Relation of dipole and angular velocity autocorrelation functions

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A truncated Mori expansion for the angular velocity autocorrelation function is used as a starting-point to calculate the orientational auto-correlation function for a disk and a sphere using the newly developed methods of Lewis et al. [9]. Assuming the angular velocity to be a gaussian process, one obtains for the first few terms of a development in powers of time. In the free rotor and Debye limits this series can be rearranged to agree with the corresponding terms of the expansion in powers of time of the known limiting expressions. A closed form is obtained for the disk which does the same. It becomes clear that this three-variable Kivelson/Keyes formalism [3] when used for the angular velocity is equivalent to the inertia-corrected itinerant oscillator in two dimensions [24]. Thus it is possible now to relate analytically a realistic, oscillatory angular velocity autocorrelation function to a realistic orientational autocorrelation function for the same molecular symmetry.

1. Introduction

In several recent articles [1–5] on brownian motion the Langevin equation for the angular velocity ω of a molecule, viz.

$$I\dot{\omega} + I\beta_t\omega = I\dot{\Gamma}, \qquad (1)$$

has been used in a more general form [6] to allow the original friction coefficient, β_t to become time-dependent. In equation (1), I is the moment of inertia and $I\beta_t$, the frictional couple written as $\zeta\omega$ by Debye [7]. $I\dot{\Gamma}$ is the torque due to random driving forces caused by thermal fluctuation in the environment. In this paper a more flexible integro-differential formalism due to Kubo [8] and Mori [6] is used to calculate an expression for the autocorrelation function of orientation for a dipole unit vector $\mathbf{u}$ embedded (i) in a sphere ; (ii) in a disk. The method used is that of Lewis et al. [9], and is a more complete calculation than one outlined by Evans [10] in a previous paper, where a cumulant expansion [11] was used to relate $\langle\omega(t) \cdot \omega(0)\rangle$ to $\langle\mathbf{u}(t) \cdot \mathbf{u}(0)\rangle$ for a two-dimensional rotor. The type of calculation presented here, though tedious and intricate, is needed to attempt a match with the results of computer molecular dynamics [12], where $\langle\omega(t) \cdot \omega(0)\rangle$ is often shown to be an oscillatory function of time, sometimes with negative portions, while $\langle\omega(t) \cdot \omega(0)\rangle$ from equation (1) is simply $\exp(-\beta_t t)$, a form that violates the fundamental axiom of time reversibility for classical autocorrelation functions [2 c]. Below, we use a more realistic, oscillatory, angular velocity autocorrelation function derived from a Mori continued fraction [6].

2. THE DIPOLE EMBEDDED IN A SPHERE

Consider the brownian motion of a spherical molecule containing a rigid dipole passing through its centre. Independently of the shape of the body we have

$$\dot{u}(t) = \omega(t) \times u(t). \quad (2)$$

Since the ω's are gaussian random variables we have

$$\langle \omega_{i_1}^{(a_1)} \ldots \omega_{i_{2n+1}}^{(a_{2n+1})} \rangle = 0 \quad (3)$$

$$\langle \omega_{i_1}^{(a_1)} \ldots \omega_{i_{2n}}^{(a_{2n})} \rangle = \sum \prod_{i_r > i_s} \langle \omega_{i_r}^{(a_r)} \omega_{i_s}^{(a_s)} \rangle, \quad (4)$$

where the superscripts denote components. So that repeated integration of equation (2) gives, on averaging (and writing the conditional expectation value $\langle u(t)|u(0)\rangle$ as $\langle u(t)\rangle$):

$$\langle u(t) \rangle = u_0 + \int_{0 \leq t_1 \leq t} \int \langle (\omega_2 \times (\omega_1 \times u_0)) \rangle \, dt_1 \, dt_2$$
$$+ \int_{0 \leq t_1 \ldots \leq t_4 \leq t} \int \langle (\omega_4 \times (\omega_3 \times (\omega_2 \times (\omega_1 \times u_0)))) \rangle \, dt_1 \ldots dt_4 + \ldots, \quad (5)$$

which converges to the unique solution of equation (2) provided $\omega(t)$ is a continuous function of t and $u(0) = u_0$. Using the Dirac notation of Lewis et al. [9], then, for example:

$$\omega_2 \times (\omega_1 \times u_0) = \omega_1(\omega_2 \cdot u_0) - (\omega_2 \cdot \omega_1) u_0 = (|1\rangle(2| - (2|1\rangle)|0\rangle.$$

In one very popular form [1-4] of the generalized Langevin equation we have

$$I\dot{\omega} + I \int_0^t K_0(t-\tau) \omega(\tau) \, d\tau = I\Theta, \quad (6)$$

where K is the memory function [2 c] defined by

$$K_0(t) = \langle \Theta(t) \cdot \Theta(0) \rangle / \langle \omega(0) \cdot \omega(0) \rangle.$$

The variate Θ is gaussian and non-markovian. According to Mori [6], K may be replaced by a continued fraction which we truncate here at a level commensurate with Kivelson/Keyes three variable theory [4], so that in Laplace transform space (p):

$$\bar{K}_0(p) = \frac{K_0(0)}{p + \bar{K}_1(p)} = \frac{K_0(0)}{p + \dfrac{K_1(0)}{p+\gamma}},$$

where $K_0(0)$ and $K_1(0)$ are equilibrium averages (variances), and γ is defined by

$$K_1(t) = K_1(0) \exp(-\gamma t).$$

It follows that

$$\dot{\Theta}(t) + \int_0^t K_1(t-\tau)\Theta(\tau) \, d\tau = \Theta_1 \quad (7)$$

and

$$\dot{\Theta}_1(t) + \gamma\Theta_1(t) = \dot{\Theta}_2(t). \quad (8)$$

Solving equations (6)-(8) we have

$$\bar{\omega}(p) = \frac{\omega(0)}{p + \bar{K}_0(p)} + \frac{\Theta(0)}{(p+\bar{K}_1(p))(p+\bar{K}_0(p))}$$
$$+ \frac{\Theta_1(0) + \mathcal{L}(\dot{\Theta}_2(t))}{p^3 + p^2\gamma + p(K_0(0)+K_1(0)) + \gamma K_0(0)}. \quad (9)$$

In equation (8), $\Theta_2(t)$ is assumed to be a Wiener process [13], so that:

$$\langle \Theta_2(t) \rangle = 0; \quad (10)$$

$$\langle (\Theta_2(t) \cdot e_i)(\Theta_2(t') \cdot e_j) \rangle = c^2 \min(t, t') \delta_{ij},$$

where c is a constant and e_i, e_j two of three mutually perpendicular unit vectors in 3-D space. For time intervals Δ, Δ'; letting

$$\Theta_2(t_k) - \Theta_2(t_l) = \xi(t_k - t_l),$$

we have

$$\langle \xi(\Delta) \rangle = 0, \quad (11)$$

$$\langle (\xi(\Delta) \cdot e_i)(\xi(\Delta') \cdot e_j) \rangle = c^2 \delta_{ij} |\Delta \cap \Delta'|.$$

Considering the roots of the cubic in equation (9); a cubic equation with real coefficients has three distinct real roots, a single real root, or at least two equal real roots, according as its discriminant is positive, negative or zero. The discriminant of our cubic is

$$\Delta_0 = 18 b_0 c_0 d_0 - 4 b_0^3 d_0 + b_0^2 c_0^2 - 4 c_0^3 - 27 d_0^2;$$

where

$$b_0 = \gamma; \quad c_0 = K_0(0) + K_1(0); \quad d_0 = \gamma K_0(0).$$

In the case where $\Delta_0 > 0$ the roots (which we designate in this case as α_1, α_2 and α_3) must be found numerically (using, for example, the comprehensive N.A.G. library available for most computers), and the steady-state solution for $\omega(t)$ from equation (9) becomes

$$\omega(t) = \int_{-\infty}^t \sum_n^3 D_n \exp[-\alpha_n(t-\tau)] \xi(dt), \quad (12)$$

where the pre-exponential D_n can be expressed in terms of α_n using partial fractions.

In the case where $\Delta_0 \leq 0$ the roots (which we designate in this case by $(p+\alpha_2')(p+\alpha_1'+i\beta')(p+\alpha_1'-i\beta')$ may be found by Cardan's formula, and may be related to $K_0(0)$, $K_1(0)$ and γ as in the Appendix. The steady-state solution is now

$$\omega(t) = \int_{-\infty}^t y_0 \exp(-(t-\tau)\alpha_2') + [y_1 \sin[\beta'(t-\tau)] + y_2 \cos[\beta'(t-\tau)]]$$
$$\times \exp(-(t-\tau)\alpha_1') \xi(d\tau)$$

$$= \int_{-\infty}^t [C_1 \cos(\beta_0(t-\tau) + \phi) \exp[-\xi_0(t-\tau)]$$
$$+ C_2 \exp[-\alpha_0(t-\tau)]] \xi(d\tau), \quad (14)$$

where $y_0 = -y_1 = [(\alpha_2' - \alpha_1')^2 + \beta'^2]^{-1}$

$$y_2 = \frac{1}{\beta'}\left(\frac{\alpha_2' - \alpha_1'}{(\alpha_1' - \alpha_2')^2 + \beta'^2}\right).$$

3. CALCULATION OF $\langle\boldsymbol{\mu}(t)\rangle$

we can proceed in the mathematically less onerous case of $\Delta_0 = -4A^3 - 27B^2 > 0$ (see Appendix) to calculate, by equation (11),

Defining

$$f_i(\tau) = \begin{cases} \sum_n^3 D_n \exp[-\alpha_n(t-\tau)], & \tau \leq t, \\ 0 & \tau > t, \end{cases}$$

$$\langle \omega_k^{(i)} \omega_1^{(j)}\rangle = c^2 \delta_{ij}(D_1^2/2\alpha_1 + D_1 D_2/(\alpha_1 + \alpha_2) + D_1 D_3/(\alpha_1 + \alpha_3))$$
$$\times \exp(-\alpha_1|t_k - t_1|) + (D_2^2/2\alpha_2^2 + D_2 D_1/(\alpha_1 + \alpha_2)$$
$$+ D_2 D_3/(\alpha_2 + \alpha_3))\exp(-\alpha_2|t_k - t_1|)$$
$$+ (D_3^2/2\alpha_3^2 + D_1 D_3/(\alpha_1 + \alpha_3) + D_2 D_3/(\alpha_2 + \alpha_3))$$
$$\times \exp(-\alpha_3|t_k - t_1|),$$ (15)

$$= c^2 \delta_{ij} \int_{-\infty}^{\infty} f_{1_k}(\tau) f_{1_l}(\tau)\, d\tau.$$ (16)

So we have

$$\langle \boldsymbol{\omega}_k \cdot \boldsymbol{\omega}_1\rangle = 3\langle \omega_k^{(i)} \omega_1^{(j)}\rangle.$$

In the case $t_k = t_1 = t$ equation (15) reduces to

$$\langle \omega^{(i)}(t)^2\rangle = \left[\frac{D_1}{2\alpha_1} + \frac{D_2}{2\alpha_2} + \frac{D_3}{2\alpha_3} + \frac{2D_1 D_2}{(\alpha_1 + \alpha_2)} + \frac{2D_1 D_3}{(\alpha_1 + \alpha_3)} + \frac{2D_2 D_3}{(\alpha_2 + \alpha_3)}\right] c^2$$ (17)
$$\equiv c^2/2\beta$$ (18)

for brevity. (N.B. in our notation β' is unrelated to β and is not its derivative.) The constant c may now be evaluated using the equation

$$\tfrac{1}{2}I\langle \boldsymbol{\omega}(t)^2\rangle = \tfrac{3}{2}kT,$$ (19)

so that

$$c^2 = 2\beta kT/I.$$ (20)

A frictional relaxation time (τ_2) and a mean thermal angular period (τ_1) may now be defined as

$$\tau_2 = 1/\beta; \quad \tau_1 = (I/kT)^{1/2}.$$ (21)

Considering the component $\langle u^{(1)}(t)\rangle$ of $\langle \mathbf{u}(t)\rangle$, the contribution to it from equation (6) can be written as

$$\int_{0 \leq t_1 \leq t_2 \leq t}\int \langle(\boldsymbol{\omega}_2 \cdot \mathbf{u}_0)\omega_1^{(1)} - (\boldsymbol{\omega}_2 \cdot \boldsymbol{\omega}_1)u_0^{(1)}\rangle\, dt_1\, dt_2,$$ (22)

from which it follows from equation (21) that the c^2 term is

$$-2c^2 u_0^{(1)} \int_{0 \leq t_1 \leq t_2 \leq t}\int A_0 \exp[-\alpha_1(t_2 - t_1)] + B_0 \exp[-\alpha_2(t_2 - t_1)]$$
$$+ C_0 \exp[-\alpha_3(t_2 - t_1)]\, dt_1\, dt_2,$$ (23)

where A_0, B_0 and C_0 denote the pre-exponential factors of equation (21). Denoting the integral in (23) by $I_1^{(2)}(t)$ and evaluating it by means of Laplace transformation we have

$$I_1^{(2)}(t) = t\left(\frac{A_0}{\alpha_1} + \frac{B_0}{\alpha_2} + \frac{C_0}{\alpha_3}\right) - \left(\frac{A_0}{\alpha_1^2} + \frac{B_0}{\alpha_2^2} + \frac{C_0}{\alpha_3^2}\right)$$
$$+ \left(\frac{A_0 \exp(-\alpha_1 t)}{\alpha_1^2} + \frac{B_0 \exp(-\alpha_2 t)}{\alpha_2^2} + \frac{C_0 \exp(-\alpha_3 t)}{\alpha_3^2}\right)$$ (24)

and so the contribution to $\langle \mathbf{u}(t)\rangle$ is

$$-2c^2 \mathbf{u}_0 I_1^{(2)}(t) = -2(2\beta kT/I)\mathbf{u}_0 I_1^{(2)}(t).$$ (25)

Next we evaluate the c^4 integral:

$$\int_{0 \leq t_1 \leq \ldots \leq t_4 \leq t}\langle(|3\rangle\langle4| - \langle4|3\rangle)(|1\rangle\langle2| - \langle2|1\rangle)|0\rangle\rangle\, dt_1 \ldots dt_4.$$

The integrand reduces, after some algebra, to

$$4\langle \omega_4^{(1)} \omega_3^{(1)}\rangle\langle \omega_2^{(1)} \omega_1^{(1)}\rangle + 4\langle \omega_4^{(1)} \omega_1^{(1)}\rangle\langle \omega_3^{(1)} \omega_2^{(1)}\rangle$$
$$+ 2\langle \omega_4^{(1)} \omega_2^{(1)}\rangle\langle \omega_3^{(1)} \omega_1^{(1)}\rangle,$$ (26)

where equation (4) has been used for the fourth-order averages. Equation (25) may now be evaluated using equation (16) and the theorem

$$(f_1 * f_2 * \ldots * f_n) = \int \ldots \int_{0 \leq t_1 \leq \ldots \leq t_{n-1} \leq t} f_1(t - t_{n-1}) f_2(t_{n-1} - t_{n-2}) \ldots f_n(t_1)$$
$$\times [dt_1 \ldots dt_{n-1}],$$ (27)

where $*$ denotes convolution. Therefrom in Laplace space the integral (25) is

$$\begin{aligned}
&A_0^2(4(p^3(p+\alpha_1)^2)^{-1}+6(p^2(p+\alpha_1)^2(p+2\alpha_1))^{-1})+B_0^2(4(p^3(p+\alpha_2)^2)^{-1}\\
&+6(p^2(p+\alpha_2)^2(p+2\alpha_2))^{-1})+C_0^2(4(p^3(p+\alpha_3)^2)^{-1}+6(p^2(p+\alpha_3)^2)^{-1}\\
&\times(p+2\alpha_3))^{-1})+4A_0B_0(2(p^3(p+\alpha_1)(p+\alpha_2))^{-1}+(p^2(p+\alpha_1)(p+\alpha_2)^2)^{-1}\\
&\times(p+\alpha_1+\alpha_2))^{-1}+(p^2(p+\alpha_1)(p+\alpha_1+\alpha_2))^{-1}+(p^2(p+\alpha_2)^2(p+\alpha_1+\alpha_2))^{-1}\\
&\times(p+\alpha_1+\alpha_2))^{-1}+4A_0C_0(2(p^3(p+\alpha_1)(p+\alpha_3))^{-1}+(p^2(p+\alpha_1)(p+\alpha_3)^2)^{-1}\\
&\times(p+\alpha_1+\alpha_3))^{-1}+(p^2(p+\alpha_3)^2(p+\alpha_1+\alpha_3))^{-1}+4B_0C_0(2(p^3(p+\alpha_2)(p+\alpha_3))^{-1}\\
&\times(p+\alpha_1+\alpha_3))^{-1}+(p^2(p+\alpha_2)(p+\alpha_3)^2)^{-1}\\
&\times(p+\alpha_2+\alpha_3))^{-1}+(p^2(p+\alpha_3)^2(p+\alpha_2+\alpha_3))^{-1}+(p^2(p+\alpha_2)^2(p+\alpha_2+\alpha_3))^{-1})\\
&\times(p+\alpha_3)(p+\alpha_2+\alpha_3))^{-1}).
\end{aligned}$$

Taking inverse transforms we have, for example:

$$\mathcal{L}^{-1}((p^3(p+\alpha_1)^2)^{-1}) = \frac{t^2}{2\alpha_1^2} - \frac{2t}{\alpha_1^3} + \frac{3}{\alpha_1^4} - \frac{t\exp(-\alpha_1 t)}{\alpha_1^3} - 3\frac{\exp(-\alpha_1 t)}{\alpha_1^4},$$

$$\mathcal{L}^{-1}((p^2(p+\alpha_1)(p+2\alpha_1))^{-1}) = \frac{t}{2\alpha_1^3} - \frac{5}{4\alpha_1^4} + t\frac{\exp(-\alpha_1 t)}{\alpha_1^3} + \frac{\exp(-\alpha_1 t)}{\alpha_1^4} + \frac{\exp(-2\alpha_1 t)}{4\alpha_1^4},$$

$$\mathcal{L}^{-1}((p^3(p+\alpha_1)(p+\alpha_2))^{-1}) = {}^0x_1 + {}^0x_2 t + {}^0x_3 t^2 + {}^0x_4 \exp(-\alpha_1 t) + {}^0x_5 \exp(-\alpha_2 t),$$

$$\mathcal{L}^{-1}((p^2(p+\alpha_1)^2(p+\alpha_2))^{-1}) = {}^1x_1 + {}^1x_2 t + {}^1x_3 \exp(-\alpha_1 t) + {}^1x_4 t\exp(-\alpha_1 t) + {}^1x_5 \exp(-(\alpha_1+\alpha_2)t),$$

$$\mathcal{L}^{-1}((p^2(p+\alpha_2)^2(p+\alpha_1+\alpha_2))^{-1}) = {}^1x_1' + {}^1x_2' t + {}^1x_3' \exp(-\alpha_2 t) + {}^1x_4' t\exp(-\alpha_2 t) + {}^1x_5' \exp(-(\alpha_1+\alpha_2)t),$$

$$\mathcal{L}^{-1}((p^2(p+\alpha_1)(p+\alpha_2)(p+\alpha_1+\alpha_2))^{-1}) = {}^2x_1 + {}^2x_2 t + {}^2x_3 \exp(-\alpha_1 t) + {}^2x_4 \exp(-\alpha_2 t) + {}^2x_5 \exp(-(\alpha_1+\alpha_2)t).$$

Here the x's are complicated combinations of α_1 and α_2. Denoting by y and z the equivalent functions for the pairs (α_1, α_3) and (α_2, α_3) respectively, the fourth-order contribution to $\langle \mathbf{u} \rangle$ is given finally by

$$\mathbf{u}_0 c^4 \{2t^2(A_0^2/\alpha_1 + B_0^2/\alpha_2 + C_0^2/\alpha_3 + \Lambda_1) - t(5(A_0^2/\alpha_1 + B_0^2/\alpha_2 + C_0^2/\alpha_3) - \Lambda_2)$$
$$+ \tfrac{9}{2}(A_0^2/\alpha_1^4 + B_0^2/\alpha_2^4 + C_0^2/\alpha_3^4) + \Lambda_3 + t(\exp(-\alpha_3 t)(2A_0^2/\alpha_3^3 + \Lambda_4)$$
$$+ \exp(-\alpha_2 t)(2B_0^2/\alpha_2^3 + \Lambda_5) + \exp(-\alpha_1 t)(2C_0^2/\alpha_3^3 + \Lambda_6))$$
$$- \exp(-\alpha_1 t)(6A_0^2/\alpha_1^4 - \Lambda_7) - \exp(-\alpha_2 t)(6B_0^2/\alpha_2^4 - \Lambda_8)$$
$$- \exp(-\alpha_3 t)(6C_0^2/\alpha_3^4 - \Lambda_9) + \tfrac{3}{2}(A_0^2 \exp(-2\alpha_1 t)/\alpha_1^4$$
$$+ B_0^2 \exp(-2\alpha_2 t)/\alpha_2^4 + C_0 \exp(-2\alpha_3 t)/\alpha_3^4) + 4(\exp(-(\alpha_1+\alpha_2)t)\Lambda_{10}$$
$$+ \exp(-(\alpha_1+\alpha_3)t)\Lambda_{11} + \exp(-(\alpha_2+\alpha_3)t)\Lambda_{12})\}. \quad (28)$$

In equation (28) the Λ factors are cross terms of $A_0 B_0$, $A_0 C_0$ and $B_0 C_0$ involving α_1, α_2 and α_3. The full expression, which is cumbersome, is available on request. We also indicate below the basic structure of the next term, which is

$$-\mathbf{u}_0 c^6 \{\tfrac{4}{3} t^3 (A_0^4/\alpha_1^3 + B_0^4/\alpha_2^3 + C_0^4/\alpha_3^3 + \Xi_1) - 6t^2 (A_0^4/\alpha_1^4 + B_0^4/\alpha_2^4 + C_0^4/\alpha_3^4 + \Xi_2)$$
$$+ \tfrac{23}{9} t(A_0^4/\alpha_1^5 + B_0^4/\alpha_2^5 + C_0^4/\alpha_3^5 + \Xi_3) - \tfrac{95}{9}(A_0^4/\alpha_1^6 + B_0^4/\alpha_2^6 + C_0^4/\alpha_3^6 + \Xi_4)$$
$$+ \exp(-\alpha_1 t)(A_0^4(t^2/\alpha_1^4 - 6t/\alpha_1^5 + 15/\alpha_1^6) + \Xi_5)$$
$$+ \exp(-\alpha_2 t)(B_0^4(t^2/\alpha_2^4 - 6t/\alpha_2^5 + 15/\alpha_2^6) + \Xi_6)$$
$$+ \exp(-\alpha_3 t)(C_0^4(t^2/\alpha_3^4 - 6t/\alpha_3^5 + 15/\alpha_3^6) + \Xi_7)$$
$$+ \exp(-2\alpha_1 t)(A_0^4(t/2\alpha_1^5 - 5/\alpha_1^6) + \Xi_8)$$
$$+ \exp(-2\alpha_2 t)(B_0^4(t/2\alpha_2^5 - 5/\alpha_2^6) + \Xi_9)$$
$$+ \exp(-2\alpha_3 t)(C_0^4(t/2\alpha_3^5 - 5/\alpha_3^6) + \Xi_{10})$$
$$+ \tfrac{5}{9}(\exp(-3\alpha_1 t)A_0^4/\alpha_1^6 + \exp(-3\alpha_2 t)B_0^4/\alpha_2^6 + \exp(-3\alpha_3 t)C_0^4/\alpha_3^6$$
$$+ \Xi_{11}) + \Xi_{12}\}, \quad (29)$$

where Ξ_{12} represents cross terms of the exponentials:

$$\exp(-(\alpha_1+\alpha_2)t), \quad \exp(-(\alpha_1+2\alpha_2)t), \quad \exp(-(\alpha_1+\alpha_2+\alpha_3)t), \quad \text{etc.}$$

and all possible permutations of the indices among α_1, α_2 and α_3. The other Ξ's represent cross terms proportional to $A_0^2 B_0^2$, $A_0^3 B_0$, $A_0^2 B_0 C_0$, $A_0 B_0^2 C_0$, etc., in permutation.

This series expansion for $\langle \mathbf{u}(t) \rangle$ simplifies considerably in two limiting cases which illuminate certain of its properties and physical significance.

(1) If α_1, α_2 and α_3 are each small enough for the exponential components of (24), (28) and (29) to remain comparable to the others in magnitude, and also for $(\alpha_m t)^{2n+1}/(2n+1)!$ to be negligible compared with $(\alpha_m t)^{2n}/(2n)!$, where n here refers to the c^nth term and $m = 1, 2, 3$ and relevant permutations and combinations thereof we have $\tau_2 \gg t$ (equation (19)), and equation (5) becomes, after a great deal of algebra:

$$\langle \mathbf{u}(t) \rangle = \mathbf{u}_0[1 - c^2 t^2 (A_0 + B_0 + C_0) + c^4 t^4 (5(A_0^2 + B_0^2 + C_0^2)/12$$
$$+ 5(A_0 B_0 + A_0 C_0 + B_0 C_0)/6) - c^6 t^6 (7(A_0^4 + B_0^4 + C_0^4)/72$$
$$+ 7(A_0^3(B_0 + C_0) + B_0^3(A_0 + C_0) + C_0^3(A_0 + B_0))/9$$
$$+ 7(A_0^2 B_0^2 + A_0^2 C_0^2 + B_0^2 C_0^2)/12 + 9(A_0^2 B_0 C_0 + B_0^2 A_0 C_0$$
$$+ C_0^2 A_0 B_0)/8) + \cdots]$$

$$= \mathbf{u}_0[1 - c^2 t^2 (A_0 + B_0 + C_0) + \tfrac{5}{12} c^4 t^4 (A_0 + B_0 + C_0)^2$$
$$- \tfrac{7}{72} c^6 t^6 (A_0 + B_0 + C_0)^4 + \cdots].$$

Using $c^2 = 2\beta(kT/I)$ and $(A_0 + B_0 + C_0) = 1/2\beta$, we have, finally, for a very long frictional relaxation time:

$$\langle \mathbf{u}(t) \rangle = \mathbf{u}_0 \left[1 - \frac{kTt^2}{I} + \frac{5}{12} \left(\frac{kT}{I}\right)^2 t^4 - \frac{7}{72} \left(\frac{kT}{I}\right)^3 t^6 + \cdots \right]. \quad (30)$$

In this limit the orientational autocorrelation function is:

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle = \langle \mathbf{u}(t) \cdot \mathbf{u}_0; \quad (31)$$

and is expanded as in the right-hand side of equation (30), since $\langle \mathbf{u}(0) \cdot \mathbf{u}(0) \rangle = 1$.

Now the classical autocorrelation function for the free rotation of a spherical top molecule is obtainable from Desplanques' expansion for a symmetric top [17]:

$$\langle \mathbf{u}(t) \rangle \cdot \mathbf{u}_0 = 1 - \frac{kTt^2}{I} + \left[\frac{1}{3} \left(\frac{kT}{I}\right)^2 \left(1 + \frac{I'}{4I}\right) + \frac{\langle N^2 \rangle}{24 I^2}\right] t^4 \quad (32)$$

in the limit where the mean square torque $\langle N^2 \rangle \to 0$, and the moments of inertia I' and I become equal. Then we have

$$\langle \mathbf{u}(t) \rangle \cdot \mathbf{u}_0 = 1 - \frac{kTt^2}{I} + \frac{5}{12} \left(\frac{kT}{I}\right)^2 t^4 - \cdots,$$

giving exact agreement with equation (30) up to the t^4 term.

(2). When α_1, α_2 and α_3 each become very large, the dominant term in each coefficient of the expansion will be the t term, t^2 term, etc, so that

$$\langle \mathbf{u}(t)\rangle \cdot \mathbf{u}_0 = 1 - 2\left(\frac{A_0}{\alpha_1} + \frac{B_0}{\alpha_2} + \frac{C_0}{\alpha_3}\right) tc^2 + 2c^4\left(\frac{A_0^2}{\alpha_1^2} + \frac{B_0^2}{\alpha_2^2} + \frac{C_0^2}{\alpha_3^2} + \Lambda_1\right)t^2$$
$$- \tfrac{4}{3}c^6\left(\frac{A_0^4}{\alpha_1^3} + \frac{B_0^4}{\alpha_2^3} + \frac{C_0^4}{\alpha_3^3} + \Xi_1\right)t^3 + \cdots. \quad (33)$$

However, we have

$$\Lambda_1 = 2\left(\frac{A_0 B_0}{\alpha_1\alpha_2} + \frac{A_0 C_0}{\alpha_1\alpha_3} + \frac{B_0 C_0}{\alpha_2\alpha_3}\right)$$

and

$$\Xi_1 = 6\frac{A_0 B_0 C_0}{\alpha_1\alpha_2\alpha_3} + 2\left[\frac{A_0^2}{\alpha_1^2}\left(\frac{B_0}{\alpha_2}+\frac{C_0}{\alpha_3}\right) + \frac{B_0^2}{\alpha_2^2}\left(\frac{A_0}{\alpha_1}+\frac{C_0}{\alpha_3}\right) + \frac{C_0^2}{\alpha_3^2}\left(\frac{B_0}{\alpha_2}+\frac{A_0}{\alpha_1}\right)\right].$$

so that it is plausible that equation (33) becomes

$$\langle \mathbf{u}(t)\rangle \cdot \mathbf{u}_0 = \exp\left[-2c^2\left(\frac{A_0}{\alpha_1}+\frac{B_0}{\alpha_2}+\frac{C_0}{\alpha_3}\right)t\right]$$
$$\equiv \exp(-t/\tau_D) \quad (34)$$

where τ_D is the Debye time.

Thus our orientation a.c.f. reduces to the free rotor and Debye limits for $\tau_2 \geq t$ and $\tau_2 \ll t$ respectively, although the angular velocity a.c.f., containing a coefficient in t^5 in its Maclaurin expansion [10] is theoretically imperfect. The expansion of $\langle \mathbf{u}(t)\rangle$ in the general case is cumbersome, and applicable experimentally in the far infra-red/microwave only for dipolar 'accidental' spherical tops such as CD_3CF_3. An approximate closed form, exact up to the t^2 term is

$$\exp\left[\left[-4\beta\frac{kT}{I}\left[t\left(\frac{A_0}{\alpha_1}+\frac{B_0}{\alpha_2}+\frac{C_0}{\alpha_3}\right) - \left(\frac{A_0}{\alpha_1^2}+\frac{B_0}{\alpha_2^2}-\frac{C_0}{\alpha_3^2}\right)\right.\right.\right.$$
$$\left.\left.\left. + \left(A_0\frac{\exp(-\alpha_1 t)}{\alpha_1^2} + B_0\frac{\exp(-\alpha_2 t)}{\alpha_2^2} + C_0\frac{\exp(-\alpha_3 t)}{\alpha_3^2}\right)\right]\right]\right] \quad (35)$$

and the spectrum

$$\left(\int_0^\infty \langle \mathbf{u}(t)\rangle \cdot \mathbf{u}_0 \exp(-i\omega t)\, dt\right)$$

may be found to the necessary accuracy by using Laplace transforms and the method of successive convergents [14]. In the case $\alpha_1 = \alpha_2 = \alpha_3 = \tau$, $D_1 = D_2 = D_3 = \frac{1}{3}$, our expansion reduces to that of Lewis et al. [9] and therefore to that of Sack [15], who investigated the problem of the rotating sphere using a diffusion equation derived from a generalized Liouville equation. We now consider the disc, where it is possible to derive the orientational a.c.f. for $\Delta_0 < 0$ in a closed form and also for $\Delta_0 > 0$, given the analytical angular velocity a.c.f. of the Mori expansion.

4. THE DIPOLE EMBEDDED IN A DISK

Consider the motion of a molecule that contains a dipole whose axis rotates in a plane, and whose $\mathbf{u}(t)$ in the dipole axis. Then

$$\omega(t) = \omega(t)\mathbf{k},$$

where $\mathbf{k}$ is a unit vector and $\omega(t) = |\omega(t)|$. Let I be the moment of inertia of the disc about $\mathbf{k}$. Since

$$\mathbf{k}\cdot\mathbf{u}_0 = 0; \quad \mathbf{k}\times(\mathbf{k}\times\mathbf{u}_0) = -\mathbf{u}_0,$$

then it follows that [8]

$$\langle\mathbf{u}(t)\rangle = \mathbf{u}_0\Big[1 - \int_{0\leq t_1\leq t_2\leq t}\int \langle\omega_2\omega_1\rangle\, dt_1\, dt_2 + \int\cdots\int_{0\leq t_1\leq\ldots\leq t_4\leq t}\langle\omega_4\omega_3\omega_2\omega_1\rangle\, dt_1\ldots dt_4$$
$$- \int\cdots\int_{0\leq t_1\leq\ldots\leq t_6\leq t}\langle\omega_6\omega_5\omega_4\omega_3\omega_2\omega_1\rangle\, dt_1\ldots dt_6 + \cdots\Big]. \quad (36)$$

For scalar ω, equation (15) becomes

$$\langle\omega_k\omega_l\rangle = c^2[A_0\exp(-\alpha_1|t_k - t_l|) + B_0\exp(-\alpha_2|t_k-t_l|)$$
$$+ C_0\exp(-\alpha_3|t_k-t_l|)]$$

in the case $\Delta_0 < 0$. We shall consider the whole domain of Δ_0 below. So the first integral in equation (36) is

$$-c^2\left[t\left(\frac{A_0}{\alpha_1}+\frac{B_0}{\alpha_2}+\frac{C_0}{\alpha_3}\right) - \left(\frac{A_0}{\alpha_1^2}+\frac{B_0}{\alpha_2^2}+\frac{C_0}{\alpha_3^2}\right)\right.$$
$$\left. + \left(A_0\frac{\exp(-\alpha_1 t)}{\alpha_1^2} + B_0\frac{\exp(-\alpha_2 t)}{\alpha_2^2} + C_0\frac{\exp(-\alpha_3 t)}{\alpha_3^2}\right)\right]. \quad (37)$$

Since the second integral can be written [9] as

$$\frac{3}{4!}\left[2\int_0^t dt_2\int_0^{t_2}\langle\omega(t_2)\omega(t_1)\rangle\, dt_1\right]^2 \quad (38)$$

and all successive integrals as

$$\frac{1}{r!}\left[c^2\left[t\left(\frac{A_0}{\alpha_1}+\frac{B_0}{\alpha_2}+\frac{C_0}{\alpha_3}\right) - \left(\frac{A_0}{\alpha_1^2}+\frac{B_0}{\alpha_2^2}+\frac{C_0}{\alpha_3^2}\right)\right.\right.$$
$$\left.\left. + \left(A_0\frac{\exp(-\alpha_1 t)}{\alpha_1^2} + B_0\frac{\exp(-\alpha_2 t)}{\alpha_2^2} + C_0\frac{\exp(-\alpha_3 t)}{\alpha_3^2}\right)\right]\right]^r, \quad (39)$$

then immediately we have

$$\langle\mathbf{u}(t)\rangle\cdot\mathbf{u}_0 = \exp\left[-2\beta\frac{kT}{I}\left[t\left(\frac{A_0}{\alpha_1}+\frac{B_0}{\alpha_2}+\frac{C_0}{\alpha_3}\right) - \left(\frac{A_0}{\alpha_1^2}+\frac{B_0}{\alpha_2^2}+\frac{C_0}{\alpha_3^2}\right)\right.\right.$$
$$\left.\left. + \left(A_0\frac{\exp(-\alpha_1 t)}{\alpha_1^2} + B_0\frac{\exp(-\alpha_2 t)}{\alpha_2^2} + C_0\frac{\exp(-\alpha_3 t)}{\alpha_3^2}\right)\right]\right]. \quad (40)$$

Turning to the case where $\Delta_0 = 0$ we have

$$\langle \omega^{(0)}(t)^2 \rangle \to \left[\frac{C_1^2}{2\xi_0} + \frac{C_2^2}{2\alpha_0} + \frac{2C_1 C_2}{\xi_0 + \alpha_0} \right] c^2$$

$$= \frac{c^2}{\beta_z} \text{ as } t \to \infty;$$

so that $c^2 = 2\beta_z kT/I$ $\tau_2 = 1/\beta_z$ as for equation (18). In the special case where $\beta_0 = 0$ (which implies $\gamma = 3(3K_0(0))^{1/2}$ in the Mori continued fraction) we have

$$\langle u(t) \rangle \cdot u_0 = \exp\left[-2\beta_z \frac{kT}{I} \left[t \left(A_1 \frac{\exp(-\xi_0 t)}{\xi_0^2} + A_2 \frac{\exp(-\alpha_0 t)}{\alpha_0^2} \right) - \left(\frac{A_1}{\xi_0^2} + \frac{A_2}{\alpha_0^2} \right) + \left(A_1 \frac{\exp(-\xi_0 t)}{\xi_0^2} + A_2 \frac{\exp(-\alpha_0 t)}{\alpha_0^2} \right) \right] \right] \quad (41)$$

with

$$A_1 = \frac{C_2^2}{2\alpha_0} + \frac{C_1 C_2}{\xi_0 + \alpha_0};$$
$$A_2 = \frac{C_1^2}{2\xi_0} + \frac{C_1 C_2}{\xi_0 + \alpha_0}.$$

Discussing limiting forms of equation (40), then, when

$$\frac{\alpha_1^3 t^3}{3!} \ll \frac{\alpha_1^2 t^2}{2!}; \quad \frac{\alpha_2^3 t^3}{3!} \ll \frac{\alpha_2^2 t^2}{2!}; \quad \frac{\alpha_3^3 t^3}{3!} \ll \frac{\alpha_3^2 t^2}{2!},$$

equation (40) reduces to

$$\langle u(t) \cdot u_0 = \exp(-kTt^2/2I), \quad (42)$$

which is the orientational autocorrelation function for a free planar rotor [16]. On the other hand, when

$$\left(\frac{A_0}{\alpha_1} + \frac{B_0}{\alpha_2} + \frac{C_0}{\alpha_3} \right)$$

is very large, then equation (40) becomes

$$\langle u(t) \rangle \cdot u_0 = \exp\left[-c^2 \left(\frac{A_0}{\alpha_1} + \frac{B_0}{\alpha_2} + \frac{C_0}{\alpha_3} \right) t \right] \quad (43)$$

$$= \exp(-t/2\tau_0), \quad (44)$$

so that the Debye relaxation time for the disk is twice that for a sphere with the same moment of inertia and 'drag coefficient', represented in this paper by the continued fraction coefficients $K_0(0)$, $K_1(0)$ and γ. We have $[2c]$ $\dot{K}_0(0)$ proportional to a mean square torque, and $K_1(0)$ proportional to its derivative for the classical angular velocity autocorrelation function. Finally, we note that a form for $\langle u(t) \rangle \cdot u_0$ with $\Delta_0 > 0$ in the case of the disk has been given by Evans [10], whose notation (subscripted E) we link to ours below:

$$C_1 \cos \phi = (1 + \Gamma_E)^{-1};$$

$$C_1 \sin \phi = -\frac{1}{\beta_E} ((\alpha_{1,E} + \Gamma_E \alpha_{2,E})/(1 + \Gamma_E));$$

$$\alpha_{1,E} = \xi_0; \quad \alpha_{2,E} = \alpha_0.$$

5. Discussion

It is necessary to indicate briefly which physical models lead to an angular velocity autocorrelation function of the form $\sum_n D_n \exp(-\alpha_n t)$. Lassier and Brot [18] have shown that

$$\langle \omega(t) \cdot \omega(0) \rangle = \frac{\tau_1}{\tau_1 - \tau_2} \exp(-t/\tau_2) - \frac{\tau_2}{\tau_1 - \tau_2} \exp(-t/\tau_1) \quad (45)$$

is an analytic consequence of considering the motion of a classical *linear* rotator hindered by a two-well potential and submitted to random torques in a plane perpendicular to the rotator. These leave the component of ω parallel to the torque vector unchanged by the torque impulse, a condition equivalent to that of a smooth, hard sphere, rigidly bound to the origin, in collision with an identical free sphere. The torque impulse is perpendicular to the line of centres of the spheres, and only the velocities along this line are exchanged. In this case we have after certain approximations [18]:

$$\langle u(t) \rangle \cdot u_0 = \frac{\tau_1}{\tau_1 - \tau_2} \exp(-t/\tau_1) - \frac{\tau_2}{\tau_1 - \tau_2} \exp(-t/\tau_2). \quad (46)$$
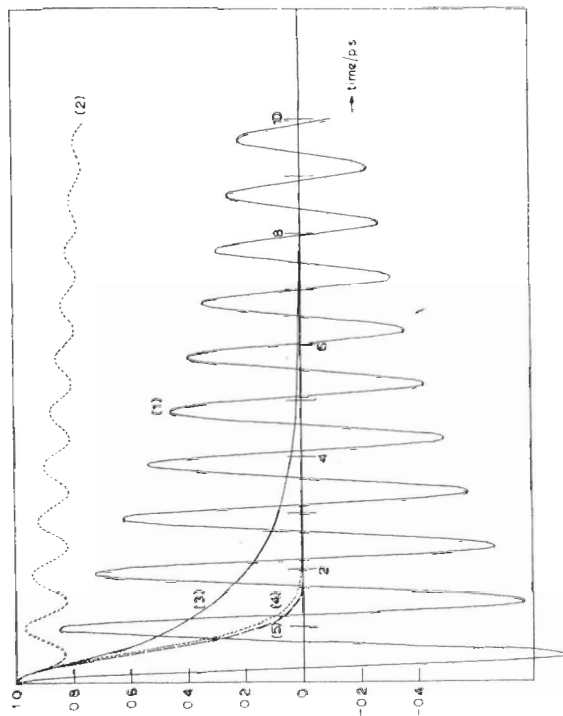

Figure 1. Angular velocity and orientational autocorrelation functions for motion in two dimensions of the itinerant oscillator. ——: $\langle \omega(t) \cdot \omega(0) \rangle$; (1) $K_0(0) = 10$ $K_1(0) = 10$ kT/I s^{-2}; (3) $K_1(0) = 10$ $K_0(0) = 10$ kT/I s^{-2} $\gamma = 4$ $(kT/I)^{1/2}$ s^{-1}; ——: $\langle u(t) \rangle \cdot u_0$; (2) corresponding to (1); (4) corresponding to (3). ————: (5) $\exp(-kTt^2/2I)$, the orientational auto correlation function for free rotation of an ensemble in two dimensions. For (1)-(5), $T = 296$ K, $I = 10^{-38}$ g cm^2. Ordinate: $f(t)$; abscissa: time (t)/ps.
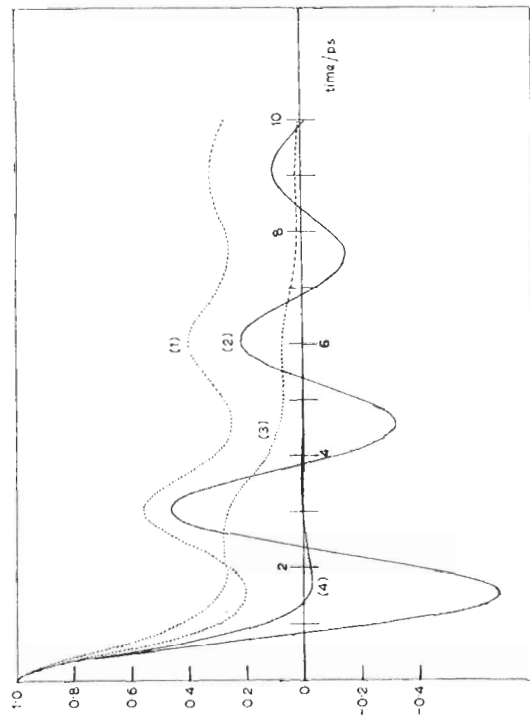
Figure 2. As for figure 1. The parameters for (1) and (2) are $K_0(0)=K_1(0)=kT/I \, s^{-2}$, $\gamma=4 (kT/I)^{1/2} s^{-1}$; those for (3) and (4) are $K_1(0)=5 K_0(0)=5 \, kT/I \, s^{-2}$, $\gamma=4 (kT/I)^{1/2} s^{-1}$. Ordinate: $f(t)$; abscissa: time (t)/ps.

The Maclaurin expansions of both equations (45) and (46) contain a non-zero, unphysical $[2 c] t^3$ coefficient, so that equation (46) cannot reduce to the free rotor hypergeometric Kummer function:

$$\sum_0^\infty (-1)^k (t^2 kT/I)^k/(1.3.5 \ldots (2k-1)).$$

This model is entirely equivalent to the *J*-diffusion mechanism of Gordon [19], extended to spherical and symmetric tops by McClung [20]. It has been extensively tested against far infra-red/microwave results by Larkin et al. [21], and in the time domain by Evans [22]. It does not predict a fast enough return to transparency at high frequencies, and has been criticized by O'Dell and Berne [23] using rough sphere molecular dynamics experiments, where all the model conditions can be fulfilled precisely.

In the case $n=3$ dealt with above, Coffey et al. [24] have shown recently that this form arises from consideration of an itinerant oscillator model for the motion of an annulus concentric with a disk. Thus, in treating the sphere, we have extended the itinerant oscillator model to three dimensions, albeit in an unclosed expansion for the orientational autocorrelation function. In two dimensions the disk carries a dipole μ lying along one of its diameters, whose position in space is specified by an angle $\theta(t)$ relative to a fixed axis (the direction of an applied field, for example). The dipole is then attracted towards the direction in space specified by $\psi(t)$ by a restoring torque proportional to $(\theta(t) - \psi(t))$. It is assumed that the damping and random torques arising from the surroundings of the system act only on the annulus.

In conclusion, it is possible to obtain expressions for $\langle \mathbf{u}(t) \rangle$. $\mathbf{u}_0$ given a truncated Mori approximation for $\langle \boldsymbol{\omega}(0) \cdot \boldsymbol{\omega}(t) \rangle$ for the sphere and disk which both reduce to the correct free rotor limit and to a Debye limit of rotational diffusion (see figures 1 and 2). Equation (40) is a closed form for the orientational autocorrelation function of the itinerant oscillator in two dimensions, which may be matched against the experimental data such as those for the far infra-red/GHz absorption/dispersion of disk-like molecules such as trimethyl-trichlorobenzene in the plastic crystalline phase, where the loss spectrum consists of two, distinct, and well separated peaks. It will be interesting also to investigate the Brownian motion of disks with computer molecular dynamics and compare the computed $\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0) \rangle$ and $\langle \mathbf{u}(t) \rangle \cdot \mathbf{u}_0$ with the theoretical Brownian model, and, if possible, the experimental (spectroscopic) evidence.

APPENDIX

Considering the domain of $\Delta_0 \leq 0$ for the disk, the coefficients y_0, y_1 and y_2 may be related to $K_0(0)$, $K_1(0)$ and γ as follows:

$$
\begin{aligned}
\alpha_1' &= (s_1 + s_2)/2 + \gamma/3; \\
\alpha_2' &= -s_1 - s_2 + \gamma/3; \\
\beta' &= (\sqrt{3}/2)(s_1 - s_2); \\
s_1 &= [-B/2 + (A^3/27 + B^2/4)^{1/2}]^{1/3}; \\
s_2 &= [-B/2 - (A^3/27 + B^2/4)^{1/2}]^{1/3}; \\
A &= K_0(0) + K_1(0) - \gamma^2/3; \\
B &= (\gamma/3)(2\gamma^2/9 + 2K_0(0) - K_1(0)).
\end{aligned}
\qquad (A1)
$$

Equation (16) becomes

$$
\begin{aligned}
\langle \omega_k \omega_l \rangle = c^2 \int_{-\infty}^{\min(t_k, t_l)} &([y_2 \cos[\beta'(t_k - \tau) + y_1 \sin[\beta'(t_k - \tau)]] \exp[-\alpha_1'(t_k - \tau)] \\
&+ y_0 \exp[-\alpha_2'(t_k - \tau)][y_2 \cos[\beta'(t_l - \tau)] \\
&+ y_1 \sin[\beta'(t_l - \tau)] \exp[-\alpha_1'(t_l - \tau)] + y_0 \exp[-\alpha_2'(t_l - \tau)]] \, d\tau \\
= c^2 [A_0' \exp(-&|t_k - t_l|\alpha_2') \\
+ \exp(-&|t_k - t_l|\alpha_1')(C_0' \cos(\beta'|t_k - t_l|) \\
&+ D_0' \sin(\beta'|t_k - t_l|))]; \qquad (A2)
\end{aligned}
$$

where

$$
\begin{aligned}
A_0' &= y_0 \left(\frac{y_0}{2\alpha_2'} + \frac{y_2\alpha_2' + y_1\beta'}{(\alpha_2'^2 + \beta'^2)} \right); \\
C_0' &= \frac{(y_2^2 + y_1^2)}{4\alpha_1'} + \frac{\alpha_1'(y_2^2 - y_1^2) + 2y_1y_2\beta'}{4(\alpha_1'^2 + \beta'^2)}; \\
D_0' &= \frac{\beta'(y_1^2 - y_2^2) + 2y_1y_2\alpha_1'}{4(\alpha_1'^2 + \beta'^2)}.
\end{aligned}
$$

When $t_k = t$, $t_i = t$, we have

$$c^2(A_0' + C_0') = kT/I. \qquad (A\ 3)$$

Using the relation derived above for the disc; viz.

$$\langle \mathbf{u}(t) \rangle \cdot \mathbf{u}_0 = \exp\left[-\int_0^t (t-\tau)\langle \omega(\tau)\omega(0)\rangle \, d\tau \right],$$

we have

$$\langle \mathbf{u}(t) \rangle \cdot \mathbf{u}_0 = \exp\left[-c^2 \int_0^t (t-\tau)(A_0' \exp(-\alpha_2'\tau) \right.$$

$$\left. + \exp(-\alpha_1'\tau)(C_0' \cos \beta'\tau + D_0' \sin \beta'\tau)) \, d\tau \right]$$

$$= \exp\left[-c^2\left[t\left(\frac{A_0'}{\alpha_2'} + \frac{\alpha_1 C_0' + \beta D_0'}{\alpha_1'^2 + \beta'^2} \right) + \frac{A_0'}{\alpha_2'^2}(\exp(-\alpha_2't)-1) \right.\right.$$

$$+ \frac{\left(C_0'(\alpha_1'^2 - \beta'^2) + 2\alpha_1'\beta' D_0'\right)}{(\alpha_1'^2 + \beta'^2)^2}(\exp(-\alpha_1't)\cos\beta't - 1)$$

$$\left.\left. + \frac{\left(D_0'(\alpha_1'^2 - \beta'^2) - 2\alpha_1'\beta' C_0'\right)}{(\alpha_1'^2 + \beta'^2)^2}\exp(-\alpha_1't)\sin\beta't \right]\right]. \qquad (A\ 4)$$

This equation is the previously underived closed form for the orientational autocorrelation function of the Coffey/Calderwood [24] *inertia-corrected* two-dimensional itinerant oscillator, and should be compared with the expression given by Evans [10].

Expanding the exponent in a Taylor series, there are no linear or t coefficients, and

$$\langle \mathbf{u}(t) \rangle \cdot \mathbf{u}_0 \rangle = \exp(-kT t^2/2I + O(t^3))$$

$$\rightarrow \exp(-kT t^2/2I),$$

the free rotor limit, at very short times when $O(t^3)$ is negligibly small. At long times, we have

$$\langle \mathbf{u}(t) \rangle \cdot \mathbf{u}_0 \rightarrow \exp\left[-t\frac{kT}{I}(A_0' + B_0' + C_0')^{-1}\left(\frac{A_0'}{\alpha_2'} + \frac{\alpha_1'C_0' + \beta'D_0'}{\alpha_1'^2 + \beta'^2} \right) \right]$$

$$= \exp(-t/2\tau_D)$$

in accord with equation (44).

Given γ, $K_0(0)$, and $K_1(0)$, equation (A 4) may be computed easily and compared with exponential data, and writing it as

$$\langle \mathbf{u}(t) \rangle \cdot \mathbf{u}_0 = \exp(-f(t)) \qquad (A\ 5)$$

an approximate form for the sphere, for this Δ_0 is

$$\langle \mathbf{u}(t) \rangle \cdot \mathbf{u}_0 = \exp(-2f(t)). \qquad (A\ 6)$$

The following equations link γ, $K_0(0)$ and $K_1(0)$ to the corresponding parameters in the itinerant oscillator:

$$K_0(0) = \omega_0^2 = \text{angular frequency of the disk when the annulus is held stationary}$$

$$K_1(0) = (I_2/I_1)\omega_0^2 ;$$

where

    $I_1 =$ moment of inertia of the annulus,

    $I_2 =$ moment of inertia of the disk,

    $\gamma = kT\tau_D/I_1$; where τ_D is the Debye relaxation time.

REFERENCES

[1] (a) ROWLINSON, J. S., and EVANS, M., 1975, *Ann. Rep. chem. Soc. A*, **72**, 5. (b) EVANS, M., 1977, *Dielectric and Related Molecular Processes*, Vol. 3 (Chemical Society Specialist Periodical Report) (in the press).
[2] (a) KIVELSON, D., and MADDEN, P., 1975, *Molec. Phys.*, **30**, 1749. (b) QUENTREC, B., and BEZOT, P., 1974, *Molec. Phys.*, **27**, 839. (c) BERNE, B. J., and HARP, G. D., 1970, *Adv. chem. Phys.*, **17**, 63.
[3] EVANS, G. J., and EVANS, M., 1976, *J. chem. Soc. Faraday II*, **72**, 1169 ; 1977, *Ibid.*, **73**, 285 ; 1976, *Adv. molec. rel. Proc.*, **9**, 85.
[4] KEYES, T., and KIVELSON, D., 1972, *J. chem. Phys.*, **56**, 1057 ; **57**, 4599.
[5] (a) ADELMAN, S. A., 1976, *J. chem. Phys.*, **64**, 124. (b) DEUTCH, J. M., and OPPENHEIM, I., 1971, *J. chem. Phys.*, **54**, 3457.
[6] MORI, H., 1965, *Prog. theor. Phys.*, **33**, 423.
[7] DEBYE, P., 1929, *Polar molecules* (Dover).
[8] KUBO, R., 1965, *Statistical Mechanics of Equilibrium and non-Equilibrium* (North-Holland).
[9] LEWIS, J. T., MCCONNELL, J., and SCAIFE, B. K. P., 1976, *Proc. R. Ir. Acad. A*, **76**, 43.
[10] EVANS, M., 1976, *Chem. Phys. Lett.*, **39**, 601.
[11] SHIMIZU, H., 1968, *J. chem. Phys.*, **48**, 2494.
[12] (a) HANSEN, J.-P., and MCDONALD, I. R. 1976, *Theory of Simple Liquids* (Academic Press), Chap. 3. (b) BAROJAS, J., LEVESQUE, D., and QUENTREC, B., 1973, *Phys. Rev. A*, **7**, 1092. (c) CHEUNG, P. S. Y., and POWLES, J. G., 1975, *Molec. Phys.*, **30**, 921. (d) EVANS, G. J., WEGDAM, G. H., and EVANS, M., 1977, *Adv. molec. rel. Proc.* (in the press).
[13] PARZEN, E., 1962, *Stochastic Processes* (Holden-Day).
[14] WALL, H. S., 1948, *Analytical Theory of Continued Fractions* (van Nostrand).
[15] SACK, R. A., 1957, *Proc. phys. Soc.*, **70**, 402.
[16] WYLLIE, G., 1972, *Dielectric and Related Molecular Processes* (Chemical Society Specialist Periodical Reports, London, 1972, edited by M. Davies) **1**, 21.
[17] DESPLANQUES, P., 1974, These d'Etat, Universite de Lille.
[18] LASSIER, B., and BROT, C., 1969, *Discuss. Faraday Soc.*, **48**, 39.
[19] GORDON, R. G., 1966, *J. chem. Phys.*, **44**, 1830.
[20] MCCLUNG, R. E. D., 1972, *J. chem. Phys.*, **57**, 5478.
[21] LARKIN, I. W., 1972, *J. chem. Soc. Faraday Symposia*, **6**, 112 ; 1973, *J. chem. Soc. Faraday II*, **69**, 1278 ; 1974, *Ibid.*, **70**, 1457. HAFFMANNS, R., and LARKIN, I. W., 1972, *J. chem. Soc. Faraday II*, **68**, 1729. EVANS, M., DAVIES, M., and LARKIN, I. W., 1973, *J. chem. Soc. Faraday II*, **69**, 1011. LARKIN, I. W., and EVANS, M., 1974, *J. chem. Soc. Faraday II*, **70**, 477.
[22] EVANS, M., 1975, *J. chem. Soc. Faraday II*, **71**, 2051.
[23] O'DELL, J., and BERNE, B. J., 1975, *J. chem. Phys.*, **63**, 2376.
[24] (a) COFFEY, W. T., AMBROSE, T., and CALDERWOOD, J. H., 1976, *J. Phys. D*, **9**, L115. (b) COFFEY, W. T., and CALDERWOOD, J. H., 1977, *Proc. R. Soc.* (in the press).