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BROWNIAN MOTION WITH SUPERIMPOSED INTERACTION: COSINE POTENTIAL AND MOLECULAR DYNAMICS SIMULATION

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ABSTRACT

A molecular dynamics simulation of 108 C_{2v} triatomics is used to evaluate a model of the molecular liquid based on the Evans and Calderwood/Coffey itinerant oscillator concepts. Several weaknesses of the original models are investigated using P_n Legendre a.c.f.'s of orientation and the related angular momentum a.c.f. The harmonic binding between cage and encaged molecule is clearly shown to be an oversimplification. Replacement by a cosine potential gives a better result after a numerical analysis due to Ferrario.

INTRODUCTION

An useful form of the itinerant librator theory of liquid state molecular dynamics was introduced via the Mori continued fraction by Evans [1] in 1976 and in greater physical and mathematical detail by Calderwood and Coffey [2] in 1977. In order to keep the number of phenomenological parameters to a minimum certain constraints have to be made. A major assumption is that the motion of the dipole vector is planar, only θ of the Euler angles (θ, ϕ, χ) is involved. Another is that the dipolar asymmetric top under consideration is bound harmonically to a cage of neighbours which revolves according to Langevin's interpretation of the Brownian motion. Since the appearance of these papers the model has been tested very thoroughly both experimentally (by Reid et al [3], using zero-THz spectroscopy) and by computer simulation [4]. An extensive data

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correlation exercise (involving some fifty solute molecules) has just been completed by Reid and Evans [5] involving liquid, ultra-viscous and glassy-state specimens.

In this letter we use a molecular dynamics simulation of 108 triatomic molecules of C_{2v} symmetry to develop a more realistic version of the original model. There are several weaknesses of the original analysis which need to be investigated.

(i) The restriction $(\theta, \phi, \chi) \rightarrow (\theta)$ is a source of concern which may be investigated in several ways. One of the most straightforward is to simulate by computer the P_n (cos $\theta(t)$) functions. Here $P_1 \equiv \langle \cos\theta(t)\cos\theta(0)\rangle$ is the autocorrelation function of the dipole vector's orientation (θ) with respect to an arbitrary initial axis. The second Legendre polynomial is denoted P_2 and its relation to P_1 is model dependent (see, for example, Berne and Harp 6 . An assumption such as $(\theta, \phi, \chi) \rightarrow (\theta)$ can be tested directly by matching the model $P_1, \ldots, P_n$ against the simulated $P_1, \ldots, P_n$, and then looking also at the way the model and simulated angular momentum auto-correlation functions behave. The results of this exercise are given later in this letter.

(ii) The assumption that the binding (or potential interaction), between the inner molecule and cage is harmonic is an approximation introduced for the sake of analytical tractability. More realistically the potential has a cosine dependence so that the equations of motion are simultaneous stochastic differential equations of the form

$$I_2\ddot{\theta}(t) + I_2\omega_o^2 \sin(\theta(t) - \phi(t)) = I_2\dot{W}(t) \qquad (1)$$

$$I_1\ddot{\phi}(t) + I_1\beta\dot{\phi}(t) - I_2\omega_o^2 \sin(\theta(t) - \phi(t)) = I_1\dot{W}(t) \qquad (2)$$

Here W(t) is a Wiener process [2] representing the effect of Brownian noise on the rotating cage, of moment of inertia I_1. I_2 is the moment of inertia of the reference molecule, ω_o^2 a coupling constant between it and its cage of nearest neighbours. β is the friction coefficient governing the Brownian motion of the cage. θ and ϕ are the angles defined by Calderwood and Coffey. Eqns. (1) and (2) are soluble numerically (appendix) by matrix diagonalisation methods. There is no known analytical solution except in the case $\sin(\theta(t) - \phi(t)) \doteq (\theta(t) - \phi(t))$ when the original concept is regained. In this letter we report that eqns. (1) and (2) lead to a more realistic match with the molecular dynamics simulation than the original model of 1976 and 1977.

EXPERIMENTAL

The far infra-red broad-band results of Reid, obtained by interferometry, have been checked in representative cases with an Apollo Instruments tunable far infra-red laser. This consists of a model 560 CO_2 laser, emitting 85 frequencies of up to 50 watts C/W output on some lines, pumping a resonance cavity filled with methanol vapour, or in some instances $CF_2{=}CH_2$ vapour. The monochromatic far infra-red output is mW in power. Far infra-red frequencies were estimated by Michelson interferometry with a melinex beam divider. Power absorption coefficients of the Beer-Lambert law were estimated by attenuation of the radiation reaching a pyrroelectric detector through a VC-01 variable path length liquid cell. Reid's broad band results were substantiated by spot frequency measurements with standard deviations in the range $\pm$(2.5 to 10% (and, exceptionally, bigger) of the original broad band value at that frequency. The mean difference between spot frequency (laser) and broad-band ("cube" interferometer) is of the order of $\pm$ 4%.

Simulation details

An algorithm written originally by Renaud and Singer [7] was modified to produce the P_n autocorrelation functions for n up to 5, together with the angular momentum autocorrelation function $\langle \underline{J}(t).\underline{J}(0)\rangle$. A 3 x 3 centre Lennard-Jones atom-atom potential was used for each of 108 molecules with periodic boundary conditions. The a.c.f.'s were computed with 2000 time steps, each of 0.01 ps, using a running time-average. Further details are available in the literature [8]. (T = 100 K, molar vol. = $10^{-4}m^3$).

Matching of model and simulation

This was carried out as follows. With the original idea $\sin(\theta(t) - \phi(t)) \doteq (\theta(t) - \phi(t))$ the simulated P_2 function (fig. (1)) was fitted with a non-linear l.m.s. method iterating on β, ω_0^2 and $(I_1/I_2)\omega_0^2$ as parameters. These paramters are (in reduced units of kT/I_2 or $(kT/I_2)^{\frac{1}{2}}$ 12.2, 4.8 and 10.2. Using these it is possible analytically to calculate P_2 to P_5, using the theorem of Calderwood and Coffey [2]. Also tractable with the same set of parameters is $\langle \underline{J}(t).\underline{J}(0)\rangle$. A self-consistent comparison (fig.(1)) is therefore possible. The outcome may be interpreted as follows.

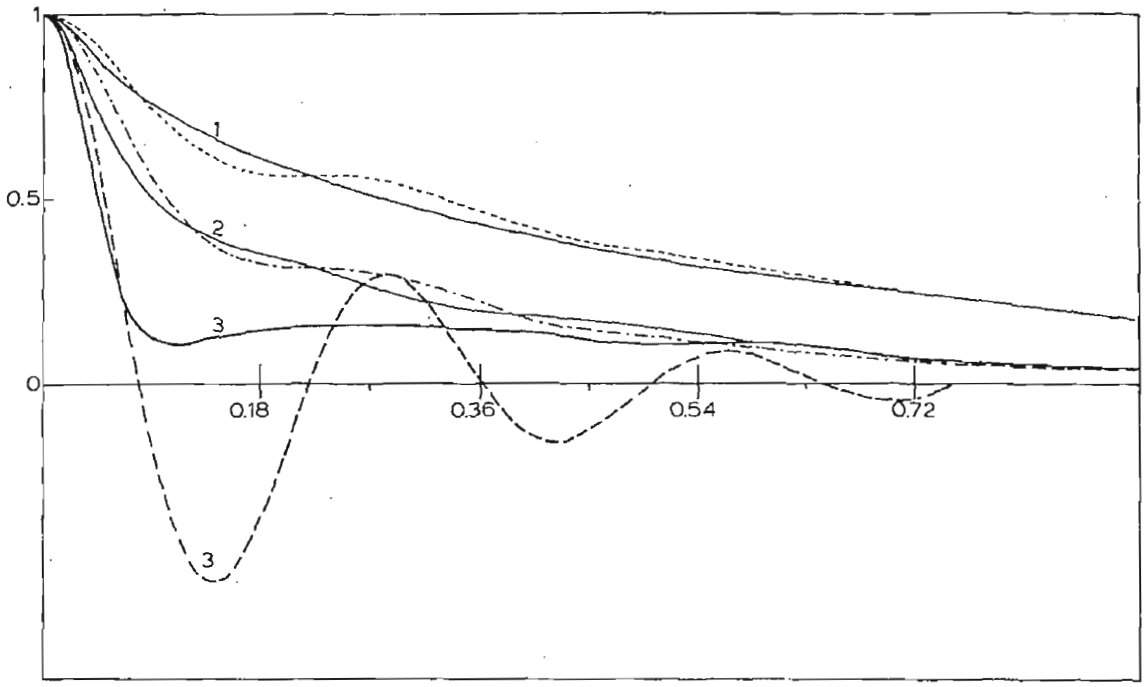


Fig. 1a.

——— Simulated

– – – Modelled with harmonic potential

(1) P_1; (2) P_2; (3) angular momentum.

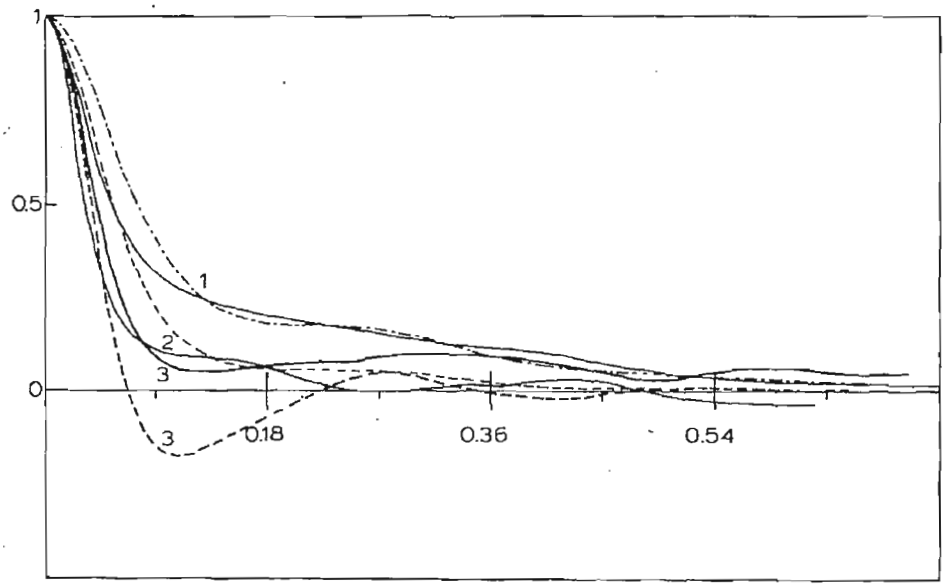


Fig. 1b.

As for figure 1(a): (1) P_3; (2) P_5; (3) rotational velocity.

Ordinate f(t); Abscissa time/ps.

(i) By fitting P_2, P_1 is reproduced fairly accurately, especially at long times, where the decay of both P_1 and P_2 with time is roughly exponential. P_3 and P_5 are followed less closely. These are always markedly non-exponential in nature. The fact that $(\theta, \phi, \chi) \rightarrow (\theta)$ is therefore not as restrictive as the harmonic assumption $\sin(\theta(t) - \phi(t)) \doteq (\theta(t) - \phi(t))$ in the original model. This is shown clearly by comparing the simulated and analytical angular momentum a.c.f.'s using the set of parameters derived from P_2. The model $\langle \underline{J}(t).\underline{J}(0) \rangle$ is <u>far too oscillatory</u>. This is a clear cut indication that eqns. (1) and (2) should be used as a starting point for the analytical analysis.

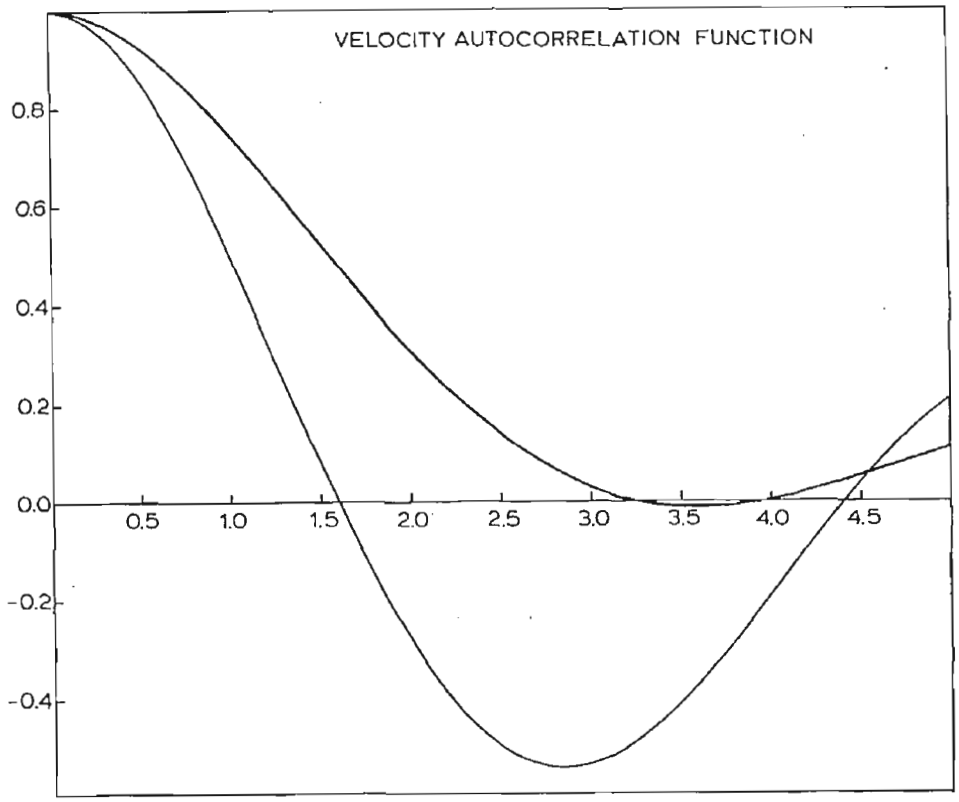


Fig. 2.

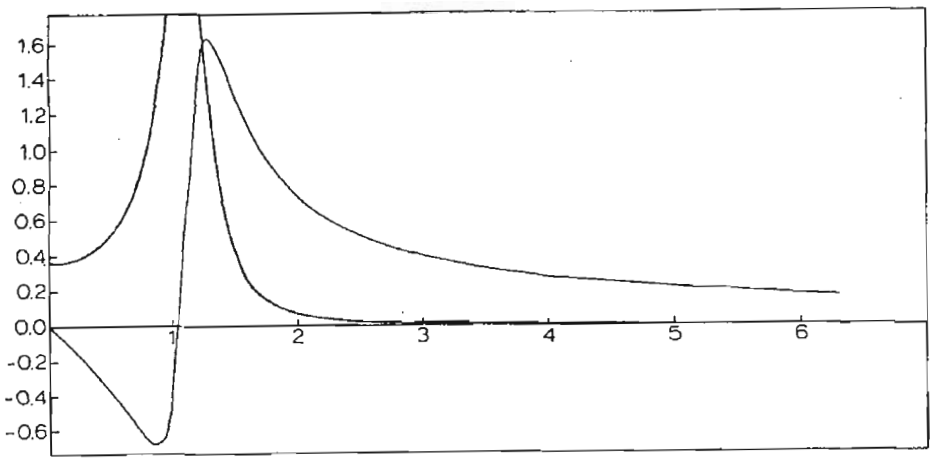
(a) Itinerant librator model, angular momentum autocorrelation function.

Model parameters as in figure 1.

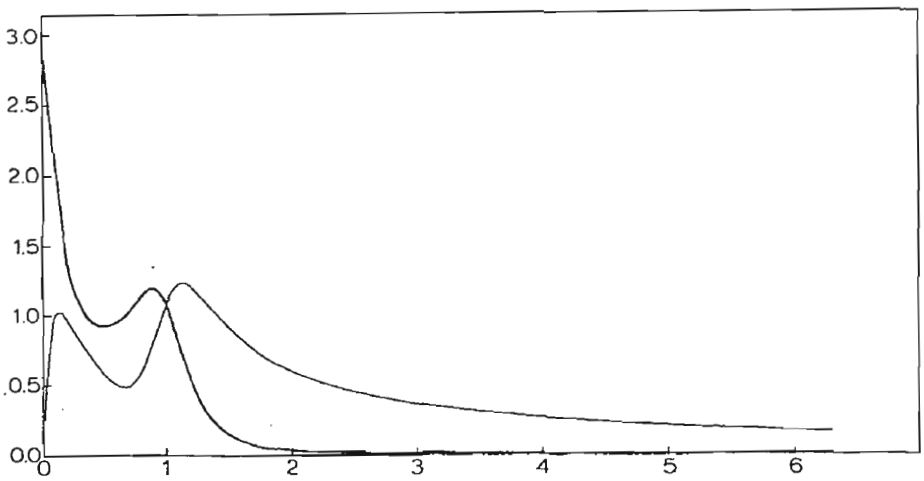
——— Cosine potential

– – – – Harmonic potential

Abscissa: time/ps.



(b) Real (———) and imaginary (▬▬) parts of the Fourier transform of the harmonic potential angular momentum a.c.f.



(c) As for (b), Cosine Potential. Abscissa: frequency/THz.

Using a Hermite polynomial basis set and Ferrario's method (appendix) it is just possible on the UMRCC CDC 7600 to solve eqns. (1) and (2) numerically. For the same parameters β, ω_o^2 and $(I_2/I_1)\omega_o^2$ and for two other sets the results are shown in figs. (2) - (3). It can be seen that $\langle \underline{J}(t).\underline{J}(0)\rangle$, i.e. $I_2^2\langle\theta(t).\theta(0)\rangle$ is damped out, but not enough. Further refinements of the modelling technique are therefore needed, as is always the case of course, but these should be made without the use of more phenomenological variables. The fact that (I_2/I_1) is greater than one from the P_2 fitting is echoed and well-

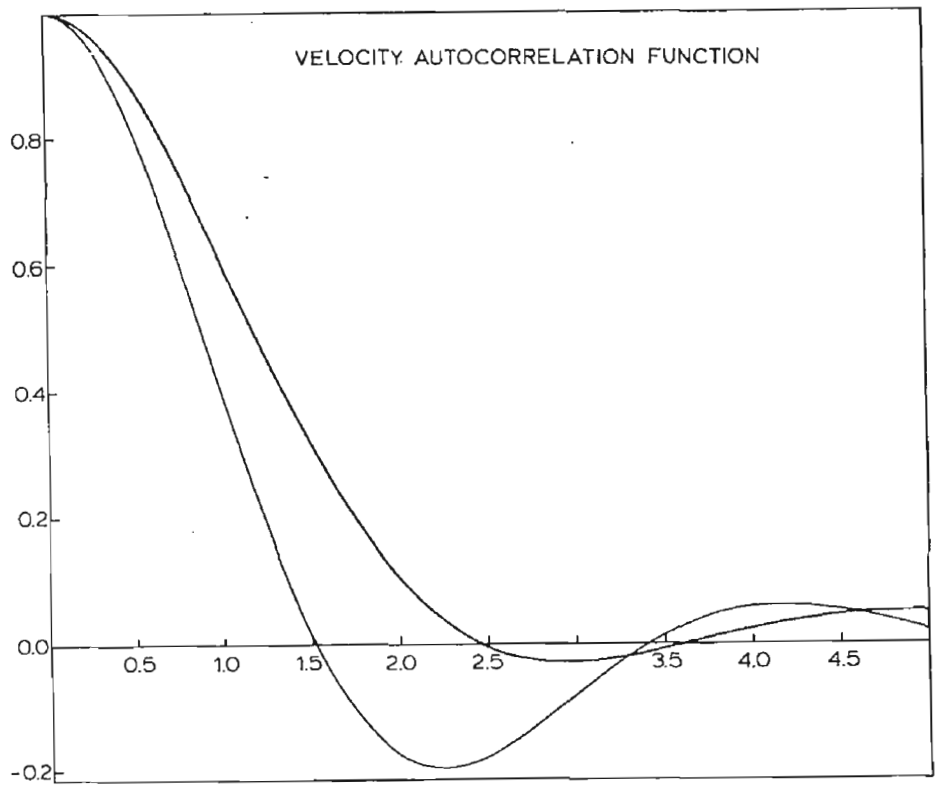


Fig. 3.
As for figure 2, $\omega_o = 1.66$, $(I_2/I_1)^{\frac{1}{2}}\omega_o = 3.27$; $\beta^{\frac{1}{2}} = 2.82$ (in reduced units, see text).

known from the zero-THz work of Evans et al. Reid [9] has offered an explanation to the effect that the cage is intuitively tenuous in nature and not a rigid entity. This should be inforporated into the mathematical details of the modelling. Copies of Ferrario's Fortran algorithm are available on request. This solves eqns. (1) and (2) for the following autocorrelation functions.

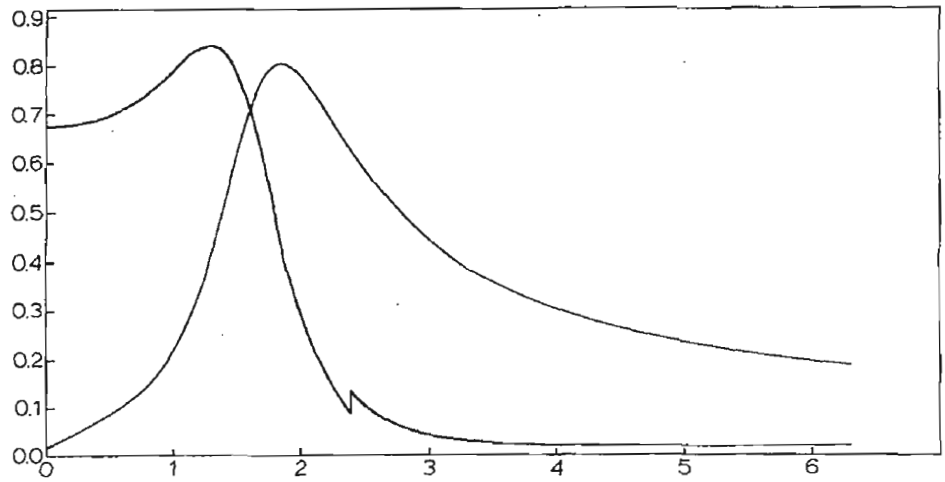
(1) $\langle\theta(t)\theta(0)\rangle/\langle\theta(0)\theta(0)\rangle$; (angular velocity).

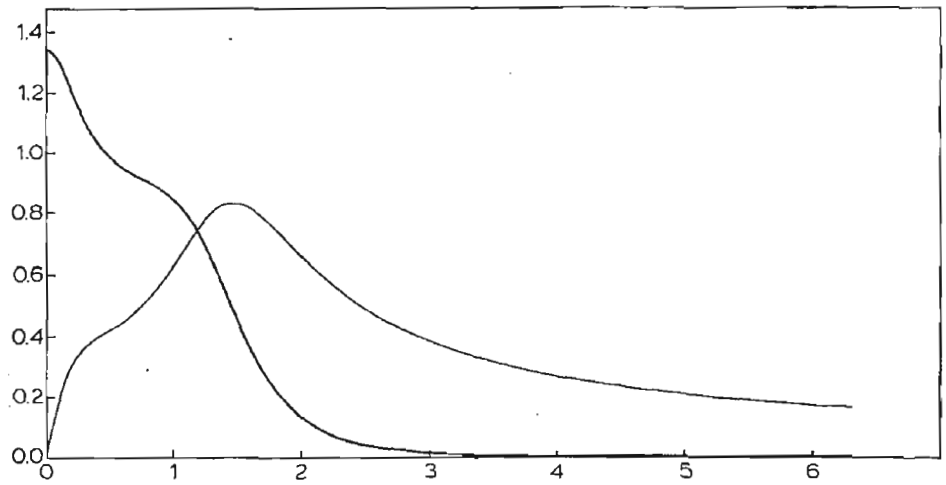
(2) $\left\langle \frac{d}{dt}\cos\theta(t)\ \frac{d}{dt}\cos\theta(t) \right\rangle_{t=0}$ (rotational velocity).

(3) $\langle\cos\theta(t)\cos\theta(0)\rangle$ (orientation).

(4) $\langle\cos 2\theta(t)\cos 2\theta(0)\rangle$ (planar P_2).

(5) $\langle\cos 3\theta(t)\cos 3\theta(0)\rangle$ (planar P_3).





APPENDIX

The Fokker-Planck equation describing the process is

$$\frac{\partial}{\partial t} P(\psi_1, \psi_2, \dot{\theta}, \dot{\phi}, t/0) = L P \tag{A1}$$

where the F.-P. operator L is

$$\frac{1}{2}\frac{\partial}{\partial \psi_1}(\dot{\theta}+\dot{\phi}) + \frac{1}{2}\frac{\partial}{\partial \psi_2}(\dot{\theta}-\dot{\phi}) - \frac{1}{2I_2}\frac{\partial}{\partial \theta} V'(\psi_2)$$

$$+ \frac{1}{2I_1}\frac{\partial}{\partial \phi} V'(\psi_2) + \frac{\partial}{\partial \dot{\theta}}\dot{\theta} + \frac{kT}{I_2}\frac{\partial^2}{\partial \dot{\theta}^2} + \frac{\partial}{\partial \dot{\phi}}\dot{\phi} + \frac{kT}{I_1}\frac{\partial^2}{\partial \dot{\phi}^2}$$

Here $\psi_1 \equiv (\theta+\phi)/2$; $\psi_2 \equiv (\theta-\phi)/2$; $V(\psi_2) = -I_2\omega_o^2 \cos(2\psi_2)$.

The equilibrium solution of eqn. (A1) is given by

$$P_{eq}(\psi_1, \psi_2, \dot{\theta}, \dot{\phi}) = \frac{1}{N'} \exp\left[-\frac{\dot{\theta}^2 I_2}{2kT} - \frac{\dot{\phi}^2 I_1}{2kT} + \frac{I_2\omega_o^2}{kT}\cos(2\psi_2)\right] \tag{A2}$$

We solve eqn. (A1) with a method which is generally applicable and is described basically by Risken and Volmer [10]. It allows us to compute any correlation function of interest by the integral

$$\langle \alpha_1(0)\alpha_2(t)\rangle = \int \phi_1(\Omega, 0)\phi_1(\Omega, t)d\Omega \tag{A3}$$

where

$$[\Omega] = [\psi_1, \psi_2, \dot{\theta}, \dot{\phi}]$$

are physical observable of the system and can be expressed in terms of $[\Omega(t)]$. $\phi_2(\Omega, t)$ is the solution of the equation

$$\frac{\partial}{\partial t}\phi = L_F \phi \tag{A4}$$

with the diffusion operator

$$L_F = \psi^{-1}(\Omega) L_F \psi(\Omega) \tag{A5}$$

and

$$\psi(\Omega) = \frac{1}{\sqrt{N'}} \exp\left[-\frac{1}{4kT}\left(I_2\dot{\theta}^2 + I_1\dot{\phi}^2\right) + \frac{I_2\omega_0^2}{2kT}\cos(2\psi_2)\right] \tag{A6}$$

subjected to the initial condition

$$\phi_2(0, \Omega) = \alpha_2(\Omega)\psi(\Omega) \tag{A7}$$

The solution of eqn. (A4) is achieved by using the following expansion on the set of Hermite polynomials and on the plane waves of the function ϕ

$$\phi(\Omega) = \sum_{n=0}^{\infty} \sum_{n_1,n_2=-\infty}^{\infty} \left[A_{kq}^{n_1 n_2}(t)\, He_{n_1}(\dot{\theta})\, He_{n_2}(\dot{\phi})\right.$$

$$\left. X \exp\left[ik\psi_1 + iq\psi_2\right] \psi(\Omega)\right] \tag{A8}$$

which transforms eqn. (A4) into a linear differential matrix equation:

$$\dot{\underline{A}}(t) = \underline{C}\,\underline{A}(t) \tag{A9}$$

where

$$\underline{A}(t) = \begin{bmatrix} A_{00}^{00}(t) \\ A_{00}^{10}(t) \\ A_{10}^{10}(t) \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ A_{\bar{k}\,\bar{q}}^{\bar{n}_1\bar{n}_2} \end{bmatrix} \tag{A10}$$

and $\underline{C}$ is the matrix expansion of the operator L_F on the basis set given by (A8).

Eqn. (A9) is solved by diagonalising the matrix $\underline{C}$. The solution is:

$$\underline{A}(t) = \exp\left[\underline{C}t\right]\underline{A}(0) = \sum_i \underline{F}_i \exp\left[\underline{C}_i t\right]\left[\underline{F}_i, \underline{A}(0)\right] \qquad (A11)$$

where $\underline{F}_i$ and $\underline{F}_i$ are the right and left eigenvectors and $\underline{C}_i$ the eigenvalues of the matrix $\underline{C}$, and the brackets $[\ ,\ ]$ mean the scalar product. In evaluating the integrals (A3) we have used the fact that

$$g_q = \int \cos q \exp\left[\frac{I_2\omega_O^2}{kT} \cos 2x\right] dx$$

$$= 0 \text{ if } n \text{ is odd}; \quad = I_{q/2}\,(I_2\omega_O^2/kT) \text{ if } n \text{ is even or zero.}$$

Here $I_n(z)$ is the modified Bessel function of integer order, n = 0, 1, 2 ....

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