a_n t + 3)e^{-a_n t}}{a_n^4}\right] \tag{A8}$$

$$L^{-1}I_2^{(4)}(t) = \sum_{n=1}^{m} \frac{A_n}{B_n'} \left[\frac{\frac{1}{2}(a_n t) - 5/4 + (a_n t + 1)e^{-a_n t} + 1/4e^{-2a_n t}}{a_n^4}\right]. \tag{A9}$$

Other integrals may be evaluated straightforwardly from Ref. [7].

APPENDIX B

Calculation of $(kT/I)^2$ correction term to Mori–Evans theory

$$2\left(\frac{kT}{I}\right)^2 \sum_{n=1}^{m} \frac{A_n}{B'_n}\left[\frac{\frac{1}{2}a_n t-5/4+(a_n t+1)e^{-a_n t}+\frac{1}{4}e^{-2a_n t}}{a_n^4}\right].$$

In 3 variable Mori–Evans theory we have:

$$m=3; \quad \frac{A_1}{B'_1}=Z=\frac{\Gamma}{1+\Gamma}; \quad \frac{A_2}{B'_2}=X+iY; \quad \frac{A_3}{B'_3}=X-iY;$$

$$X=\frac{1}{2(1+\Gamma)}; \quad Y=\frac{(\alpha_1+\alpha_2\Gamma)}{2\beta(1+\Gamma)};$$

$$a_1=\alpha_2; \quad a_2=\alpha_1+i\beta; \quad a_3=\alpha_1-i\beta.$$

The correction term should be purely real.
Constant term (1):

$$-\tfrac{5}{4}\left[\frac{Z}{\alpha_2^4}+\frac{X+iY}{(\alpha_1+i\beta)^4}+\frac{X-iY}{(\alpha_1-i\beta)^4}\right]$$

$$=-\tfrac{5}{4}\left[\frac{Z}{\alpha_2^4}+\frac{2(X(\alpha_1^4-6\alpha_1^2\beta^2+\beta^4)+Y(4\alpha_1^3\beta-4\alpha_1\beta^3))}{(\alpha_1^2+\beta^2)^4}\right]$$

t term (2):

$$\frac{t}{2}\left[\frac{Z}{\alpha_2^3}+(X+iY)\left(\frac{\alpha_1-i\beta}{\alpha_1^2+\beta^2}\right)^3+(X-iY)\left(\frac{\alpha_1+i\beta}{\alpha_1^2+\beta^2}\right)^3\right]$$

$$=\frac{t}{2}\left[\frac{Z}{\alpha_2^3}+\frac{2(X(\alpha_1^3-3\alpha_1\beta^2)+Y(3\alpha_1^2\beta-\beta^3))}{(\alpha_1^2+\beta^2)^3}\right]$$

Exponential term (3):

$$+\left[\frac{Ze^{-\alpha_2 t}}{\alpha_2^4}+\frac{(X+iY)e^{-(\alpha_1+i\beta)t}}{(\alpha_1+i\beta)^4}+\frac{(X-iY)e^{-(\alpha_1-i\beta)t}}{(\alpha-i\beta)^4}\right]$$

$$=\left[\frac{Ze^{-\alpha_2 t}}{\alpha_2^4}+\frac{2e^{-\alpha_1 t}\cos\beta t}{(\alpha_1^2+\beta^2)^4}(X(\alpha_1^4-6\alpha_1^2\beta^2+\beta^4)+Y(4\alpha_1^3\beta-4\alpha_1\beta^3))\right.$$

$$\left.+\frac{2e^{-\alpha_1 t}\sin\beta t}{(\alpha_1^2+\beta^2)^4}(X(4\alpha_1^3\beta-4\alpha_1\beta^3)-Y(\alpha_1^4-6\alpha_1^2\beta^2+\beta^4))\right]$$

Exponential term (4):

$$+\tfrac{1}{4}\left[\frac{Ze^{-2\alpha_2 t}}{\alpha_2^4}+\frac{(X+iY)e^{-2(\alpha_1+i\beta)t}}{(\alpha_1+i\beta)^4}+\frac{(X-iY)e^{-2(\alpha_1-i\beta)t}}{(\alpha_1-i\beta)^4}\right]$$

$$=\tfrac{1}{4}\left[\frac{Ze^{-2\alpha_2 t}}{\alpha_2^4}+\frac{2e^{-2\alpha_1 t}\cos 2\beta t}{(\alpha_1^2+\beta^2)^4}(X(\alpha_1^4-6\alpha_1^2\beta^2+\beta^4)+Y(4\alpha_1^3-4\alpha_1\beta^3))\right.$$

$$\left.+2e^{-2\alpha_1 t}\sin 2\beta t(X(4\alpha_1^3\beta-4\alpha_1\beta^3)-Y(\alpha_1^4-6\alpha_1^2\beta^2+\beta^4))\right]/(\alpha_1^2+\beta^2)$$

t term (5):

$$t\left[\frac{Ze^{-\alpha_2 t}}{\alpha_2^3}+\frac{2e^{-\alpha_1 t}\cos\beta t}{(\alpha_1^2+\beta^2)^3}(X(\alpha_1^3-3\alpha_1\beta^2)+Y(3\alpha_1^2\beta-\beta^3))\right.$$

$$\left.+\frac{2e^{-\alpha_1 t}\sin\beta t}{(\alpha_1^2+\beta^2)^3}(X(3\alpha_1^2\beta-\beta^3)-Y(\alpha_1^3-3\alpha_1\beta^2))\right]$$

We have the usual relations between (Z, X, Y, α_1, α_2 and β) and (K_0, K_1 and γ of the angular velocity a.c.f.). The expression is now ready for evaluation because K_0, K_1 and γ have been evaluated carefully in the uncorrected theory by Reid and Evans. Correction to order $(kT/I)^4$ is possible but laborious.

1976 Evans theory is equivalent to:

$$\langle u(t)\cdot u(0)\rangle = \exp\left[\frac{-2kT}{I}\,I^{(2)}(t)\right]$$

and $m = 3$. This is Shimizu's equation (1964), quoted by Wyllie (1972) and rigorously valid only for planar libration (the Coffey case), when the factor 2 is replaced by 1.

APPENDIX C

Rotation/translation

In this case we have:

$$\frac{A(p)}{B(p)} = (p+\gamma^{(t)})/[p^2+(\gamma^{(r)}+\gamma^{(t)})p+(\gamma^{(r)}\gamma^{(t)}-\gamma^{(rt)}\gamma^{(tr)})].$$

The roots of the denominator may be written as:

$$\tfrac{1}{2}[-(\gamma^{(r)}+\gamma^{(t)})\pm[(\gamma^{(r)}+\gamma^{(t)2}-4(\gamma^{(r)}\gamma^{(t)}-\gamma^{(rt)}\gamma^{(tr)})]^{1/2}]$$

so that $a_1 = x+iy, \quad a_2 = x-iy$

where

$$x = -(\gamma^{(r)}+\gamma^{(t)})/2;$$

$$y = \tfrac{1}{2}[(\gamma^{(r)}+\gamma^{(t)})^2-4(\gamma^{(r)}\gamma^{(t)}-\gamma^{(rt)}\gamma^{(rt)})]^{1/2}$$

when

$$(\gamma^{(r)}+\gamma^{(t)})^2 < 4(\gamma^{(r)}\gamma^{(t)}-\gamma^{(rt)}\gamma^{(tr)}).$$

We have:

$$\frac{A_1}{B_1'} = \frac{(x+\gamma^{(t)})\,(2x+\gamma^{(r)}+\gamma^{(t)})+2y^2+iy(\gamma^{(r)}-\gamma^{(t)})}{(2x+\gamma^{(r)}+\gamma^{(t)})^2+4y^2} \equiv X+iY$$

and

$$\frac{A_2}{B_2'} = X-iY.$$

We have therefore:

$$I^{(2)}(t) = \sum_{n=1}^{m} \frac{A_n}{B_n'}\,\frac{(a_n t-1+e^{-a_n t})}{a_n^2} = \frac{-[2X(x^2-y^2)+4Yxy]}{(x^2-y^2)^2+4x^2y^2} + \frac{2t[xX+yY]}{(x^2+y^2)}$$

$$+\frac{2X(x^2-y^2)+4Yxy}{(x^2-y^2)^2+4x^2y^2}\,e^{-xt}\cos yt+\frac{2Y(x^2-y^2)-4Xxy}{(x^2-y^2)^2+4x^2y^2}\,e^{-xt}\sin yt.$$

$$I_2^{(4)}(t) = \frac{-10}{4}\left[\frac{X(x^4-6x^2y^2+y^4)+Y(4x^3y-4xy^3)}{(x^2+y^2)^4}\right]$$

$$+t\left[\frac{X(x^3-3xy^2)+Y(3x^2y-y^3)}{(x^2+y^2)^3}\right]$$

$$+\frac{2e^{-xt}\cos yt}{(x^2+y^2)^4}\,[X(x^4-6x^2y^2+y^4)+Y(4x^3y-4xy^3)]$$

$$+\frac{2e^{-xt}\sin yt}{(x^2+y^2)^4}\,[X(4x^3y-4xy^3)-Y(x^4-6x^2y^2+y^4)]$$

$$+\tfrac{1}{2}\,\frac{e^{-2xt}\cos 2yt}{(x^2+y^2)^4}\,[X(x^4-6x^2y^2+y^4)+Y(4x^3y-4xy^3)]$$

$$+\tfrac{1}{2}\,\frac{e^{-2xt}\sin 2yt}{(x^2+y^2)^4}\,[X(4x^3y-4xy^3)-Y(x^4-6x^2y^2+y^4)]$$

$$+\frac{2te^{-\alpha_1 t}\cos yt}{(x^2+y^2)^3}\,[X(x^3-3xy^2)+Y(3x^2y-y^3)]$$

$$+\frac{2te^{-\alpha_1 t}\sin yt}{(x^2+y^2)^3}\,[X(3x^2y-y^3)-Y(x^3-3xy^2)].$$

We have:

$$\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle = \exp\left[-2\left(\frac{kT}{I}I^{(2)}(t)+\left(\frac{kT}{I}\right)^{2}I_2^{(4)}(t)\right)\right]$$

in this approximation.

REFERENCES

[1] M. W. Evans, *Chem. Phys. Lett.* **39**, 601 (1976).

[2] M. W. Evans, W. T. Coffey, G. J. Evas, P. Grigolini, *Molecular Dynamics*, Wiley Interscience, N. Y., in press, chapter 5; M. W. Evans, G. J. Evans, A. R. Davies, *Adv. Chem. Phys.* **44**, 285 (1980).

[3] C. J. Reid, M. W. Evans, *Mol. Phys.* **40**, 1357 (1980).

[4] M. W. Evans, *J. Chem, Phys.*, submitted.

[5] H. Benoit, *Ann. Phys.* (France) **6**, 561 (1951); *J. Chem. Phys.* **49**, 517 (1952).

[6] G. R. Luckhurst, T. E. Faber, *Ann. Rep., Chem. Soc. (London)* 1975, p. 31; Ref. [2], chapter 8.

[7] G. W. Ford, J. T. Lewis, J. McConnell, *Proc. Roy. Irish Acad.* **76A**, 117 (1976); J. T. Lewis, J. McConnell, B. K. P. Scaife, *Proc. Roy. Irish Acad.* **76A**. 43 (1976).

[8] H. Mori, *Prog. Theor. Phys.* **34**, 399 (1965).

[9] N. G. van Kampen, *Phys. Rep.* **24C**, 171 (1976).

[10] P. Debye, *Polar Molecules*, Chem. Cat. Co, New York 1929.

[11] M. Abramowitz, I. A. Stegun, *Handbook of Mathematical Functions*, Dover, New York 1965.

[12] H. Shimizu, *J. Chem. Phys.* **41**, 2329 (1964). See also M. Ferrario, M. W. Evans, *Adv. Mol. Rel. Int. Proc.*, in press (1981); and Ref. [2], chapter 2.

[13] B. J. Berne, R. Pecora, *Light Scattering with Applications to Chemistry, Physics and Biology*, Wiley Interscience, New York 1976.

[14] R. P. Feynman, *Lectures in Physics*, Addison-Wesley, Reading, Mass. 1965.

[15] A. D. Buckingham, *Chem. Soc. Quart. Rev.* **13**, 183 (1959).

[16] G. T. Evans, *J. Chem. Phys.* **65**, 3030 (1976); P. G. Wolynes, J. M. Deutch, *J. Chem. Phys.* **65**, 450 (1976).

[17] M. W. Evans, M. Ferrario, P. Crigolini, *Mol. Phys.* **39**, 1369, 1391 (1980); M. Ferrario, M. W. Evans, *Physica A*, in press.

[18] W. B. Streett, K. K. Gubbins, *Ann. Rev. Phys. Chem.* **28**, 373 (1977); *Faraday Disc., Chem. Soc.* (London), No. 66 (1978).

[19] J. H. van Vleck, *Theory of Electric and Magnetic Susceptibility*.