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THE CALCULATION OF THE ORIENTATIONAL FROM AN OSCILLATORY ANGULAR VELOCITY a.c.f.

by

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Short Title

Orientational linked to angular velocity a.c.f.

Proofs to: Dr. M.W. Evans

No diagrams.

ABSTRACT

A truncated Mori expansion for the angular velocity autocorrelation function is used as a starting point to calculate the orientational autocorrelation function for a disk and sphere using the newly developed methods of Lewis et. al.[9]. A series expansion is obtained for the sphere which reduces to the free rotor and Debye limits, and 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 disk angular velocity, is equivalent to the inertia-corrected two dimensional itinerant oscillator[24]. Thus it is now possible to relate analytically a realistic, oscillatory angular velocity autocorrelation function to a realistic orientational autocorrelation function for the same molecular symmetry.

Introduction

In several recent articles[1-5] on Brownian motion the Langevin equation for the angular velocity $\underset{\sim}{\omega}$ of a molecule, viz :

$$I\dot{\underset{\sim}{\omega}} + I\beta_f\underset{\sim}{\omega} = I\dot{\underset{\sim}{\Gamma}} \qquad \ldots \qquad (1)$$

has been used in a more general form[6] to allow the original friction coefficient, β_f, to become time dependent. In equation (1) I is the moment of inertia and $I\beta_f$ the frictional couple written as $\zeta\underset{\sim}{\omega}$ by Debye [7]. $I\dot{\underset{\sim}{\Gamma}}$ 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 $\underset{\sim}{u}$ 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 $\langle\underset{\sim}{\omega}(t)\cdot\underset{\sim}{\omega}(0)\rangle$ to $\langle\underset{\sim}{u}(t)\cdot\underset{\sim}{u}(0)\rangle$ 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 $\langle\underset{\sim}{\omega}(t)\cdot\underset{\sim}{\omega}(0)\rangle$ is often shown to be an oscillatory function of time, sometimes with negative portions, while $\langle\underset{\sim}{\omega}(t)\cdot\underset{\sim}{\omega}(0)\rangle$ from equation (1) is simply $\exp(-\beta_f t)$, a form that violates the fundamental axiom of time reversibility for classical autocorrelation functions[2c]. Below, we use a more realistic, oscillatory, angular velocity autocorrelation function derived from a Mori continued fraction[6].

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:

$$\dot{\underset{\sim}{u}}(t) = \underset{\sim}{\omega}(t) \times \underset{\sim}{u}(t) \qquad \ldots \qquad (2)$$

Since the ω's are Gaussian random variables we have

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

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

where the superscripts denote components. So that repeated integration of equation (2) gives, on averaging:

$$\langle \underset{\sim}{u}(t) \rangle = \underset{\sim}{u}_0 + \iint\limits_{0 \leq t_1 \leq t_2 \leq t} \langle (\underset{\sim}{\omega}_2 \times (\underset{\sim}{\omega}_1 \times \underset{\sim}{u}_0)) \rangle dt_1 dt_2$$

$$+ \int\limits_{0 \leq t_1 .. \leq t_4 \leq t} \cdot \int \langle (\underset{\sim}{\omega}_4 \times (\underset{\sim}{\omega}_3 \times (\underset{\sim}{\omega}_2 \times (\underset{\sim}{\omega}_1 \times \underset{\sim}{u}_0)))) \rangle dt_1 \ldots dt_4$$

$$+ \ldots .. \qquad \ldots \qquad \ldots \qquad \ldots \qquad (5)$$

which converges to the unique solution of equation (2) provided $\underset{\sim}{\omega}(t)$ is a continuous function of t and $\underset{\sim}{u}(0) = \underset{\sim}{u}_0$. Using the Dirac notation of Lewis et. al.[9] then, for example:

$$\underset{\sim}{\omega}_2 \times (\underset{\sim}{\omega}_1 \times \underset{\sim}{u}_0) = \underset{\sim}{\omega}_1(\underset{\sim}{\omega}_2 \cdot \underset{\sim}{u}_0) - (\underset{\sim}{\omega}_2 \cdot \underset{\sim}{\omega}_1)\underset{\sim}{u}_0$$

$$= (|1)(2| - (2|1))|0).$$

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

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

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

$$K_0(t) = \langle\underset{\sim}{\Theta}(t)\cdot\underset{\sim}{\Theta}(0)\rangle/\langle\underset{\sim}{\omega}(0)\cdot\underset{\sim}{\omega}(0)\rangle \ .$$

The variate $\underset{\sim}{\Theta}$ 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) :

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

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:

$$\dot{\underset{\sim}{\Theta}}(t) + \int_0^t K_1(t-\tau)\underset{\sim}{\Theta}(\tau)\,d\tau = I\,\underset{\sim}{\Theta}_1 \ . \quad \ldots \quad (7)$$

and:

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

Solving equations (6) - (8) we have:

$$\tilde{\underset{\sim}{\omega}}(p) = \frac{\underset{\sim}{\omega}(0)}{p + \tilde{K}_0(p)} + \frac{\underset{\sim}{\Theta}(0)}{(p + \tilde{K}_1(p))(p + \tilde{K}_0(p))} + \frac{\underset{\sim}{\Theta}_1(0) + L(\dot{\underset{\sim}{\Theta}}_2(t))}{p^3 + p^2\gamma + p(K_0(0) + K_1(0)) + \gamma K_0(0)} \quad \ldots \quad (9)$$

In equation (8) $\underset{\sim}{\Theta}_2(t)$ is assumed to be a Wiener process[13], so that:

$$\langle \underset{\sim}{\Theta}_2(t) \rangle = 0 \ ;$$

$$\langle (\underset{\sim}{\Theta}_2(t) \cdot \underset{\sim}{e}_i)(\underset{\sim}{\Theta}_2(t') \cdot \underset{\sim}{e}_j) \rangle = c^2 \min(t,t') \delta_{ij}$$

where c is a constant and e_i, e_j two of three mutually perpendicular unit vectors in 3-D space. δ_{ij} is the Kronecker delta. For time intervals Δ, Δ'; letting:

$$\underset{\sim}{\Theta}_2(t_k) - \underset{\sim}{\Theta}_2(t_\ell) = \underset{\sim}{\xi}(t_k - t_\ell), \quad \ldots \quad (10)$$

we have:

$$\left. \begin{aligned} &\langle \underset{\sim}{\xi}(\Delta) \rangle = 0 \ , \\ &\langle (\underset{\sim}{\xi}(\Delta) \cdot \underset{\sim}{e}_i)(\underset{\sim}{\xi}(\Delta') \cdot \underset{\sim}{e}_j) \rangle = c^2 \, \delta_{ij} |\Delta \cdot \Delta'| \end{aligned} \right\} . \quad (11)$$

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

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 $\underset{\sim}{\omega}(t)$ from equation (9) becomes:

$$\underset{\sim}{\omega}(t) = \int_{-\infty}^{t} \sum_{n}^{3} D_n e^{-\alpha_n (t-\tau)} \underset{\sim}{\xi}(d\tau) \quad \ldots \quad (12)$$

where the preexponential D_n can be expressed in terms of α_n using partial fractions.

In the case where $\Delta_0 \leqslant 0$ 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:

$$\underset{\sim}{\omega}(t) = \int_{-\infty}^{t} y_0 e^{-(t-\tau)\alpha_2'} + [y_1 \sin[\beta'(t-\tau)] + y_2 \cos[\beta'(t-\tau)]]$$

$$\times e^{-(t-\tau)\alpha_1'} \underset{\sim}{\xi}(d\tau)$$

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

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

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

<u>Calculation of $\langle \underset{\sim}{u}(t) \rangle$</u>

Defining:

$$f_t(\tau) = \begin{cases} \sum_n^3 D_n e^{-\alpha_n(t-\tau)} , & \tau \leqslant t \\ 0 & \tau > t, \end{cases}$$

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

$$\langle \omega_k^{(i)} \omega_\ell^{(j)} \rangle = c^2 \delta_{ij} \, (D_1^2/2\alpha_1 + D_1 D_2/(\alpha_1+\alpha_2) + D_1 D_3/(\alpha_1+\alpha_3))$$

$$\times \exp(-\alpha_1 |t_k - t_\ell|) + (D_2^2/2\alpha_2^2 + D_1 D_2/(\alpha_1+\alpha_2)$$

$$+ D_2 D_3/(\alpha_2+\alpha_3)) \exp(-\alpha_2 |t_k - t_\ell|)$$

$$+ (D_3^2/2\alpha_3^2 + D_1 D_3/(\alpha_1+\alpha_3) + D_2 D_3/(\alpha_2+\alpha_3))$$

$$\exp(-\alpha_3 |t_k - t_\ell|) \quad \ldots \quad \ldots \quad \ldots \quad (15)$$

$$= c^2 \delta_{ij} \int_{-\infty}^{\infty} ft_k(\tau)\, ft_\ell(\tau)\, d\tau \ . \qquad (16)$$

So we have:

$$<\underset{\sim}{\omega}_k \cdot \underset{\sim}{\omega}_\ell> \ = \ 3<\omega_k^{(i)} \omega_\ell^{(j)}> \ .$$

In the case $t_k = t_\ell = t$ equation (15) reduces to:

$$<\omega^{(i)}(t)^2> \ = \left[\frac{D_1}{2\alpha_2} + \frac{D_2}{2\alpha_2} + \frac{D_3}{2\alpha_3} + \frac{2D_1D_2}{(\alpha_1+\alpha_2)} + \frac{2D_1D_3}{(\alpha_1+\alpha_3)} + \frac{2D_2D_3}{(\alpha_2+\alpha_3)}\right] c^2 \qquad \ldots \qquad \ldots \qquad (17)$$

$$\equiv c^2/2\beta \qquad \ldots \qquad \ldots \qquad \ldots \qquad (18)$$

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:

$$\frac{1}{2} I<\underset{\sim}{\omega}(t)^2> \ = \frac{3}{2} kT, \qquad \ldots \qquad \ldots \qquad (19)$$

so that $\quad c^2 = 2\beta kT/I$. $\qquad \ldots \qquad \ldots \qquad \ldots \qquad (20)$

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

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

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

$$\iint\limits_{0\leqslant t_1\leqslant t_2\leqslant t} (\underset{\sim}{\omega}_2\cdot\underset{\sim}{u}_0)\omega_1^{(1)} - (\underset{\sim}{\omega}_2\cdot\underset{\sim}{\omega}_1)u_0^{(1)}\rangle \, dt_1\, dt_2 \qquad \ldots \qquad (22)$$

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

$$-2c^2u_0^{(1)} \iint\limits_{0\leqslant t_1\leqslant t_2\leqslant t} A_0e^{-\alpha_1(t_2-t_1)} + B_0e^{-\alpha_2(t_2-t_1)} + C_0e^{-\alpha_3(t_2-t_1)} dt_1dt_2 \qquad \ldots \qquad (23)$$

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

$$I_1^{(2)}(t) = t\left(\frac{A_0}{\alpha_1} + \frac{B_0}{\alpha_2} + \frac{C_0}{\alpha_3}\right) - \left(\frac{A_0}{\alpha_1^2} + \frac{B_0}{\alpha_2^2} + \frac{C_0}{\alpha_3^2}\right). + \left(\frac{A_0e^{-\alpha_1t}}{\alpha_1^2} + \frac{B_0e^{-\alpha_2t}}{\alpha_2^2} + \frac{C_0e^{-\alpha_3t}}{\alpha_3^2}\right)$$

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

$$-2c^2 \underset{\sim}{u}_0 I_1^{(2)}(t) = -2(2\beta kT/I)\underset{\sim}{u}_0 I_1^{(2)}(t) . \qquad (24)$$

Next we evaluate the c^4 integral :

$$\underset{0\leqslant t_1\leqslant \dots \leqslant t_4 \leqslant t}{\int \cdots \int} \langle (|3)(4| - (4|3))(|1)(2| - (2|1))|0)\rangle \, dt_1 \dots dt_4 . \qquad (25)$$

The integrand reduces, after a deal of algebra, to :

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

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

where equation (4) has been used for the fourth order averages.

Equation (25) may now be evaluated using equation (21) and the theorem :

$$(f_1 * f_2 * \dots * f_n) = \underset{0\leqslant t_1 \leqslant \dots \leqslant t_{n-1} \leqslant t}{\int \cdots \int} f_1(t-t_{n-1}) f_2(t_{n-1} - t_{n-2}) \dots f_n(t_1)$$

$$[dt_1 \dots dt_{n-1} \qquad (27)$$

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

$$A_0^2(4(p^3(p+\alpha_1)^2)^{-1} + 6(p^2(p+\alpha_1)^2(p+2\alpha_1))^{-1}) + B_0^2(4(p^3(p+\alpha_2)^2)^{-1}$$

$$+ 6(p^2(p+\alpha_2)^2(p+2\alpha_2))^{-1}) + C_0^2(4(p^3(p+\alpha_3)^2)^{-1} + 6(p^2(p+\alpha_3)^2(p+2\alpha_3))^{-1})$$

$$+ 4A_0B_0(2(p^3(p+\alpha_1)(p+\alpha_2))^{-1} + (p^2(p+\alpha_1)^2(p+\alpha_1+\alpha_2))^{-1}$$

$$+ (p^2(p+\alpha_2)^2(p+\alpha_1+\alpha_2))^{-1} + (p^2(p+\alpha_1)(p+\alpha_2)(p+\alpha_1+\alpha_2))^{-1})$$

$$+ 4A_0C_0(2(p^3(p+\alpha_1)(p+\alpha_3))^{-1} + (p^2(p+\alpha_1)^2(p+\alpha_1+\alpha_3))^{-1}$$

$$+ (p^2(p+\alpha_3)^2(p+\alpha_1+\alpha_3))^{-1} + (p^2(p+\alpha_1)(p+\alpha_3)(p+\alpha_1+\alpha_3))^{-1})$$

$$+ 4B_0C_0(2(p^3(p+\alpha_2)(p+\alpha_3))^{-1} + (p^2(p+\alpha_2)^2(p+\alpha_2+\alpha_3))^{-1}$$

$$+ (p^2(p+\alpha_3)^2(p+\alpha_2+\alpha_3))^{-1} + (p^2(p+\alpha_2)(p+\alpha_3)(p+\alpha_2+\alpha_3))^{-1}).$$

Taking inverse transforms we have, for example :

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

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

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

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

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

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

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 $<\underset{\sim}{u}>$ is given finally by :

$$\begin{aligned}
\underset{\sim}{u}_0 c^4 \Big\{ & 2t^2(A_0^2/\alpha_1 + B_0^{\,2}/\alpha_2 + C_0^2/\alpha_3 + \Lambda_1) - t(5(A_0^2/\alpha_1 + B_0^2/\alpha_2 + C_0^2/\alpha_3) - \Lambda_2) \\
& + \frac{9}{2}(A_0^2/\alpha_1^{\,4} + B_0^2/\alpha_2^{\,4} + C_0^2/\alpha_3^{\,4}) + \Lambda_3 + t(e^{-\alpha_1 t}(2A_0^2/\alpha_1^{\,3} + \Lambda_4) \\
& + e^{-\alpha_2 t}(2B_0^{\,2}/\alpha_2^{\,3} + \Lambda_5) + e^{-\alpha_3 t}(2C_0^{\,2}/\alpha_3^{\,3} + \Lambda_6)) \\
& - e^{-\alpha_1 t}(6A_0^2/\alpha_1^{\,4} - \Lambda_7) - e^{-\alpha_2 t}(6B_0^2/\alpha_2^{\,4} - \Lambda_8) - e^{-\alpha_3 t}(6C_0^2/\alpha_3^{\,4} - \Lambda_9) \\
& + \frac{3}{2}(A_0^2 e^{-2\alpha_1 t}/\alpha_1^{\,4} + B_0^2 e^{-2\alpha_2 t}/\alpha_2^{\,4} + C_0\, e^{-2\alpha_3 t}/\alpha_3^{\,4}) \\
& + 4(e^{-(\alpha_1+\alpha_2)t}\Lambda_{10} + e^{-(\alpha_1+\alpha_3)t}\Lambda_{11} + e^{-(\alpha_2+\alpha_3)t}\Lambda_{12}) \Big\}. \qquad \ldots \quad (28)
\end{aligned}$$

In equation (28) the Λ factors are cross terms of A_0B_0, A_0C_0 and B_0C_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

$$
\begin{aligned}
- \underset{\sim}{u}_0 c^6 \Big\{ & \frac{4}{3} t^3 (A_0^4/\alpha_1^3 + B_0^4/\alpha_2^3 + C_0^4/\alpha_3^3 + \Xi_1) \\
& - 6t^2 (A_0^4/\alpha_1^4 + B_0^4/\alpha_2^4 + C_0^4/\alpha_3^4 + \Xi_2) \\
& + \frac{73}{6} t (A_0^4/\alpha_1^5 + B_0^4/\alpha_2^5 + C_0^4/\alpha_3^5 + \Xi_3) \\
& - \frac{95}{9} (A_0^4/\alpha_1^6 + B_0^4/\alpha_2^6 + C_0^4/\alpha_3^6 + \Xi_4) \\
& + e^{-\alpha_1 t} (A_0^4 (t^2/\alpha_1^4 - 6t/\alpha_1^5 + 15/\alpha_1^6) + \Xi_5) \\
& + e^{-\alpha_2 t} (B_0^4 (t^2/\alpha_2^4 - 6t/\alpha_2^5 + 15/\alpha_2^6) + \Xi_6) \\
& + e^{-\alpha_3 t} (C_0^4 (t^2/\alpha_3^4 - 6t/\alpha_3^5 + 15/\alpha_3^6) + \Xi_7) \\
& + e^{-2\alpha_1 t} (A_0^4 (t/2\alpha_1^5 - 5/\alpha_1^6) + \Xi_8) \\
& + e^{-2\alpha_2 t} (B_0^4 (t/2\alpha_2^5 - 5/\alpha_2^6) + \Xi_9) \\
& + e^{-2\alpha_3 t} (C_0^4 (t/2\alpha_3^5 - 5/\alpha_3^6) + \Xi_{10}) \\
& + \frac{5}{9} (e^{-3\alpha_1 t} A_0^4/\alpha_1^6 + e^{-3\alpha_2 t} B_0^4/\alpha_2^6 + e^{-3\alpha_3 t} C_0^4/\alpha_3^6 \\
& + \Xi_{11}) + \Xi_{12} \Big\} , \qquad \ldots \qquad (29)
\end{aligned}
$$

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

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

and all possible permutations of the indices among α_1, α_2, and α_3. The other Ξ's represent cross terms proportional to $A_0^2B_0^2$, $A_0^3B_0$, $A_0^2B_0C_0$, $A_0B_0^2C_0$, etc., in permutation.

This series expansion for $\langle \underset{\sim}{n}(t) \rangle$ 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 $\frac{(\alpha_m t)^{2n+1}}{(2n+1)!}$ to be negligible compared with $\frac{(\alpha_m t)^{2n}}{(2n)!}$, where n here refers to the c^nth term and m = 1, 2, 3 and relevant permutations and combinations thereof we have $\tau_2 >> t$ (equation 19), and equation (5) becomes, after a great deal of algebra:

$$\begin{aligned}\langle \underset{\sim}{u}(t) \rangle = \underset{\sim}{u}_0 [1 - & c^2t^2(A_0+B_0+C_0) + c^4t^4(5(A_0^2+B_0^2+C_0^2)/12 \\ & + 5(A_0B_0+A_0C_0+B_0C_0)/6) - c^6t^6(7(A_0^4+B_0^4+C_0^4)/72 \\ & + 7(A_0^3(B_0+C_0)+B_0^3(A_0+C_0)+C_0^3(A_0+B_0))/9 \\ & + 7(A_0^2B_0^2+A_0^2C_0^2+B_0^2C_0^2)/12+9(A_0^2B_0C_0+B_0^2A_0C_0+C_0^2A_0B_0)/8) + \ldots] \\ = \underset{\sim}{u}_0 [1 - & c^2t^2(A_0+B_0+C_0) + \frac{5}{12}c^4t^4(A_0+B_0+C_0)^2 \\ & - \frac{7}{72}c^6t^6(A_0+B_0+C_0)^4 + \ldots].\end{aligned}$$

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:

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

In this limit the orientational autocorrelation function is:

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

and is expanded as in equation (30).

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

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

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:

$$\langle \underset{\sim}{u}(t)\rangle \cdot \underset{\sim}{u}_0 = 1 - \frac{kTt^2}{I} + \frac{5}{12}\left(\frac{kT}{I}\right)^2 t^4 - \ldots\ldots.$$

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:

$$\begin{aligned}\langle \underset{\sim}{u}(t)\rangle \cdot \underset{\sim}{u}_0 = 1 &- 2\left(\frac{A_0}{\alpha_1} + \frac{B_0}{\alpha_2} + \frac{C_0}{\alpha_3}\right)tc^2 \\ &+ 2c^4\left(\frac{A_0^2}{\alpha_1^2} + \frac{B_0^2}{\alpha_2^2} + \frac{C_0^2}{\alpha_3^2} + \Lambda_1\right)t^2 \\ &- \frac{4}{3}c^6\left(\frac{A_0^4}{\alpha_1^3} + \frac{B_0^4}{\alpha_2^3} + \frac{C_0^4}{\alpha_3^3} + \Xi_1\right)t^3 + \ldots\ldots. \quad (33)\end{aligned}$$

However, we have $\Lambda_1 = 2\left(\frac{A_0B_0}{\alpha_1\alpha_2} + \frac{A_0C_0}{\alpha_1\alpha_3} + \frac{B_0C_0}{\alpha_2\alpha_3}\right)$

and $\Xi_1 = 6\frac{A_0B_0C_0}{\alpha_1\alpha_2\alpha_3} + 2\left[\frac{A_0^2}{\alpha_1^2}\left(\frac{B_0}{\alpha_2} + \frac{C_0}{\alpha_3}\right) + \frac{B_0^2}{\alpha_2^2}\left(\frac{A_0}{\alpha_1} + \frac{C_0}{\alpha_3}\right) + \frac{C_0^2}{\alpha_3}\left(\frac{B_0}{\alpha_2} + \frac{A_0}{\alpha_1}\right)\right]$

so that equation (33) becomes, by inspection:

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

$\simeq e^{-t/\tau_D}$ where τ_D is the Debye time.

Thus our orientation a.c.f. reduces to the free rotor and Debye limits for $\tau_2 \gg t$ 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 $\langle \underset{\sim}{u}(t) \rangle$ 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, correct up to the t^2 term is:

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

$$\left.\left.+\left(A_0\frac{e^{-\alpha_1 t}}{\alpha_1^2}+B_0\frac{e^{-\alpha_2 t}}{\alpha_2^2}+C_0\frac{e^{-\alpha_3 t}}{\alpha_3^2}\right)\right)\right] \qquad \ldots \qquad (35)$$

and the spectrum $\left(\int_0^\infty \langle \underset{\sim}{u}(t)\rangle\cdot\underset{\sim}{u}_0 \exp(-i\omega t)dt\right)$ may be found to the necessary accuracy by using Laplace transforms and the method of successive convergents[14]. In the case $\alpha_1 = \alpha_2 = \alpha_3 = \tau$, $D_1 = D_2 = D_3 = 1/3$, 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 generalised Liouville equation. We now consider the disk, 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.

The Dipole Embedded in a Disk

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

$$\underset{\sim}{\omega}(t) = \omega(t)\underset{\sim}{k}$$

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

$$\underset{\sim}{k}.\underset{\sim}{u}_0 = 0; \quad \underset{\sim}{k} \times (\underset{\sim}{k} \times \underset{\sim}{u}_0) = -\underset{\sim}{u}_0 ,$$

then it follows that:

$$\langle\underset{\sim}{u}(t)\rangle = \underset{\sim}{u}_0\left[1 - \iint\limits_{0\leqslant t_1\leqslant t_2\leqslant t} \langle\omega_2\omega_1\rangle\, dt_1 dt_2 + \int\limits_{0\leqslant t_1\leqslant\ldots\leqslant t_4\leqslant t}\!\!\cdots\!\int \langle\omega_4\omega_3\omega_2\omega_1\rangle dt_1\ldots dt_4 \right.$$

$$\left. - \int\limits_{0\leqslant t_1\leqslant\ldots\leqslant t_6\leqslant t}\!\!\cdots\!\int \langle\omega_6\omega_5\omega_4\omega_3\omega_2\omega_1\rangle dt_1\ldots dt_6 + \ldots\right]. \qquad (36)$$

For scalar ω, equation (21) becomes:

$$\langle\omega_k\omega_\ell\rangle = c^2[A_0 e^{-\alpha_1|t_k-t_\ell|} + B_0 e^{-\alpha_2|t_k-t_\ell|} + C_0 e^{-\alpha_3|t_k-t_\ell|}]$$

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

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

Since the second integral can be written [9] as:

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

and all successive integrals as:

$$\frac{1}{r!}\Bigg\{c^2\Bigg[t\left(\frac{A_0}{\alpha_1}+\frac{B_0}{\alpha_2}+\frac{C_0}{\alpha_3}\right)-\left(\frac{A_0}{\alpha_1^2}+\frac{B_0}{\alpha_2^2}+\frac{C_0}{\alpha_3^2}\right)$$

$$+\left(A_0\frac{e^{-\alpha_1 t}}{\alpha_1^2}+B_0\frac{e^{-\alpha_2 t}}{\alpha_2^2}+C_0\frac{e^{-\alpha_3 t}}{\alpha_3^2}\right)\Bigg]\Bigg\}^r \quad \ldots \quad (39)$$

then immediately we have

$$\langle \underset{\sim}{u}(t)\rangle\cdot\underset{\sim}{u}_0 = \exp\Bigg[-2\beta\frac{kT}{I}\Bigg(t\left(\frac{A_0}{\alpha_1}+\frac{B_0}{\alpha_2}+\frac{C_0}{\alpha_3}\right)-\left(\frac{A_0}{\alpha_1^2}+\frac{B_0}{\alpha_2^2}+\frac{C_0}{\alpha_3^2}\right)$$

$$+\left(A_0\frac{e^{-\alpha_1 t}}{\alpha_1^2}+B_0\frac{e^{-\alpha_2 t}}{\alpha_2^2}+C_0\frac{e^{-\alpha_3 t}}{\alpha_3^2}\right)\Bigg)\Bigg] \quad \ldots \quad (40)$$

Turning to the case where $\Delta_0 \gtreqless 0$, we have:

$$\langle\omega^{(i)}(t)^2\rangle \to \left[\frac{C_1^2}{2\xi_0}+\frac{C_2^2}{2\alpha_0}+\frac{2C_1C_2}{\xi_0+\alpha_0}\right]c^2$$

$$\equiv \frac{c^2}{\beta\alpha} \quad \text{as } t\to\infty\ ;$$

α

so that $c^2 = 2\beta_\alpha kT/I$, $\tau_2 = 1/\beta_\alpha$ - (41) as for equation (18). In the special case where $\beta_0 = 0$ (which implies $\gamma = 3(3K_0(0))^{\frac{1}{2}}$ in the Mori continued fraction) we have:

$$\langle \underset{\sim}{u}(t)\rangle \cdot \underset{\sim}{u}_0 = \exp\left[-2\beta_\alpha \frac{kT}{I}\left\{t\left(A_1\frac{e^{-\xi_0 t}}{\xi_0^{\,2}} + A_2\frac{e^{-\alpha_0 t}}{\alpha^{\,2}}\right)\right.\right.$$

$$\left.\left. - \left(\frac{A_1}{\xi_0^{\,2}} + \frac{A_2}{\alpha_0^{\,2}}\right) + \left(A_1\frac{e^{-\xi_0 t}}{\xi_0^{\,2}} + A_2\frac{e^{-\alpha_0 t}}{\alpha_0^{\,2}}\right)\right\}\right] \quad \ldots \quad (41)$$

with
$$A_1 = \frac{C_2^{\,2}}{2\alpha_0} + \frac{C_1C_2}{\xi_0+\alpha_0}$$

$$A_2 = \frac{C_1^{\,2}}{2\xi_0} + \frac{C_1C_2}{\xi_0+\alpha_0}\,.$$

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

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

equation (40) reduces to:

$$\langle \underset{\sim}{u}(t)\rangle \cdot \underset{\sim}{u}_0 = \exp\,(-\,kTt^2/2I) \quad \ldots \quad \ldots \quad (42)$$

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:

$$\langle \underset{\sim}{u}(t)\rangle \cdot \underset{\sim}{u}_0 = \exp\left[-c^2\left(\frac{A_0}{\alpha_1} + \frac{B_0}{\alpha_2} + \frac{C_0}{\alpha_3}\right)t\right] \tag{43}$$

$$= e^{-t/2\tau_0} , \qquad \ldots \tag{44}$$

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] $K_0(0)$ 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 an approximate form for $\langle \underset{\sim}{u}(t)\rangle \cdot \underset{\sim}{u}_0$ 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:

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

$$C_1 \sin\phi = -\frac{1}{\beta E}\left[(\alpha_{1,E} + \Gamma_E\alpha_{2,E})/(1 + \Gamma_E)\right] ;$$

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

Discussion

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

$$\langle \underset{\sim}{\omega}(t)\cdot\underset{\sim}{\omega}(0)\rangle = \frac{\tau_1}{\tau_1 - \tau_2} e^{-t/\tau_2} - \frac{\tau_2}{\tau_1 - \tau_2} e^{-t/\tau_1} \qquad (45)$$

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 $\underset{\sim}{\omega}$ 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] :

$$\langle \underset{\sim}{u}(t)\rangle\cdot\underset{\sim}{u}_0 = \frac{\tau_1}{\tau_1 - \tau_2} e^{-t/\tau_1} - \frac{\tau_2}{\tau_1 - \tau_2} e^{-t/\tau_2} . \qquad (46)$$

The Maclaurin expansions of both equations (45) and (46) contain a non-zero, unphysical [2c] 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 criticised 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 $\underline{\mu}$ 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 $\langle \underset{\sim}{u}(t) \rangle \cdot u_0$ given a truncated Mori approximation for $\langle \underset{\sim}{\omega}(0) \cdot \underset{\sim}{\omega}(t) \rangle$ for the sphere and disk which both reduce to the correct free rotor limit and to a Debye limit of rotational diffusion. 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/GH_z absorption/dispersion of disk-like molecules such as trimethyltrichlorobenzene 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 $\langle \underset{\sim}{\omega}(t)\cdot\underset{\sim}{\omega}(0)\rangle$ and $\langle \underset{\sim}{u}(t)\rangle\cdot\underset{\sim}{u}_0$ with the theoretical Brownian model, and, if possible, the experimental (spectroscopic) evidence.

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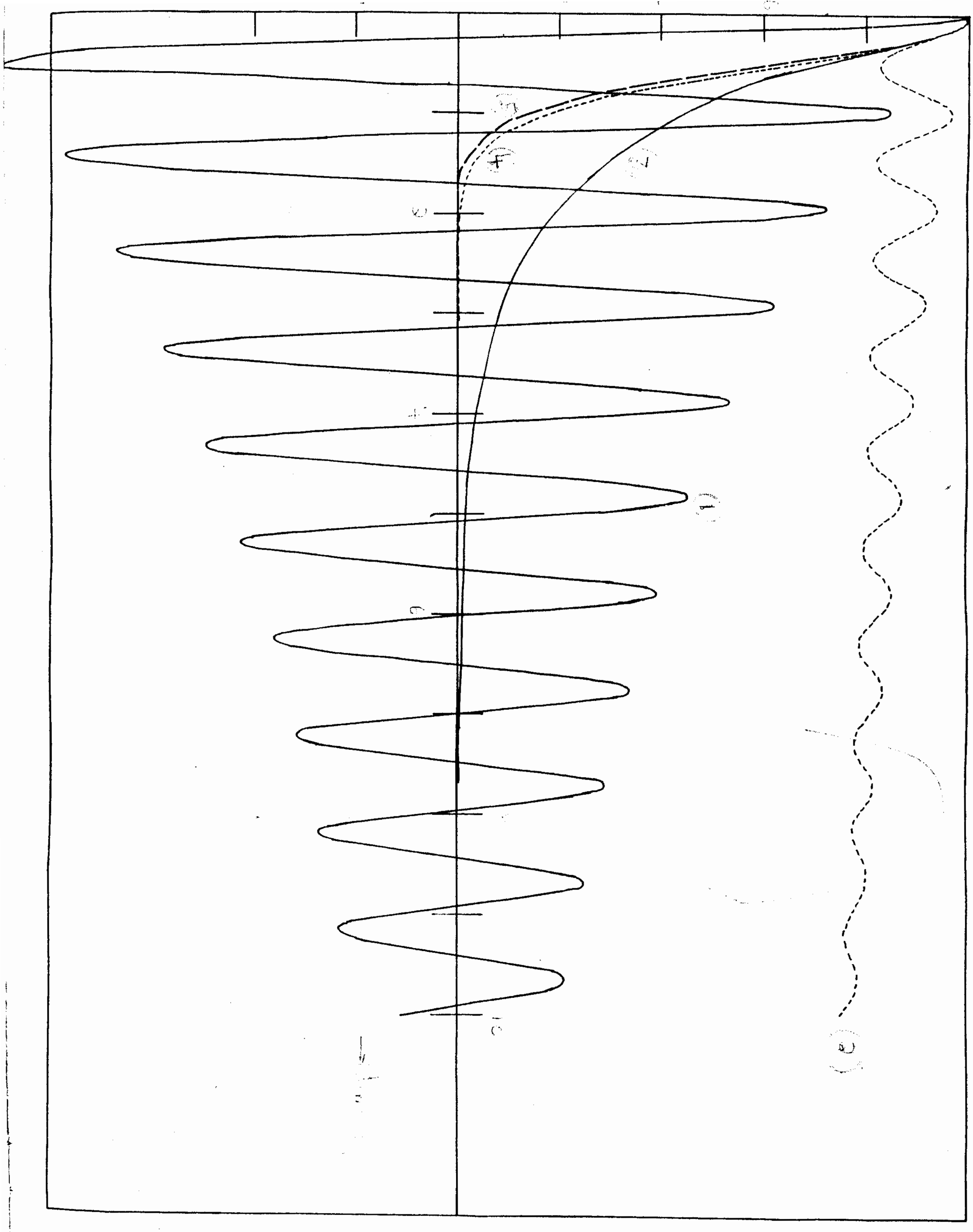

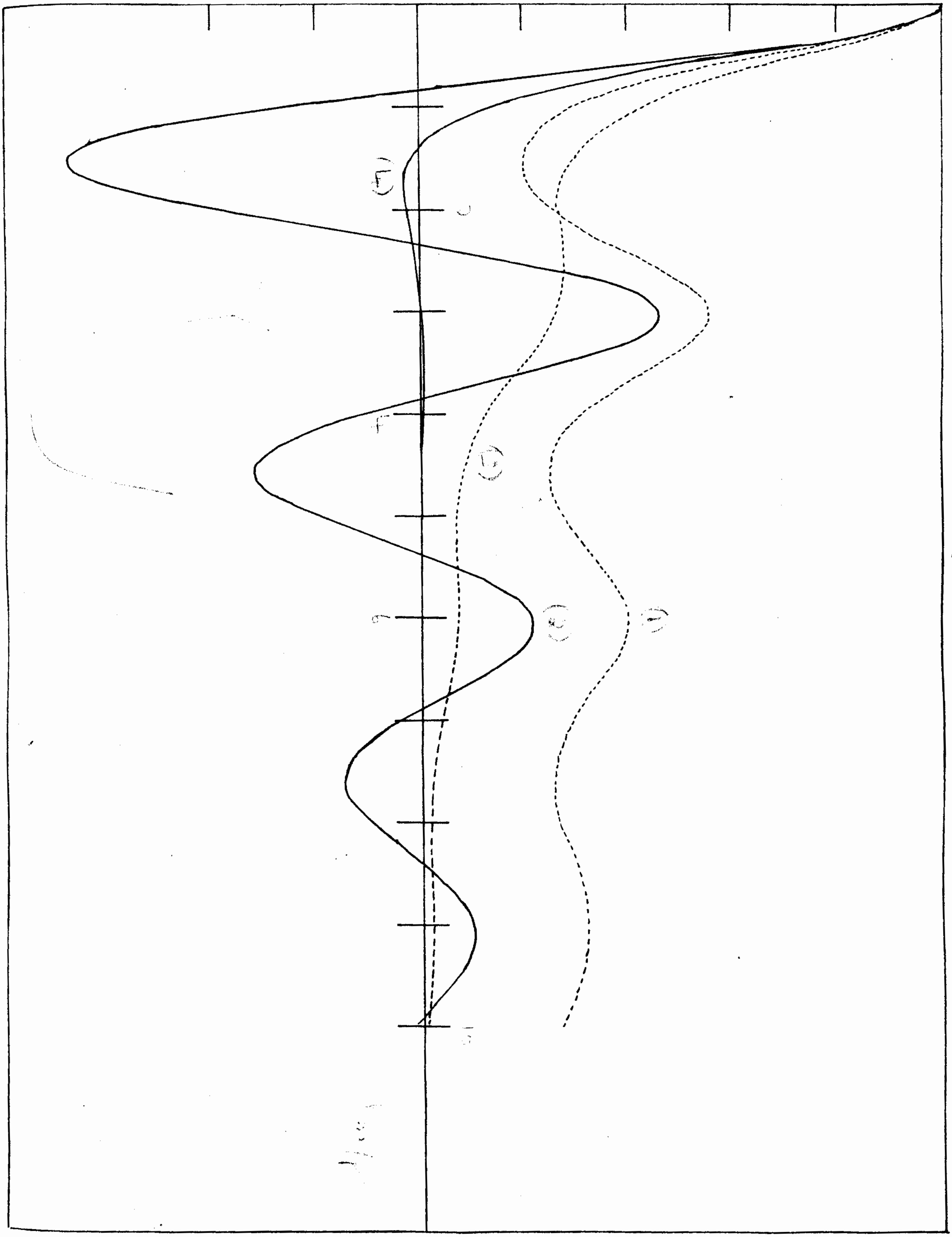

Appendix

Considering the domain of $\Delta_0 \leqslant 0$ 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:

$$\alpha_1' = (s_1 + s_2)/2 + \gamma/3 \; ; \qquad \alpha_2' = - s_1 - s_2 + \gamma/3;$$

$$\beta' = (\sqrt{3}/2)(s_1 - s_2) \; ;$$

$$s_1 = [- B/2 + (A^3/27 + B^2/4)^{\frac{1}{2}}]^{\frac{1}{3}} \; ;$$

$$s_2 = [- B/2 - (A^3/27 + B^2/4)^{\frac{1}{2}}]^{\frac{1}{3}} \; ;$$

$$A = K_0(0) + K_1(0) - \gamma^2/3; \qquad B = (\gamma/3)(2\gamma^2/9 + 2K_0(0) - K_1(0)).$$

Equation (16) becomes:

$$\langle\omega_k\omega_\ell\rangle = c^2 \int_{-\infty}^{\min(t_k,t_\ell)} ([y_2 \cos [\beta'(t_k-\tau) + y_1 \sin [\beta'(t_k-\tau)]]e^{-\alpha_1'(t_k-\tau)}$$

$$+ y_0 e^{-\alpha_2'(t_k-\tau)})(y_2 \cos [\beta'(t_\ell-\tau)]$$

$$+ y_1 \sin [\beta'(t_\ell-\tau)] \; e^{-\alpha_1'(t_\ell-\tau)} + y_0 e^{-\alpha_2'(t_\ell-\tau)})d\tau$$

$$= c^2 [A_0' \exp (-|t_k-t_\ell|\alpha_2') + B_0' \cos (\beta'|t_k-t_\ell|)$$

$$+ \exp (-|t_k-t_\ell|\alpha_1') \; (C_0' \cos (\beta'|t_k-t_\ell|) + D_0' \sin (\beta'|t_k-t_\ell|))] \; ;$$

where $A_0' = y_0\left(\dfrac{y_0}{2\alpha_2'} + \dfrac{y_2\alpha_2' + y_1\beta'}{(\alpha_2'^2 + \beta'^2)}\right)$;

$$B_0' = y_0(y_2\alpha_2' + y_1\beta')/(\alpha_2'^2 + \beta'^2) \; ;$$

$$C_0' = \frac{(y_2^2 + y_1^2)}{4\alpha_1'} + \frac{\alpha_1'(y_2^2 - y_1^2) + 2y_1y_2\beta'}{4(\alpha_1'^2 + \beta'^2)} \; ;$$

$$D_0' = \frac{\beta'(y_1^2 - y_2^2) + 2y_1y_2\alpha_1'}{4(\alpha_1'^2 + \beta'^2)} \; .$$

When $t_k = t_\ell = t$, we have:

$$c^2(A_0' + B_0' + C_0') = kT/I . \qquad \ldots \qquad (A3)$$

Using the relation derived above for the disk; viz.:

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

we have:

$$\langle \underset{\sim}{u}(t)\rangle \cdot \underset{\sim}{u}_0 = \exp\Bigg[-c^2\int_0^\tau (t-\tau)\Big(A_0' e^{-\alpha_2'\tau} + B_0'\cos\beta'\tau + e^{-\alpha_1'\tau}(C_0'\cos\beta'\tau + D_0'\sin\beta'\tau)\Big)d\tau\Bigg]$$

$$= \exp\Bigg[-c^2\Bigg(t\left[\frac{A_0'}{\alpha_2'} + \frac{\alpha_1 C_0' + \beta D_0'}{\alpha_1'^2 + \beta'^2}\right] + \frac{A_0'}{\alpha_2'^2}(e^{-\alpha_2' t} - 1) - \frac{B_0'}{\beta'^2}(\cos\beta' t - 1) + \left[\frac{C_0'(\alpha_1'^2 - \beta'^2) + 2\alpha_1'\beta' D_0'}{(\alpha_1'^2 + \beta'^2)^2}\right] \times (e^{-\alpha_1' t}\cos\beta' t - 1) + \left[\frac{D_0'(\alpha_1'^2 - \beta'^2) - 2\alpha_1'\beta' C_0'}{(\alpha_1'^2 + \beta'^2)^2}\right] \times e^{-\alpha_1' t}\sin\beta' t\Bigg)\Bigg] . \qquad \ldots \qquad \ldots \qquad (A4)$$

This equation is the previously unreported closed form for the orientational auto-correlation function of the Coffey/Calderwood[24] *inertia-corrected* two dimensional itinerant oscillator, and should supersede the approximate expression given by Evans[10].

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

$$\langle \underset{\sim}{u}(t)\cdot \underset{\sim}{u}_o\rangle = \exp(-kTt^2/2I + \mathcal{O}(t^3))$$

$$\rightarrow \exp(-kTt^2/2I),$$ the free rotor limit, at very short times when $\mathcal{O}(t^3)$ is negligibly small.

At long times, we have:

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

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

in accord with equation (44).

Given γ, $K_0(0)$, and $K_1(0)$, equation (A4) may be computed easily (figs.) and compared with exponential data, and writing it as:

$$\langle \underset{\sim}{u}(t)\rangle\cdot\underset{\sim}{u}_0 = \exp\,(-f(t)) \qquad \ldots \qquad \ldots \qquad \text{(A5)},$$

an approximate form for the sphere, for all Δ_0, is:

$$\langle \underset{\sim}{u}(t)\rangle\cdot\underset{\sim}{u}_0 = \exp\,(-2f(t)). \qquad \ldots \qquad \text{(A6)}$$

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

$K_0(0) = \omega_0^2$ = 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.