A GENERALISED FRICTION MODEL FOR THE EVALUATION OF ANGULAR MOMENTUM AUTO CORRELATION FUNCTIONS

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Received 4 February 1976

A theory of brownian motion where the friction coefficient is a finite correlation function of molecular torque is used to derive an expression for the angular velocity autocorrelation function, $\psi(t)$. This is related to the orientational a.c.f., $\phi(t)$, using an analysis of bandshapes due to Kubo and extended by Shimizu. Both functions $\phi(t)$ and $\psi(t)$ contain inherent weaknesses since $\psi(t)$ has a MacLaurin expansion even up to t^4 only, and $\phi(t)$ does not reduce to the Kummer function for an ensemble of free rotors in the so-called limit of vanishing friction. Reasons for this behaviour are discussed.

1. Introduction and theoretical considerations

To describe the process of general random rotation of a linear molecule, Shimizu [1] has used an analysis by Kubo [2] of the shape of spectral bands. This has been discussed further by Wyllie [3] whose comments are recalled briefly here as an introduction.

Let the angular velocity of the rotor at time t be $\omega(t)$, then since $t = 0$ it has been displaced through an angle:

$$\theta = \int_0^t \omega(t')\,\mathrm{d}t' , \tag{1}$$

and the normalised autocorrelation function of a unit vector in the axis of the linear molecule is:

$$\langle \cos\theta(t)\rangle \equiv \langle \cos\left[\textstyle\int_0^t \omega(t')\,\mathrm{d}t'\right]\rangle \equiv \mathrm{Re}\,\{\langle \exp\left[\mathrm{i}\textstyle\int_0^t \omega(t')\,\mathrm{d}t'\right]\rangle\} , \tag{2}$$

where the angular brackets $\langle\ \rangle$ denote an average over the different $\omega(0)$, and the different $\omega(t')$.

Regarding ω as a random variable, its equilibrium distribution (i.e. that of $\omega(0)$) will be gaussian, and we can expand $\langle\cos\theta(t)\rangle$, the general term being:

$$\langle(\mathrm{i}^n/n!)\left[\textstyle\int_0^t \omega(t')\,\mathrm{d}t'\right]^n\rangle = (\mathrm{i}^n/n!)\int_0^t \mathrm{d}t_1 \ldots \int_0^t \mathrm{d}t_n \langle\omega(t_1)\ldots\omega(t_n)\rangle .$$

The r.h.s. now involves multiple self-correlations of ω, and can be regrouped in terms of cumulant averages ($\langle\ \rangle_c$),

$$\langle\cos\theta(t)\rangle = \mathrm{Re}\left\{\exp\left[\mathrm{i}\langle\omega\rangle_c t - \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \langle\omega(t_1)\omega(t_2)\rangle_c + \ldots + \mathrm{i}^n \int_0^t \mathrm{d}t_1 \ldots \int_0^t \langle\omega(t_1)\ldots\omega(t_n)\rangle_c \mathrm{d}t_n \ldots\right]\right\} , \tag{3}$$

where, for example, $\langle\omega\rangle_c = \langle\omega\rangle$; $\langle\omega_1\omega_2\rangle_c = \langle\omega_1\omega_2\rangle - \langle\omega_1\rangle\langle\omega_2\rangle$. We can see immediately from eq. (3) that if all the odd correlations of ω vanish, then the autocorrelation function $\phi(t) = \langle\cos\theta(t)\rangle$ will be positive throughout its domain of definition, and therefore will not reproduce the well known form of $\phi(t)$ for free rotation, the hyper-

geometric Kummer function [3], which for large t approaches zero from below the time axis. The same is true if the series in eq. (3) is truncated in any way such as to delete the imaginary terms. For example, if it is assumed that the multivariate density function for $\omega(t_1) \ldots \omega(t_n)$ is a gaussian, then all cumulants beyond $\langle \omega_1 \omega_2 \rangle_c$ vanish and the process ω is statistically determined by its mean (zero) and first self-correlation alone, i.e.

$$\phi(t) = \exp\left[-\int_0^t \mathrm{d}t_1 \int_0^t \langle \omega(t_1)\, \omega(t_2) \rangle \, \mathrm{d}t_2 \right] = \exp\left[-\int_0^t (t-\tau) \langle \omega(0)\, \omega(\tau) \rangle \, \mathrm{d}\tau \right], \tag{4}$$

and $\phi(t)$ is inevitably badly behaved in the free rotor limit at long times, in that it cannot become negative.

This is a point which does not seem to have been emphasized sufficiently. For example, Kluk and Powles [4] recently used the exponential form:

$$\langle \omega(0)\, \omega(t) \rangle = \langle \omega^2(0) \rangle \exp(-\xi t/I), \tag{5}$$

which is consequential upon Langevin's treatment [3] of rotational brownian motion with ξ as the constant friction coefficient and I the molecular moment of inertia. Using eq. (5) in (4), then:

$$\phi(t) = \exp\{-(2kTI/\xi^2)[\exp(-\xi t/I) + \xi t/I - 1]\}, \tag{6}$$

a form previously given by Wyllie and others [3] for a rotator with one degree of freedom. Here we give it another (laboratory) frame so that:

$$\langle \omega^2(0) \rangle = 2kT/I .$$

Eq. (6) is identical with that of Kluk and Powles for the first harmonic of the orientational correlation function ($j = 1$ in their notation). It has the correct *initial* short time expansion [5] for the classical autocorrelation function:

$$\phi(t) = 1 - (kT/I)t^2 + \mathcal{O}(t^3), \tag{7}$$

and reduces to a pure exponential for high ξ, but not surprisingly, does not reduce [4] to the Kummer function as $\xi \to 0$ (the limit of vanishing friction).

Eq. (5) is an unsatisfactory form for at least two reasons:

(i) Gordon [5], Berne [6], and others have shown that the angular velocity correlation function is classically an even function of time, so that [6], for linear molecules:

$$\psi(t) = \langle \omega(0)\, \omega(t) \rangle / \langle \omega^2(0) \rangle = 1 - \langle O(V)^2 \rangle t^2/4IkT + \langle \dot{O}(V)^2 \rangle t^4/48kTI - \ldots ,$$

where $\langle O(V)^2 \rangle$ is the mean square torque on a molecule due to the others, and $\langle \dot{O}(V)^2 \rangle$ its derivative. $\phi(t)$ in turn ought to be even in this sense.

(ii) It truncates the series in eq. (3) so as to leave no imaginary terms, and therefore from the start has no hope of producing a $\phi(t)$ which is well behaved as the free rotor limit is approached. It seems that cumulants beyond $\langle \omega_1 \omega_2 \rangle_c$, both even and odd, must be used before $\phi(t)$ can be induced to go negative and remain an even function of time (in the sense that its MacLaurin expansion contains no odd powers of t).

An improvement over eq. (5), but one which still has the second weakness built in, is to use generalised Langevin theory in deriving $\langle \omega(0)\, \omega(t) \rangle$ instead of the simple equation used by Kluk and Powles. This would at least involve the equilibrium intermolecular properties $\langle O(V)^2 \rangle$ and $\langle \dot{O}(V)^2 \rangle$ to be used in $\phi(t)$, properties that can be simulated by computerised molecular dynamics of large molecular ensembles.

Kubo [7] and others [3,6] have presented a general form of the classical Langevin equation. This is now written as:

$$\dot{\omega}(t) = -\int_0^t K(t-\tau)\, \omega(\tau)\, \mathrm{d}\tau + \Gamma(t), \tag{8}$$

where K is a time-dependent friction coefficient known as the memory function. $m\Gamma(t)$ is the fluctuating part of the torque on a molecule of mass m. It follows from eq. (8) that:

$$\mathrm{d}\langle\omega(0)\,\omega(t)\rangle/\mathrm{d}\,t = -\int_0^t K(t-\tau)\langle\omega(0)\,\omega(\tau)\rangle\,\mathrm{d}\tau + \langle\omega(0)\,\Gamma(t)\rangle\,. \tag{9}$$

The last term is zero since $\omega(0)$ and $\Gamma(t)$ are assumed to be uncorrelated statistically.

Mori [8,6] has shown that the set of memory functions $K_0(t) \ldots K_n(t)$ obey the set of coupled Volterra equations such that:

$$\partial K_{n-1}(t)/\partial t = -\int_0^t K_n(t-\tau)\,K_{n-1}(\tau)\,\mathrm{d}\tau\,. \tag{10}$$

Solving by Laplace transformation we have:

$$\tilde{C}(p) = \frac{C(0)}{p+\tilde{K}_0(p)} = \frac{C(0)}{p+\dfrac{K_0(0)}{p+\tilde{K}_1(p)}} = \ldots\,, \tag{11}$$

with $\tilde{C}(p)$ as the Laplace transform of $C(t) = \langle\omega(0)\,\omega(t)\rangle$. Several authors [3,6,9] have shown how the method of truncating this continued fraction using simple forms for $K_N(p)$ can be used to derive complicated but more realistic forms of $C(t)$ and its Fourier transform, the complex spectral function $C(-\mathrm{i}\omega)$.

The equilibrium averages $K_0(0), K_1(0)$, etc. are related [6] to the terms in the MacLaurin expansion of $C(t)$, so that if we define:

$$\psi(t) = C(t)/\langle\omega^2(0)\rangle = \sum_n a_n\,t^{2n}/(2n)!\,, \tag{12}$$

with a_n alternatively positive and negative, we have:

$$K_0(0) = -a_1 = \langle O(V)^2\rangle/2IkT\,, \tag{13}$$

$$K_1(0) = a_1 - a_2/a_1 = \langle\dot{O}(V)^2\rangle/\langle O(V)^2\rangle - \langle O(V)^2\rangle/2kTI\,, \tag{14}$$

and so on.

Here, we truncate the series (11) with:

$$K_1(t) = K_1(0)\exp(-\gamma t)\,, \tag{15}$$

where γ^{-1} is an empirical correlation time, and find that $\psi(t)$ is even up to the t^4 term in its series expansion, but thereafter contains all the odd powers. Higher order truncations than that of eq. (15) merely introduce higher derivatives of $\langle O(V)^2\rangle$, which in general is unknown analytically. Therefore, by using eq. (15) we introduce the "empirical" terms $\langle O(V)^2\rangle$ and $\langle\dot{O}(V)^2\rangle$. The advantage of using this form for $K_1(t)$ and $\psi(t)$ is that $\phi(t)$ will have the odd powers only after t^6, and will be very well behaved at short times away from the free rotor limit.

From eqs. (11) and (15), we have:

$$\psi(t) = \left[\frac{\cos\beta t}{1+\Gamma} + \frac{1}{\beta}\left(\frac{\alpha_1+\Gamma\alpha_2}{1+\Gamma}\right)\sin\beta t\right]\exp(-\alpha_1 t) + \frac{\Gamma}{1+\Gamma}\exp(-\alpha_2 t)\,, \tag{16}$$

where

$$\Gamma = 2\alpha_1(2\beta^2-\alpha_1^2)/\alpha_2(3\alpha_1^2-\beta^2-\alpha_2^2);\quad \alpha_1 = \tfrac{1}{2}(s_1+s_2)+\tfrac{1}{3}\gamma;\quad \alpha_2 = -s_1-s_2+\tfrac{1}{3}\gamma;\quad \beta = (3^{1/2}/2)(s_1-s_2)\,.$$

The terms s_1 and s_2 are defined by:

$$s_1 = [-\tfrac{1}{2}B + (\tfrac{1}{27}A^3 + \tfrac{1}{4}B^2)^{1/2}]^{1/3}, \quad s_2 = [-\tfrac{1}{2}B - (\tfrac{1}{27}A^3 + \tfrac{1}{4}B^2)^{1/2}]^{1/3},$$

with

$$A = K_0(0) + K_1(0) - \tfrac{1}{3}\gamma^2, \quad B = \tfrac{1}{3}\gamma[\tfrac{2}{9}\gamma^2 + 2K_0(0) - K_1(0)].$$

The angular velocity correlation time, τ_ω, is now:

$$\tau_\omega = \int_0^\infty \langle\omega(0)\,\omega(t)\rangle\,\mathrm{d}t = \frac{2kT}{I(1+\Gamma)}\left[\frac{2\alpha_1 + \Gamma\alpha_2}{\alpha_1^2+\beta^2} + \frac{\Gamma}{\alpha_2}\right]. \tag{17}$$

Using eq. (4), we have:

$$\phi(t) = \exp\{-(2kT/I)\,[A_1(\mathrm{e}^{-\alpha_1 t}\cos\beta t - 1) - B_1\mathrm{e}^{-\alpha_1 t}\sin\beta t + \Gamma(\mathrm{e}^{-\alpha_2 t} - 1)/(1+\Gamma)\alpha_2^2 + C_1 t]\}, \tag{18}$$

where

$$A_1 = \frac{3\alpha_1^2 + 2\alpha_1\alpha_2\Gamma - \beta^2}{(1+\Gamma)(\alpha_1^2+\beta^2)^2}; \quad B_1 = \frac{2\beta^2\alpha_1 + (\alpha_1 + \Gamma\alpha_2)(\beta^2 - \alpha_1^2)}{\beta(1+\Gamma)(\alpha_1^2+\beta^2)^2}; \quad C_1 = \frac{2\alpha_1}{(1+\Gamma)(\alpha_1^2+\beta^2)} + \frac{\Gamma}{1+\Gamma}\left[\frac{\alpha_2}{\alpha_1^2+\beta^2} + \frac{1}{\alpha_2}\right].$$

2. Discussion

Some idea of the forms of $\phi(t)$ and $\psi(t)$ is given in fig. 1 for reasonable values of $\langle O(V)^2\rangle$ and its derivative. It is seen that as the torque is increased $\psi(t)$ oscillates about the time axis and $\phi(t)$ develops damped oscillations at short times, becoming exponential (logarithmic) thereafter. As $\langle O(V)^2\rangle \to 0$, $\psi(t)$ should, by eq. (5), become constant at unity for all positive t, and $\phi(t)$ should show a negative region. The former is true for all γ, but the latter is not observed in the limit of vanishing torque, since $\psi(t)$ contains all the odd powers after t^4.

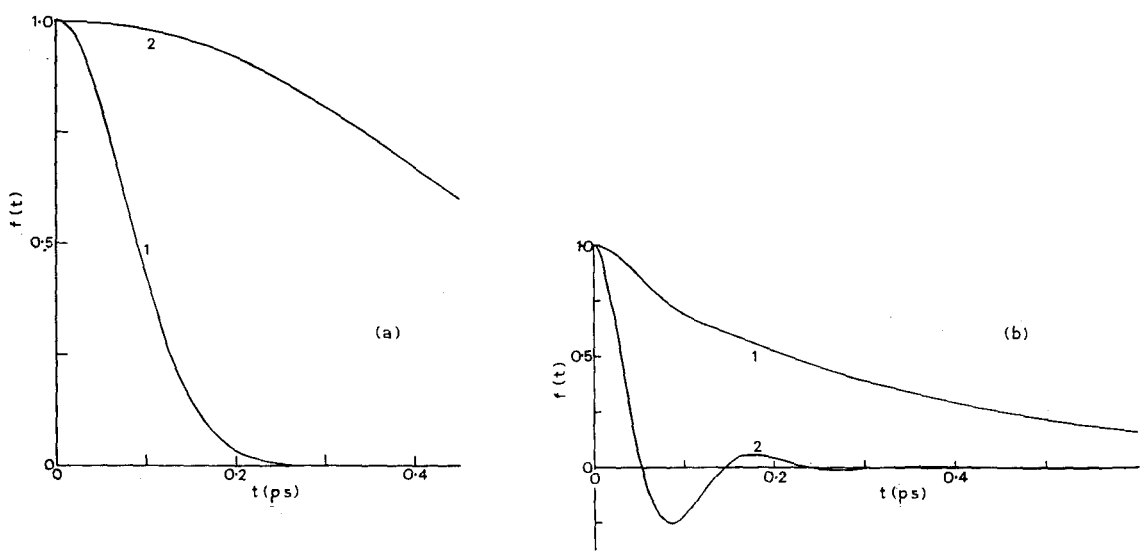

Fig. 1. (a) $\phi(t)$ (curve 1) and $\psi(t)$ (curve 2) for $K_0(0) = 0.65\,I/2kT$; $K_1(0) = 2.25\,I/2kT$; $\gamma = 1.85\,(I/2kT)^{1/2}$, where I = moment of inertia = 6.31×10^{-39} g cm^2, T = temperature = 298 K. (b) $\phi(t)$ (curve 1) and $\psi(t)$ (curve 2) for $K_0(0) = 79.9\,I/2kT$; $K_1(0) = 247.6\,I/2kT$; $\gamma = 32.7\,(I/2kT)^{1/2}$; I and T as for fig. 1a.

It would be fruitful for further work in this field to apply generalised Langevin theory to approximate odd cumulants such as $\langle\omega(t_1)\omega(t_2)\omega(t_3)\rangle_c$, and to abandon the idea that the multivariate density function for $\omega(t_1) \ldots \omega(t_n)$ is a gaussian.

Acknowledgement

SRC is thanked for a fellowship.

Appendix

The overall memory function $K_\psi(t)$ corresponding to $\psi(t)$, related by the equation:

$$\dot{\psi}(t) = -\int_0^t K_\psi(t-\tau)\,\psi(\tau)\,\mathrm{d}\tau\,,$$

is given [using eq. (15)] by:

$$\begin{aligned} K_\psi(t) &= \exp(-\gamma t)\,(\cos at + \tfrac{1}{2}\gamma a \sin at)\,K_0(0)\,, && \text{for } K_1(0) > \tfrac{1}{4}\gamma^2\,; \\ &= \exp(-\gamma t)\,(1+\tfrac{1}{2}\gamma t)K_0(0)\,, && \text{for } K_1(0) = \tfrac{1}{4}\gamma^2\,; \\ &= \exp(-\gamma t)\,(\cosh bt + \tfrac{1}{2}\gamma b \sinh bt)\,K_0(0)\,, && \text{for } K_1(0) < \tfrac{1}{4}\gamma^2\,. \end{aligned}$$

Berne and Harp have shown that the ideal $K_\psi(t)$ has a MacLaurin series starting:

$$K_\psi(t) = \frac{\langle O(V)^2\rangle}{2IkT} + \tfrac{1}{2}t^2\left[\left(\frac{\langle O(V)^2\rangle}{2IkT}\right)^2 - \frac{\langle \dot{O}(V)^2\rangle}{2IkT}\right] - \ldots\,,$$

so that in the absence of molecular interaction, $K_\psi(t)$ should reduce to zero, i.e. it can be looked upon as representing the "molecular memory" of past interaction. From eqs. (13) and (14) we have $K_0(0)$ and $K_1(0)$ of our approximate $\psi(t)$ disappearing in this limit of collision free angular motion.

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