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NUMERICAL SOLUTION OF FOKKER/PLANCK/KRAMERS EQUATIONS

M. FERRARIO and M. W. EVANS

Chemistry Department, University College of Wales, Aberystwyth SY23 1NE, Wales (Gt. Britain)

and W. T. COFFEY

School of Engineering, Trinity College, Dublin 2, Ireland.

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ABSTRACT

Some Fokker/Planck/Kramers equations of current interest are solved numerically for autocorrelation functions and spectra. It is demonstrated that uncritical use of these equations should be avoided because of the neglect of memory effects inherent in their make-up. Only in the case discussed by Evans (1976) does this type of equation produce realistic spectra, and then only over a limited range of temperature and viscosity. The way to proceed in problems involving molecular diffusion of this type is to use molecular dynamics simulation

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INTRODUCTION

In a series of articles [1-5] we have recently been attempting to describe the relation of spectroscopic profiles to molecular motions in the liquid state and related condensed phases. In particular, the combination of far infra-red spectroscopy with dielectric measurements at microwave and lower frequencies has provided us with a sensitive means of evaluating probability

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diffusion equations of the Fokker-Planck-Kramers (FPK) type [6]. These are descriptions of the motion of a particle, or molecule, subjected to disturbances of stochastic origin, such as in Brownian motion and also to a superimposed potential energy. The latter may be attributed to various causes and several articles have recently appeared stressing the importance of the FPK type of equation in many branches of physics [7].

In this article we compute from FPK formalism autocorrelation functions of molecular dipole reorientation. These are Fourier transform pairs with the electromagnetic spectrum of dipolar liquids from static to THz (or far infra-red) frequencies provided that linear response theory is applicable, i.e. that the external measuring field can be regarded as a perturbation. We have developed specific forms of the general FPK equations previously [8] for comparison with the zero-THz bandshapes of a series of dipolar liquids, and have extended the analysis to Rayleigh and neutron scattering. In so doing we have assumed that the potential appearing in the FPK equation arises from intermolecular interactions of various kinds. For example:

(i) Potential well interaction, leading to molecular torsional oscillation, or libration. The form of the resultant intermolecular potential is of course complicated, depending in an intricate manner on the structure of each molecule but progress is possible through the use of simple functions. In this context a harmonic potential has been discussed in detail by Coffey et al. [9], and evaluated experimentally by Reid et al. [10] under a wide range of conditions. It emerges that this theory is successful in reproducing also the basic features of far infra-red spectroscopy, the Poley absorption, but not in describing the experimentally observed shift to higher frequencies in the peak absorption frequency $\bar{\nu}_{max}$ (cm^{-1}).

Calderwood, Coffey et al.[8,9] have improved upon this aspect of the theory by developing a model of the FPK formalism known as itinerant libration or oscillation (i.o), because the dynamical equations are those of a librator harmonically bound and encaged with a group of neighbours undergoing rotational diffusion as rigid entity. This is an FPK system in $\mathbb{R}^4$ space

where the intermolecular potential well is again assumed to be harmonic. In its simplest form this model is capable of reproducing the shift in $\bar{\nu}_{max}$ and also of defining properly the intermolecular mean square torque essentially because the encaged molecule is shielded from impulsive collisions by its neighbours. Evans, Grigolini and Ferrario [11] have discussed in detail its relationship with the Mori continued fraction of which it is an approximation Coffey [12] discussed its relation with Budo's theory of diffusing molecules subjected to internal dipole-dipole interaction of cosinal form. In this paper we use FPK formalism to generalise the i.o. equations for use with an arbitrary intermolecular potential form.

(ii) Zero-THz spectroscopy can be used incisively to investigate the molecular dynamics of liquid crystals. In this respect Evans and Price [13] have recently used a Smoluchowski equation similar to that of Coffey and Budo to explain the loss features at microwave and MHz frequencies of the nematogen 4-cyano-4 n-heptyl biphenyl (7CB) without assuming the presence of a hydrodynamic director. In this work the intermolecular potential was cosine, but used with geometrical constraints. Chaturvedi and Shibata [14] using convolutionless Mori formalism, have shown how this restriction may be lifted.

SECTION I: NUMERICAL SOLUTION OF KRAMERS EQUATIONS

In a paper by Brinkman [15] often quoted by authors in this field the Fokker-Planck-Kramers equation is written as:

$$-\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial p}\left(F\rho - \frac{\rho}{\tau}p - \frac{mkT}{\tau}\frac{\partial \rho}{\partial p}\right) + \frac{\partial}{\partial q}\left(\frac{p\rho}{m}\right) \quad - (I - 1)$$

where ρ is the particle density in phase space $1R^2(q,p)$, p being the momentum of the particle P and q its coordinate, Eqn. (I.1) is derived from the Langevin equation:

$$\frac{dp}{dt} = F(q) + A(t) \quad - (I - 2); \quad m\ddot{q} = p; \quad F(q) = -\frac{dV}{dq} \quad - (I - 3)$$

where V is the potential energy of P. This is the basic equation with which

we shall be concerned but we shall change Brinkman's equation slightly in order to concur with that more commonly used in contemporary articles. Accordingly:

$$W(q,p,t); \quad \tau \equiv \beta^{-1}, \; F \equiv -\partial V/\partial q \qquad - (I - 4)$$

We shall be interested in evaluating numerically averages of the type

$$\langle e^{iq} \rangle_{q,p}$$

In the notation (I - 4), eqn. (I - 1) becomes

$$-\frac{\partial W}{\partial t} = \frac{\partial}{\partial p}\left(-\frac{\partial V}{\partial q} W - \frac{W}{\beta^{-1}} p - \frac{mkT}{\beta^{-1}} \frac{\partial W}{\partial p}\right) + \frac{\partial}{\partial q}\left(\frac{W}{m} p\right) \qquad - (I - 5)$$

whose solution may be written as:

$$W(q,p,t) = \exp\left(\frac{-p^2}{2mkT}\right) \sum_{n=0}^{\infty} He_n \frac{p}{\sqrt{mkT}} \psi_n (q,t) \qquad - (I - 6)$$

where the He_n are the Hermite polynomials and the ψ_n are functions to be determined. We stipulate that $\psi_n = 0$ for $n<0$ and in general $n = 0,1,2,3...$ Eqns. (I.6) and (I.1) with the use of $He_n(x)$ recurrence relations result in the scheme:

$$\frac{\partial \psi_n}{\partial t} + \frac{n}{\beta^{-1}} \psi_n = \frac{F}{\sqrt{mkT}} \psi_{n-1} - \left(\frac{kT}{m}\right)^{\frac{1}{2}} \frac{\partial \psi_{n-1}}{\partial q} - (n + 1)\left(\frac{kT}{m}\right)^{\frac{1}{2}} \frac{\partial \psi_{n+1}}{\partial q} \qquad - (I - 7)$$

where m is the mass of the particle. The set (I.7) is one of differential difference equations, e.g. for $n = 0$, $n = 1$

$$\frac{\partial \psi_0}{\partial t} = \left(\frac{kT}{m}\right)^{\frac{1}{2}} \frac{\partial \psi_1}{\partial q}$$

$$\frac{\partial \psi_1}{\partial t} + \frac{\psi_1}{\beta^{-1}} = \frac{F}{(mkT)^{\frac{1}{2}}} \psi_0 - \left(\frac{kT}{m}\right)^{\frac{1}{2}} \left(\frac{\partial \psi_0}{\partial q} - 2 \frac{\partial \psi_2}{\partial q}\right) \qquad - (I - 8)$$

This is a complicated structural problem which is best tackled numerically when the potential V is at all involved. The initial conditions chosen are:

$$W(q,p,o) = \exp(-p^2/2mkT) f_0(q) \qquad - (I - 9)$$

which is meant to cover all possible physical contingencies in which we shall be interested. Here $f_0(q)$ represents the initial distribution in q space only. Clearly:

$$W(q,p,o) = \exp(-p^2/2mkT) He_0 \psi_0(q,o); \quad (\because He_0 = 1) \qquad - (I - 10)$$

Of particular interest to zero-THz spectroscopy is <u>rotational</u> diffusion.

In order to keep things simple we shall linearise the Euler equations and consider diffusion on a circular track so that $q = \theta$ and our Fokker-Planck Kramers equation becomes:

$$\frac{\partial \Psi_n}{\partial t} + \frac{n}{\beta^{-1}} \Psi_n = \frac{F}{\sqrt{IkT}} \Psi_{n-1} - \left(\frac{kT}{I}\right)^{\frac{1}{2}} \frac{\partial \Psi_{n-1}}{\partial \theta} - (n+1)\left(\frac{kT}{I}\right)^{\frac{1}{2}} \frac{\partial \Psi_{n+1}}{\partial \theta} \qquad - (I-11)$$

$$-\frac{\partial W}{\partial t} = \frac{\partial}{\partial p}\left(-\frac{\partial V}{\partial \theta} W - \frac{W}{\beta^{-1}} p - \frac{Ikt}{\beta^{-1}} \frac{\partial W}{\partial p}\right) + \frac{\partial}{\partial \theta}\left(\frac{Wp}{I}\right)$$

where $p = I\dot{\theta}$. Here I is the scalar moment of inertia. The Langevin equation corresponding to this is

$$I\ddot{\theta} + I\beta\dot{\theta} + F(\theta) = I\dot{B}(t); \quad t > o - \qquad (I-12)$$

where B is the Wiener process [6] governing the stochastic torque experienced by the librating molecule. When $F(\theta) = I\omega_o^2\theta$ the model reduces to the harmonic oscillator model of Calderwood et al. [9] , which is closely related to Gordon's m-diffusion model [1-3,16]. We suppose that static conditions have prevailed up to $t = o$, i.e. for $t < o$:

$$I\ddot{\theta} + I\beta\dot{\theta} + F(\theta) + \mu E \sin\theta = I\dot{B}(t) \; - \qquad (I-13)$$

To cover the itinerant librator and Budo formalism the FPK system in IR^4 must be constructed, i.e. involving $IR^4(\theta_1, \theta_2, \dot{\theta}_1, \dot{\theta}_2, t)$ and this is discussed in greater detail later.

In general, for the present case:

$$\langle e^{iq} \rangle = \int_0^{2\pi} \int_{-\infty}^{\infty} e^{iq} W \, dq \, dp \Big/ \int_0^{2\pi} e^{iq} \, dq \, dp$$

$$= \int_0^{2\pi} e^{iq} \Psi_o \, dq \Big/ \int_0^{2\pi} \Psi_o \, dq \qquad - (I-14)$$

because of the normalisation:

$$\int_{-\infty}^{\infty} e^{-\frac{x^2}{2}} H_{en}(x) H_{em}(x) dx = \sqrt{2\pi}\, n! \, \delta_{m,n}$$

When dealing with the scalar angular coordinate θ we have:

$$\langle e^{i\theta} \rangle = \int_0^{2\pi} e^{i\theta} \Psi_0 \, d\theta \Big/ \int_0^{2\pi} \Psi_0 \, d\theta; \quad \Psi_0 \equiv \Psi_0(\theta, t) \qquad - (I-15)$$

The problem is to calculate $\Psi_0(\theta,t)$ for any periodic $F(\theta)$ of eqn. (I-13).

We have initially:

$$W(\theta, I\dot{\theta}, 0) \equiv W(\theta, p, 0) = \exp\left(-p^2/2IkT\right)(1 + \frac{\mu E}{kT}\cos\theta)e^{-\beta V(\theta)}$$

so that:

$$\Psi_n(\theta,0) = (1 + \frac{\mu E}{kT}\cos\theta)\exp(-\beta V(o)) = \Psi_o(\theta, o)$$

To simplify eqn. (I - 11) we write:

$$\Psi_n(\theta, t) = \sum_{l=-\infty}^{l=\infty} A_l^n(t)e^{il\theta}, \quad F = \sum_{r=-\infty}^{\infty} F_r e^{ir\theta}$$

and use the implications of orthogonality to write:

$$\frac{d}{dt}A_l^n + \frac{n}{\beta}A_l^n = (IkT)^{-\frac{1}{2}}\sum_{r=-\infty}^{\infty} Fr\, A_{l-r}^{n-1}(t) - (kT/I)^{\frac{1}{2}}il\{A_l^{n-1}(t) + (n+1)A_l^{n+1}(t)\} \qquad - (I - 16)$$

so that:

$$\langle e^{i\theta}\rangle = \frac{\int_0^{2\pi}\sum_{l=-\infty}^{\infty} A_l^o(t)e^{il\theta}e^{i\theta}d\theta}{\int_0^{2\pi}\sum_{l=-\infty}^{\infty} A_l^o(t)e^{il\theta}d\theta} \qquad - (I - 17)$$

The numerator is finite only for $l = -1$ and the denominator only for $l = 0$:

$$\langle e^{i\theta}\rangle = \int_0^{2\pi} A_{-1}^o(t)e^{i\theta}e^{-i\theta}d\theta / \int_0^{2\pi} A_o^o(t)d\theta$$

$$= A_{-1}^o(t)/A_o^o(t)$$

If we now take the special case of:

$$F = I\omega_o^2 \sin\theta = I\omega_o^2(e^{i\theta} - e^{-i\theta})/2i \qquad - (I - 18)$$

this leads to the recurrence relations:

$$\frac{dA_l^n}{dt} + \frac{n}{\beta}A_l^n = \left(\frac{I}{kT}\right)^{\frac{1}{2}}\frac{\omega_o^2}{2}\, i(A_{l+1}^{n-1} - A_{l-1}^{n-1})$$

$$-\left(\frac{kT}{I}\right)^{\frac{1}{2}} il\left(A_l^{n-1}(t) + (n+1)A_l^{n+1}(t)\right) \qquad - (I - 19)$$

Numerical Solution of Eqn.(I - 19):

This is quite straightforward if we write eqn. (I - 19) in the matrix form:

$$\dot{\underline{\underline{A}}}(t) = \underline{\underline{C}}\,\underline{\underline{A}}(t) \qquad - (I - 20)$$

where $\underline{\underline{A}}(t) =$

$$\begin{bmatrix} \vdots \\ A_1^1 \\ A_o^1 \\ A_o^o \\ A_1^o \\ A_{-1}^1 \\ \vdots \end{bmatrix}$$

The formal solution is:

$$\underline{\underline{A}}(t) = \exp(\underline{\underline{C}}t)\underline{\underline{A}}(o) \qquad - (I - 21)$$

and for numerical purposes we must restrict ourselves to N components of $\underline{\underline{A}}$.

If we take the left and right eigenvectors of the matrix $\underline{\underline{C}}$: $\underline{X}_i$ (i = 1, ...,N) and $\underline{Y}_i^T$ (= 1, ...,N) respectively, with eigenvalues λ_i, we may write:

$\underline{\underline{A}}(o) = \sum_i \alpha_i \underline{X}_i$, where $\alpha_i = (\underline{Y}_i^T, \underline{\underline{A}}(o))$ the scalar product, then we have:

$\underline{\underline{C}}\,\underline{X}_i = \lambda_i \underline{X}_i$, which means:

$\exp(\underline{\underline{C}}t)\underline{X}_i = \exp(\lambda_i t)\underline{X}_i$.

We finally get:

$$\underline{\underline{A}}(t) = \sum_i e^{\lambda_i t} (\underline{Y}_i^T, \underline{\underline{A}}(o))\underline{X}_i \qquad - (I - 22)$$

This is valid only if the matrix $\underline{\underline{C}}$ has a complete set of eigenvectors,

e.g. if:

$$\sum_i \underline{X}_i \underline{Y}_i^T = \underline{\underline{1}} \qquad (I - 23)$$

Eqn. (I - 19) is now amenable to solution using methods of diagonalisation.

Next in this section we describe the method of generalising itinerant oscillator equations of Coffey and Calderwood [9] and Coffey et al [8] to remove the restriction of harmonic potential force.

FOKKER-PLANCK KRAMERS EQUATION FOR THE ITINERANT OSCILLATOR

In this case the Langevin equations of motion for scalar angular itinerant libration are, for a harmonic potential,

$$I_1 \ddot{\Psi}_1(t) + I_1\beta_1 \dot{\Psi}_1(t) - I_2\omega_0^2\left(\Psi_2(t) - \Psi_1(t)\right) = I_1\dot{W}_1(t)$$

$$I_2 \ddot{\Psi}_2(t) + I_2\beta_2 \dot{\Psi}_2(t) + I_2\omega_o^2\left(\Psi_2(t) - \Psi_1(t)\right) = I_2\dot{W}_2(t) \qquad \text{- (I - 24)}$$

These reduce to the equations of Coffey and Calderwood [9] when $\beta_2 = o$. The physical meaning of the angular functions $\Psi_2(t)$ and $\Psi_1(t)$ and of the friction coefficients β_1 and β_2 are fully explained in the literature [8,9]. We wish to accomplish the generalisation of the term:

$$I_2\omega_o^2(\Psi_2(t) - \Psi_1(t))$$

which represents the harmonic force between the inner molecule and the diffusing cage. Eqns. (I - 24) with $\beta_2 = o$ have been tested out experimentally for about fifty liquid and glassy systems by Reid and Evans [10]. They have the disadvantage that generally the Poley absorption is too sharply defined theoretically. The FPK equation corresponding to eqn. (I.24) is [11] :

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \dot{\psi}_2}(\dot{\psi}_2 f) + \frac{\partial}{\partial \dot{\psi}_1}(\dot{\psi}_1 f) - \frac{\partial}{\partial \dot{\psi}_1}(\omega_0^2(\psi_2 - \psi_1)f) = \frac{\partial}{\partial \dot{\psi}_1}(\Omega_0^2(\psi_2 - \psi_1)f)$$

$$= \beta_2 \frac{\partial}{\partial \dot{\psi}_2}(\dot{\psi}_2 f) + \beta_1 \frac{\partial}{\partial \dot{\psi}_1}(\dot{\psi}_1 f) + \beta_2 \frac{kT}{I_2}\frac{\partial^2 f}{\partial \dot{\psi}_2^2} + \beta_1 \frac{kT}{I_1}\frac{\partial^2 f}{\partial \dot{\psi}_1^2} \qquad \text{(I - 25)}$$

with initial condition:

$$f(\psi_1, \psi_2, \dot{\psi}_1, \dot{\psi}_2, o) = A \exp\left(-\frac{1}{2kT}(I_1\dot{\psi}_1^2 + I_2\dot{\psi}_2^2 + I_2\omega_0^2(\psi_2 - \psi_1)^2)\right)$$

and is soluble analytically. However our problem is to solve the FPK equation for a distribution function describing the Langevin equations:

$$\ddot{\psi}_2(t) + \frac{\xi}{I_2}\dot{\psi}_2(t) + \frac{V'}{I_2}(\psi_2 - \psi_1) = \dot{B}_2(t)$$

$$\ddot{\psi}_1(t) + \frac{\xi}{I_1}\dot{\psi}_1(t) - \frac{V'}{I_1}(\psi_2 - \psi_1) = \dot{B}_1(t) \qquad \text{(I - 26)}$$

where B_1 and B_2 are Wiener processes. As well as generalising the itinerant oscillator concept these equations also describe and generalise the Budo

theory [12] of the molecular dynamics of an assembly of molecules containing rotating dipolar groups. If these dipoles are denoted by μ_1 and μ_2 then in the Budo/Coffey theory they are compelled to rotate about an axis through their common centre normal to the plane containing the measuring field ε. In eqn. (I. 26) subsequently ψ_1 and ψ_2 are the angles μ_1 and μ_2 make with e, the direction of ε, at any time. I is the moment of inertia of each equally sized dipole and ξ is the friction coefficient arising from the Brownian movement of the surroundings, while $\lambda_1(t)$ and $\lambda_2(t)$ are the random couples acting on μ_1 and μ_2 again arising from Brownian motion.

Coffey {12} has derived the FPK equation in IR^4 corresponding to the system (I - 26). This is: (I = I_1 = I)

$$\frac{\partial W}{\partial t} + \dot{\psi}_2 \frac{\partial W}{\partial \psi_2} + \dot{\psi}_1 \frac{\partial W}{\partial \psi_1} - \frac{1}{I}\left(\frac{\partial W}{\partial \dot{\psi}_2}\frac{\partial V}{\partial \psi_2} + \frac{\partial W}{\partial \dot{\psi}_1}\frac{\partial V}{\partial \psi_1}\right) = \frac{\xi}{I}\left(\frac{\partial}{\partial \dot{\psi}_2}(\dot{\psi}_2 W) + \frac{\partial}{\partial \dot{\psi}_2}(\dot{\psi}_1 W)\right)$$

$$+ \tfrac{1}{2}\left(C_{33}^2 \frac{\partial^2 W}{\partial \dot{\psi}_2} + (C_{34}^2 + C_{43}^2)\frac{\partial^2 W}{\partial \dot{\psi}_1 \partial \dot{\psi}_2} + C_{44}^2 \frac{\partial^2 W}{\partial \dot{\psi}_1^2}\right) \qquad \text{(I - 27)}$$

solved subject to the initial conditions:

$$W(\psi_1, \psi_2, \dot{\psi}_1, \dot{\psi}_2, 0) = A \exp\{-\beta\{I/_2 (\dot{\psi}_1^2 + \dot{\psi}_2^2) + V(\psi_2 - \psi_1) + (\mu_1 \cos\psi_1 + \mu_2 \cos\psi_2)\varepsilon\}\} \qquad \text{(I - 28)}$$

In eqn. (I - 27) C_{33}^2, C_{34}^2, C_{43}^2, and C_{44}^2 are constants to be determined from the equilibrium Boltzmann distribution. Thereby eqn. (I - 27) becomes:

$$\frac{\partial W}{\partial t} + \dot{\psi}_2 \frac{\partial W}{\partial \psi_2} + \dot{\psi}_1 \frac{W}{\partial \psi_1} - \frac{1}{I}\left(\frac{W}{\partial \dot{\psi}_2}\frac{\partial V}{\partial \dot{\psi}_2} + \frac{\partial W}{\partial \psi_1}\frac{\partial V}{\partial \psi_1}\right)$$

$$= \frac{\xi}{I}\left\{\frac{\partial}{\partial \dot{\psi}_2}(\dot{\psi}_2 W) + \frac{\partial}{\partial \dot{\psi}_1}(\dot{\psi}_1 W) + \frac{kT}{I}\left(\frac{\partial^2 W}{\partial \dot{\psi}_2^2} + \frac{\partial^2 W}{\partial \dot{\psi}_1^2}\right)\right. \qquad \text{(I - 29)}$$

Coffey has shown how eqn. (I - 29) may be manipulated using two dimensional Hermite polynomials into the set of differential difference equations:

$$s\,\tilde{\psi}_{0,0} = f_0(\chi,\eta) - \left(\frac{kT}{2I}\right)^{\frac{1}{2}}\left(\frac{\partial \tilde{\psi}_{0,1}}{\partial \chi} + \frac{\partial \tilde{\psi}_{1,0}}{\partial \eta}\right);$$

$$\{s + \frac{\xi}{I}(m+n)\,\tilde{\psi}_{m,n} + (2IkT)^{-\frac{1}{2}}\frac{\partial V}{\partial \eta}\tilde{\psi}_{m,n-1} \qquad \text{(I - 30)}$$

$$+ \left(\frac{kT}{2I}\right)^{\frac{1}{2}}(m+1)\frac{\partial \tilde{\psi}_{m+1,n}}{\partial \chi} + (n+1)\frac{\partial \tilde{\psi}_{m,n+1}}{\partial \eta} + \frac{\partial \tilde{\psi}_{m-1,n}}{\partial \chi} + \frac{\partial \tilde{\psi}_{m,n-1}}{\partial \eta}\}$$

$$= 0$$

where $\chi = (\psi_1 + \psi_2)/2$; $\eta = (\psi_2 - \psi_1)/2$; and f is defined by:

$$W(\chi,\eta,\dot{\chi},\dot{\eta},0) = \exp\{-\beta I(\dot{\chi}^2 + \dot{\eta}^2)\} f_o(\chi,\eta)$$

the probability density function being given by:

$$\tilde{W} = \exp\{-I\beta(\chi 2 + \eta 2)\} \sum_{m,n} He_{m.n}\left(\left(\frac{2I}{kT}\right)^{\frac{1}{2}}\dot{\chi}, \left(\frac{2I}{kT}\right)^{\frac{1}{2}}\dot{\eta}\right) \tilde{\psi}$$

$\tilde{\psi} \equiv \tilde{\psi}(\chi,\eta,s)$. We wish to solve eqns. (I-30) numerically for $\tilde{W}$.

Details of the Numerical Solution

Problem in IR^2 Space

In this case the Kramers equation is solved in the form:

$$\frac{\partial}{\partial t} P(\Omega|\Omega_0, t) = L_F P(\Omega|\Omega_0, t) \qquad (I\text{-}31)$$

$$\{\Omega\} = \{\omega,\Theta\}$$

with the equilibrium solution:

$$Po = N' \exp\{-\phi/kT\}; \quad \phi = I\omega^2/2 + V(\Theta). \qquad (I - 32)$$

With $L = \exp\{\phi/2kT\} L_F \exp\{-\phi/2kT\}$ as the transformation

we obtain the equation:

$$\frac{\partial}{\partial t} \Xi = L \qquad \text{with} \qquad \Xi_o = \sqrt{N'} \exp(-\phi/2kT)$$

as the equilibrium distribution and:

$$\Xi = \exp \phi/2 \; P(\Omega|\Omega_0, t)/\sqrt{N'} \qquad (I - 33)$$

It is possible to show that any correlation function may be expressed as:

$$\langle W_1(o)W_2(t) = K_{12}(t) = \int \Phi_1(\Omega, o)\Phi_2(\Omega, t)\partial\Omega \qquad (I - 34)$$

where $\Phi_i(\Omega, t)$ is the solution of the equation:

$$\frac{\partial}{\partial t} \Phi_i = L \Phi_i$$

with the initial condition $\Phi_i(\Omega, o) = W_i \Xi_o(\Omega)$ (I - 35)

Risken and Vollmer [7] obtain the differential operator (kT = 1, I = 1)

$$L = -\frac{\partial}{\partial\theta}\omega + \frac{\partial}{\partial\omega}V'(\Phi) + \beta\left(\frac{1}{2} + \frac{\partial^2}{\partial\omega^2} - \frac{\omega^2}{4}\right) \qquad (I - 36)$$

which results in the equation:

$$\phi_i = \sum_{\substack{n=o \\ q=-\infty}}^{\infty} A_q^n(t) \frac{1}{\sqrt{n!}} H_{en}(\omega) \sqrt{N'} \exp(-\phi/2kT + iq\theta)$$

and the recursion relations:

$$\frac{\partial}{\partial t} A_q^n(t) = -n\beta A_q^n(t) - iq\sqrt{n+1}\, A_q^{n+1}(t)$$

$$+ \sqrt{n+1} \sum_{r=-\infty}^{\infty} ir\, f_r\, A_{q-r}^{n+1}(t) - iq\sqrt{n}\, A_q^{n-1}(t) \qquad (I - 37)$$

with

$$V(\theta) = \sum_{r=-\infty}^{\infty} f_r \exp(iqr) - \qquad (I - 38)$$

The two-time correlation functions $K_d = \left\langle \frac{d}{dt}\cos\theta(t) \frac{d}{dt}\cos\theta(t) \Big|_{t=o} \right\rangle$

$K_\omega(t) = \langle\omega(t)\omega(o)\rangle$; $K_{\cos l\theta} = \langle\cos l\theta(t)\cos l\theta(o)\rangle$ $K_d = \langle d/dt\cos\theta(t)\ d/dt\cos\theta(t)/t=o\rangle$ may now be computed. These are of spectroscopic interest because $\langle\cos\theta(t)\cos\theta(t)\rangle$ is the planar analogue of the orientational autocorrelation function, which is related to the dielectric loss, $\varepsilon''(\omega)$, by Fourier transformation, 1-5 , and $\langle\cos 2\theta(t)\cos 2\theta(o)\rangle$ is related by Fourier transformation to the intensity spectrum of depolarised scattered light. The drivative function $\langle \frac{d}{dt}\cos\theta(t)\ \frac{d}{dt}\cos\theta(t) \Big|\ t = o\rangle$ is the direct Fourier transform of the far infra-red, optical power absorption coefficient $\alpha(\omega)$ (in neper cm^{-1}). We have:

$$K_\omega(t) = \int \Phi_\omega(o,\omega,\theta)\Phi_\omega(t,\omega,\theta)\, d\omega d\theta \qquad (I - 39)$$

with $\Phi_\omega(o,\omega,\theta) = \omega\Xi_0 = \sqrt{N'}\, H_{e1}(\omega) \exp(-\phi/2kT)$;

$$K_{\cos l\theta}(t) = \int \Phi_{\cos l\theta}(o,\omega,\theta)\Phi_{\cos l\theta}(t,\omega,\theta)\, d\omega d\theta \qquad (I - 40)$$

with $\Phi_{\cos l\theta}(o,\omega,\theta) = \cos(l\theta)\Xi_0 = (\sqrt{N'}/2)(e^{il\theta} + e^{-il\theta})He_0\, e^{-\psi/2kT}$ (I - 41)

and $K_d(t) = \int \Phi_d(o,\omega,\theta)\Phi_d(t,\omega,\theta)\, d\omega d\theta$ (I - 42)

with $\Phi_d(o,\omega,\theta) = -\omega\sin\theta\,\Xi_0 = \sqrt{N'}/(2i)(e^{iq\theta} - e^{-iq\theta})H_{e\,l}\, e^{-\phi/2kT}$ (I - 43)

By defining:

$$\exp\left(-V/kT\right) = \sum_{r=-\infty}^{\infty} g_2 \exp(ir\theta)$$

it is possible (see Risken and Vollmer) to show:

$$K_\omega(t) = \frac{1}{g_0} \sum_{q=-\infty}^{\infty} A_q^l(t) g_{-q} \qquad (I - 44)$$

with

$$A_q^n(o) = \delta_{n,l}\, \delta_{q,o} \qquad (I - 45)$$

By explicit calculation we have:

$$\widehat{K\cos l\theta}(t) = \int_{\pi}^{\pi} d\theta \int_{\infty}^{\infty} d\omega \left(\frac{N}{2}' (e^{il\theta} + e^{-il\theta}) H_{\theta} e^{-V/kT} \right.$$

$$\left. \times \sum_{n,q} A_q^n(t) \frac{1}{\sqrt{n!}} He_n(\omega) \exp(iq\theta) \exp(-\omega^2/2\Delta^2) \right. \qquad \text{(I - 46)}$$

$$= \int_{\pi}^{\pi} \left[\frac{N}{2}' (e^{il\theta} + e^{-il\theta}) \exp(-V(\theta)/kT) \sum_{q} A_q^o(t) e^{iq\theta} \right] d\theta = \frac{1}{2g_o} \sum_{q=-\infty}^{\infty} A_q^o(t) \left[g_{-q-l} + g_{-q+l} \right]$$

with the initial condition:

$$A_q^n(0) = \tfrac{1}{2} \delta_{n,0} (\delta_{q,1} + \delta_{q,-1}) \qquad \text{(I - 47)}$$

and

$$K_l(t) = \int_{-\pi}^{\pi} d\theta \int_{-\infty}^{\infty} d\omega \{ -\omega \sin\theta N' e^{-V/kT} e^{-\omega^2/2\Delta^2} \sum_{n,q} A_q^n(t) He_n(\omega) e^{iq\theta} \frac{1}{\sqrt{n!}} \}$$

$$= \int_{-\pi}^{\pi} \frac{N'}{\pi 2i} \{ (e^{i\theta} - e^{-i\theta}) e^{-V(\theta)/kT} \sum_{q} A_q^l(t) e^{iq\theta} \} d\theta$$

$$= 1/(2ig_o) \sum_{q=-\infty}^{\infty} A_q^l(t) \{ g_{-l-q} - g_{l-q} \} \qquad \text{(I - 48)}$$

with the initial condition:

$$A_q^n(0) = -\frac{1}{2i} \delta_{n,1} (\delta_{q,1} - \delta_{q,-1}) \qquad \text{(I - 49)}$$

The Budo Model with Arbitrary Potential ($f(\theta)$) (IR^3 space)

In this case we have $\{\Omega\} = \omega_1, \omega_2, \theta$; $\omega_1 = \dot{\psi}_1/\Delta_1$

$\theta = \psi_1 - \psi_2$; $\omega_2 = \dot{\psi}_2/\Delta_2$

and

$$L_F = -(\Delta_1\omega_1 - \Delta_2\omega_2)\frac{\partial}{\partial\theta} + \frac{1}{kT}\left(\Delta_1\frac{\partial}{\partial\omega_1} - \Delta_2\frac{\partial}{\partial\omega_2}\right)V'(\theta)$$

$$+ \beta_1 \left(\frac{\partial}{\partial\omega_1}\omega_1 + \frac{\partial^2}{\partial\omega_1}\right) + \beta_2 \left(\frac{\partial}{\partial\omega_2}\omega_2 + \frac{\partial^2}{\partial\omega_2}\right)$$

and

$$P_0 = N \exp\{-\omega_1^2/2 - \omega_2^2/2 - V(\theta)/kT\}$$

i.e. $\phi = \omega_1^2/2 + \omega_2^2/2 + V(\theta)/kT$

The operator L becomes

$$L = -(\Delta_1\omega_1 - \Delta_2\omega_2)\,\partial/\partial\theta + 1/kT(\Delta_1\partial/\partial\omega_1 - \Delta_2\,\partial/\partial\omega_2)V'(\theta)$$

$$+ \beta_1(1/2 + \partial^2/\mu\omega_1^2 - \omega_1^2/4) + \beta_2(1/2 + \partial^2/\partial\omega_2^2 - \omega_2^2/4);$$

$$\left(e^{\phi/2}\,\frac{\partial}{\partial\omega_1}\,e^{-\phi/2} = \frac{\partial}{\partial\omega_1} - \frac{\omega_i}{2}\;;\quad e^{-\phi/2} = \frac{\partial}{\partial\theta} - \frac{V'(\theta)}{2kT}\right).$$

The numerical solution now proceeds via the expansion of the functions:

$$\phi_i(\theta,\omega_1,\omega_2,t) = \sum_{\substack{n_1=0,\\ n_2=0}}^{\infty} C^{n_1,n_2}(t,\theta)\sqrt{N'}e^{-V(\theta)/2kT}|n_1,n_2\rangle$$

where we use a quantum-like notation:

$$|n_1,n_2\rangle = (4\pi^2 n_1!n_2!)^{-1/2}H_{en1}(\omega_1)\,H_{en2}(\omega_2)\exp\{-\frac{\omega_1^2 + \omega_2^2}{4}\}$$

which exploits the properties of Hermite polynomials in the following immediate way:

$$\partial/\partial\omega_1|n_1,n_2\rangle = \tfrac{1}{2}\,(\sqrt{n_1}|n_1 - 1,\, n_2\rangle - \sqrt{n_1 + 1}|n_1 + 1,\, n_2\rangle)$$

$$\partial/\partial\omega_2|n_1,n_2\rangle = \tfrac{1}{2}\,(\sqrt{n_2}|n_1,n_2 - 1\rangle - \sqrt{n_2 + 1}|\,n_1,n_2 + 1\rangle\,)$$

$$\omega_1|n_1,n_2\rangle = (\sqrt{n_1}\,|\,n_1 - 1,\, n_2\rangle + \sqrt{n_1 + 1}|n_1 + 1,\, n_2\rangle)$$

$$\omega_2|n_1\, n_2\rangle = (\sqrt{n_2}|n_1,n_2 - 1\rangle + \sqrt{n_2 + 1}|\,n_1,n_2 + 1\rangle)$$

We obtain for the coefficient $C^{n_1n_2}(x,t)$ the following differential equation.

From $\partial/\partial t\;\phi_i = L\,\phi_i$:

$$\partial/\partial t\; C^{n_1n_2}(\theta,t)e^{-V(\theta)2kT}\sqrt{N'}|n_1,n_2\rangle = -\Delta_1(\sqrt{n_1 + 1}|n_1 + 1,\, n_2\rangle + \sqrt{n_1}|n_1 - 1,n_2\rangle$$

$$\times\quad (C^{n_1n_2}(\theta,t) - V'/(2kT)C^{n_1n_2}(\theta,t))\sqrt{N'}e^{-V(\theta)/2kT}$$

$$+\quad \Delta_1\,(\sqrt{n_2 + 1}\,|\,n_1,\, n_2 + 1\rangle + \sqrt{n_2}\,|\,n_1,\, n_2 - 1\,\rangle)$$

$$\times\quad (C^{n_1n_2}(\theta,t) - V'/(2kT)\,C^{n_1n_2}(\theta,t))\sqrt{N'}e^{-V(\theta)/2kT}$$

$$+\quad \Delta_1/(2kT)(\sqrt{n_1}\,|n_1 - 1,\, n_2\rangle - \sqrt{n_1 + 1}\,|\,n_1 + 1,\, n_2\rangle)V'(\theta)$$

$$\times\quad C^{n_1n_2}(\theta,t)\sqrt{N'}\,\exp\,(-V(\theta)/(2kT))$$

$$-\quad \Delta_2/(2kT)(\sqrt{n_2}|n_1,\, n_2 - 1\rangle - \sqrt{n_2 + 1}|\,n_1,\, n_2 + 1\rangle)V'(\theta)$$

$$\times\quad C^{n_1n_2}(\theta,t)\sqrt{N'}\,\exp(-V(\theta)/2kT))$$

$$-\quad (n_1\,\beta_1 + n_2\beta_2)C^{n_1n_2}(\theta,t)\sqrt{N'}e^{-V(\theta)/(2kT)}|\,n_1,n_2\rangle$$

Summations over n_1 and n_2 are understood in the above formula.

We obtain for the coefficient $C^{n_1, n_2}(\Theta,t)$:

$$\frac{\partial}{\partial t} C^{n_1,n_2}(\Theta,t) = -\Delta_1 (\sqrt{n_1} C^{n_1-1,n_2}(\Theta,t) + \sqrt{n_1+1}\, C^{n_1+1,n_2}(\Theta,t))$$

$$+ \Delta_2(\sqrt{n_2} C^{n_1,n_2-1}(\Theta,t) + \sqrt{n_2+1}\, C^{n_1,n_2+1}(\Theta,t))$$

$$+ (\Delta_1/kT)\sqrt{n_1+1}\, C^{n_1+1,n_2}(\Theta,t) V'(\Theta)$$

$$- (\Delta_2/kT)\sqrt{n_2+1}\, C^{n_1,n_2+1}(\Theta,t) V'(\Theta)$$

$$- (n_1\beta_1 + n_2\beta_2) C^{n_1 n_2}(\Theta,t)$$

The next step is to expand $C^{n_1,n_2}(\Theta,t)$ over a set of functions of Θ.

By denoting: $|q\rangle = e^{iq\Theta}$ we have $C^{n_1, n_2}(\Theta,t) = \sum_{q=-\infty}^{\infty} A_q^{n_1 n_2}(t)|q\rangle$

The properties of $|q\rangle$ are

$$\frac{\partial}{\partial\Theta}|q\rangle = iq|q\rangle$$

and $V'(\Theta)|q\rangle = -\frac{id}{2}(|q+1\rangle - |q$

For $V(\Theta) = \overline{1}\partial\cos\Theta$, where ∂ is a constant, we have $V'(\Theta) = \partial\sin\Theta$

$$= \partial(e^{i\theta} - e^{-i\theta})/(2i); \quad \text{and } V'(\theta)e^{iq\theta} = -\frac{id}{2}(e^{i(q+1)\theta} - e^{-i(q-1)\theta}).$$

By inserting the equation for $C^{n_1,n_2}(\theta,t)$ we obtain

$$\partial/\partial t\, A_q^{n_1,n_2}(t)|q\rangle = -\Delta_1 (\sqrt{n_1}(iq)\, A_q^{n_1-1,n_2}(t)|q\rangle + \sqrt{n_1+1}\,(iq)\, A_q^{n_1+1,n_2}(t)|q\rangle)$$

$$+ \Delta_2(\sqrt{n_2}(iq) A_q^{n_1,n_2-1}(t)|q\rangle + \sqrt{n_2+1}(iq)\, A_q^{n_1,n_2+1}(t)\, q\rangle) + (-\frac{id}{2}\frac{\Delta_1}{kT})\sqrt{n_1+1}$$

$$\times (A_q^{n_1+1,n_2}(t)\,(|q+1\rangle - |q-1\rangle)) - (-\frac{id}{2}\frac{\Delta_2}{kT})\sqrt{n_2+1}\,(A_q^{n_1,n_2+1}(t)$$

$$\times (|q+1\rangle - |q-1\rangle)) - (n_1\beta_1 + n_2\beta_2) A_q^{n_1,n_2}(t)\,|q\rangle$$

Finally we have an equation for $A_q^{n_1,n_2}(t)$ which is numerically soluble:

$$\partial/\partial t\, A_q^{n_1,n_2}(t) = -iq\,\Delta_1\sqrt{n_1}\, A_q^{n_1-1,n_2}(t) - iq\,\Delta_1\sqrt{n_1+1}\, A_q^{n_1+1,n_2}(t)$$

$$+ iq\,\Delta_2\sqrt{n_2}\, A_q^{n_1,n_2-1}(t) + iq\,\Delta_2\sqrt{n_2+1}\, A_q^{n_1,n_2+1}(t) - i\frac{\partial\Delta_1}{2kT}\sqrt{n_1+1}\,\{A_{q-1}^{n_1+1,n_2}(t)$$

$$- A_{q+1}^{n_1+1,n_2}(t)\} + i\frac{\partial\Delta_2}{2kT}\sqrt{n_2+1}\,\{A_{q-1}^{n_1,n_2+1}(t) - A_{q+1}^{n_1,n_2+1}(t)\} - (n_1\beta_1 + n_2\beta_2)\, A_q^{n_1,n_2}(t)$$

The correlation functions of spectroscopic interest are now given in terms of $A_q^{n_1,n_2}(t)$:

$$K_{\omega_1}(t) = \langle\omega_1(t)\omega_1(0)\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\omega_1 d\omega_2 \int_0^{2\pi} d\theta\{\omega_1\psi 0 e^{-V/(2kT)}\sqrt{N'}|n_1,n_2,q\rangle\}$$

$$= (1/g_0)\sum_q A_q^{1,0}(t) g_{-q}$$

with the initial condition: $A_q^{n_1,n_2}(0) = \delta_{n_1,1}\delta_{q,0}\delta_{n_2,0}$

$K_{\omega_2}(t) = 1/g_0 \sum_q A_q^{0,1}(t) g_{-q}$; with i.c. $A_q^{n_1,n_2}(0) = \delta_{n_1,0}\,\delta_{n_2,1}\,\delta_{q,0}$

$K_{\cos 1\theta}(t) = \frac{1}{2g_0} \sum_q A_q^{0,0}(t)\,(g_{-q-1} + g_{-q+1})$

with initial condition $A_q^{n_1,n_2}(0) = \frac{1}{2}\,\delta_{n_1,0}\,\delta_{n_2,0}\,(\delta_{q,1} + \delta_{q,-1})$

$K_{\partial}(t) = -\frac{1}{2ig_0} \sum_q \left[A_q^{1,0}(t) - A_q^{0,1}(t)\right](g_{-q-1} - g_{-q+1})$,

with $A_q^{n_1,n_2}(0) = -\frac{1}{2i}\,(\delta_{n_1,0}\,\delta_{n_2,1} + \delta_{n_1,1}\,\delta_{n_2,0})\,(\delta_{q,1} - \delta_{q,-1})$

Checks on the Numerical Evaluation: Normalisation Factors and $t \to \infty$ limits of the Correlation Functions

(a) Equation in IR^2 space

The normalisation factors may be calculated from the equilibrium distribution function:

$P_0(\theta,\omega) = N \exp\{-\omega^2/2 - V(\theta)\}$, $(kT = 1)$

$(N^{-1} = \int\int \exp(-\omega^2/2 - V(\theta))\,d\theta\,d\omega)$

We set once more $V(\theta) = d\cos\theta$. The initial condition on the Kramers equation is

$$P_2(\theta(t), \omega(t), t. \,|\, \theta(0), \omega(0), 0) = \delta(\omega(t) - \omega(0))\,\delta(\theta(t) - \theta(0))$$

The limiting value for $t \to \infty$ may easily be calculated because the two-time distribution functions may be replaced by the product of the two P_0 equilibrium functions, because there is no correlation between the system at $t = 0$ and at $t \to \infty$, so:

$$\lim_{\to\infty} W_2(\theta(t), \omega(t), t\,;\ \theta(0), \omega(0), 0) = P_0(\theta(t), \omega(t))\,P_0(\theta(0), \omega(0))$$

(P_0 independent of t).

So we obtain:

$$\langle\omega(0)\omega(0)\rangle = N\int\int\omega^2\exp(-\omega^2/2 + V(\theta))\,d\theta\,d\omega = 1$$

$$\langle\cos\theta(0)\cos\theta(0)\rangle = N\int\int\cos^2\theta\exp(-\omega^2/2 + \partial\cos\theta)\,d\theta d\omega$$

$$= \tfrac{1}{2}\int(1 + \cos2\theta)\exp\{\partial\cos\theta\}\,d\theta/\int\exp\{\partial\cos\theta\}\,d\theta$$

$$= 1/(2g_0)\ \{g_0 + g_2\}$$

where $g_n = \int\cos n\theta\exp\{\partial\cos\theta\}\,d\theta = I_n(\partial)$

$I_n(z)$ being the modified Bessel function of integer order (n). In addition:

$$\langle\cos2\theta(0)\cos2\theta(0)\rangle = \int\int N\cos^2 2\theta\exp(-\omega^2/2 + \partial\cos\theta)\,d\theta$$

$$= 1/(2g_0)\{g_0 + g_4\}$$

$$\langle\cos n\theta(0)\cos n\theta(0)\rangle = 1/(2g_0)\{g_0 + g_{2n}\}$$

$$\left\langle\frac{\partial}{\partial t}\cos\theta(t)\frac{\partial}{\partial t}\cos\theta(t)/_{t=0}\right\rangle = \langle\dot\theta(0)\sin\theta(0)\,\dot\theta(0)\sin\theta(0)\rangle$$

$$= N\int\int\omega^2\sin^2\theta\exp\{-\omega^2/2 + \partial\cos\theta\}\,d\theta d\omega$$

$$= \int\sin^2\theta\exp\{\partial\cos\theta\}\,d\theta/\int\exp\{\partial\cos\theta\}\,d\theta$$

$$= 1/(2g_0)\ (g_0 - g_2)$$

The limits $t \to \infty$ of the orientational a.c.f.'s are generally different from zero because of the Kramers potential. This fact is of paramount importance in the development of a molecular theory of the mesomorphic state of matter. These limits may be expressed by:

$$\lim_{t\to\infty}\langle g_1(t)g_1(o)\rangle = \lim_{t\to\infty}\int W_2(\Theta(t),\omega(t),t;\omega(o),o)$$

$$\times\, g_1(\Theta(t),\omega(t))g_2(\Theta(o),\omega(o))\,d\Theta(t)d\Theta(o)d\omega(t)d\omega(o)$$

$$/\ W_2(\ )d\Theta(o)\ .....\ d\omega(o)$$

$$= \int P_o(\Theta_1,\omega_1)g_1(\Theta_1,\omega_1)d\Theta_1 d\omega_1\int P_o(\Theta_2,\omega_2)g_2(\Theta_2,\omega_2)d\Theta_2 d\omega_2$$

$$/(\int P_o(\Theta,\omega)d\Theta d\omega)^2$$

so we obtain:

$$\lim_{t\to\infty}\langle\omega(t)\omega(o)\rangle = o, \text{ because } \int\omega P_o(\omega,\Theta)d\Theta d\omega = o$$

$$\lim_{t\to\infty}\left\langle\frac{d}{dt}\cos\theta(t)\frac{d}{dt}\cos\theta(t)/_{t=o}\right\rangle = \langle\omega(t)\omega(o)\rangle\langle\sin\theta(t)\sin\theta(o)\rangle = o$$

$$\lim_{t\to\infty}\langle\cos n\theta(t)\cos n\theta(o)\rangle = \frac{(\int\cos n\theta\exp[d\cos\theta]\,d\theta)^2}{(\int\exp[d\cos\theta]d\theta)^2} = \left(\frac{g_n}{g_o}\right)^2$$

(b) Budo's Model, Cosine Potential

In this case:

$$P_o(\omega_1,\omega_2,\theta) = \exp\left[\frac{-\omega_1^2}{2\Delta_1^2} - \frac{\omega_2^2}{2\Delta_2^2} + \frac{d}{kT}\cos\theta\right] / \int \exp \ \ldots\ d\omega_1 d\omega_2 d\theta$$

so we obtain

$$\langle\omega_1(o)\omega_1(o)\rangle = \Delta_1^2; \langle\omega_2(o)\omega_2(o)\rangle = \Delta_2^2$$

$$\langle\cos n\theta(o)\cos n\theta(o)\rangle = 1/(2g_o)\left[g_o + g_{2n}\right]$$

$$\left\langle \frac{d}{dt}\cos\theta(t)\Big|_{t=o} \frac{d}{dt}\cos\theta(t)\Big|_{t=o}\right\rangle = \langle(\omega_1(o) - \omega_2(o))\sin\theta(o)(\omega_1(o)-\omega_2(o))\sin\theta(o)\rangle$$

$$= \left[\langle\omega_1(o)\omega_1(o)\rangle + \langle\omega_2(o)\omega_2(o)\rangle\right] \langle\sin\theta(o)\sin\theta(o)\rangle$$

$$= \left[\Delta_1^2 + \Delta_2^2\right] 1/(2g_o)\ (g_o - g_2)$$

and $\lim_{t\to\infty}\langle\omega_1(t)\omega_1(o)\rangle = \lim_{t\to\infty}\langle\omega_2(t)\omega_2(o)\rangle = o$

$$\lim_{t\to\infty}\left\langle \frac{d}{dt}\cos\theta(t)\ \frac{d}{dt}\cos\theta(t)\Big|_{t=o}\right\rangle = o;$$

$$\lim_{t\to\infty}\langle\cos n\theta(t)\cos n\theta(o)\rangle = (g_n/g_o)^2.$$

Results and Discussion

The numerical results are illustrated in figs. (1) to (3) for both the IR^2 model and the more complicated set of equations in IR^3 space. An important feature is that in neither case is the velocity (or angular velocity) autocorrelation well-defined as $t\to o$. This is because the initial slope is not zero, and can be explained as follows:

(a) IR^2 Space

In this case eqn. (I-2) has no memory kernel apart from the delta function friction coefficient. A direct mathematical consequence is that the autocorrelation function of the velocity or angular velocity has a Taylor expansion which begins: $1 - \beta t + O(t^2)$ where β is the friction frequency factor.

(b) The Budo equations (I-24) can be regarded as a zeroth order approximant of the integro-differential matrix equation developed by Damle et al [17] in the context of neutron scattering, i.e. the associated memory matrix has

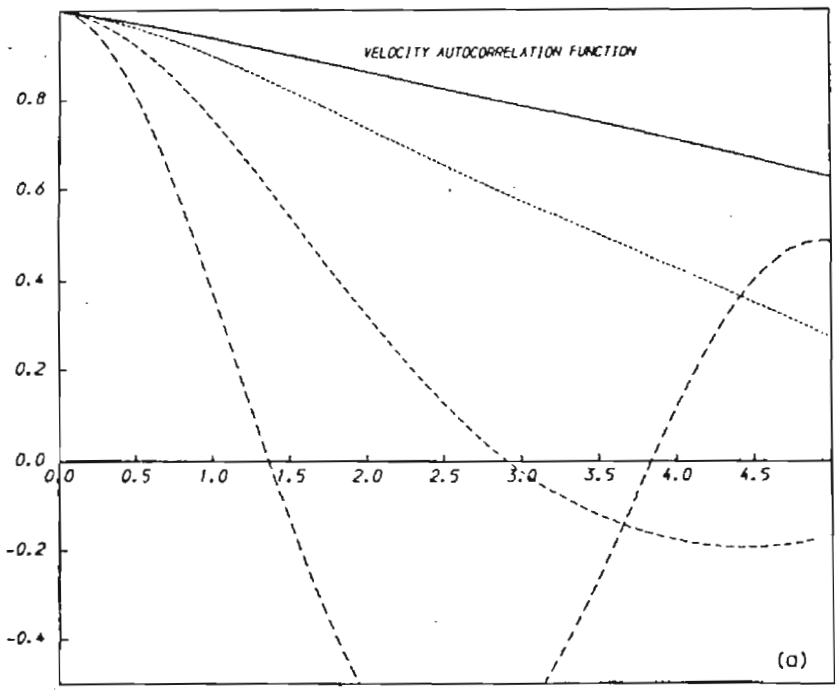


FIGURE 1

IR^2 model, normalised autocorrelation functions and spectra for various values of friction coefficient β and potential strength d. Solid like behaviour. Abscissa in reduced time units of $\left(\frac{I}{kT}\right)^{\frac{1}{2}}$ where I is the moment of inertia.

a) Angular velocity autocorrelation function.

----------β = 0.05 reduced frequency units of $\left(\frac{kT}{I}\right)^{\frac{1}{2}}$, d = 0.25.

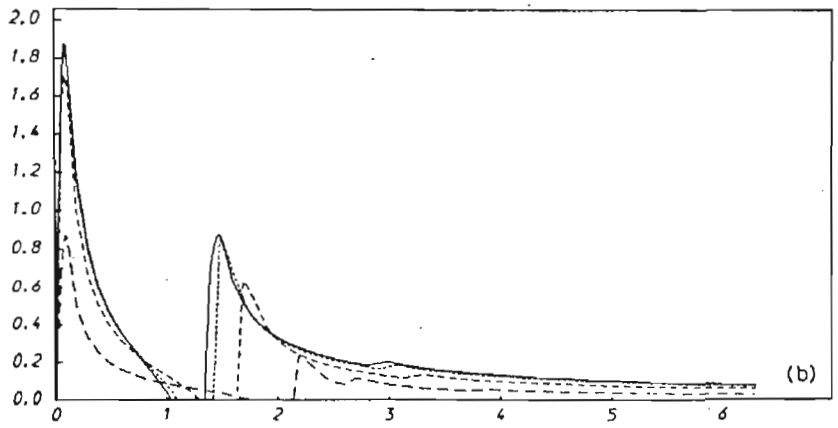
- - - - - - - - = 0.05, d = 0.50

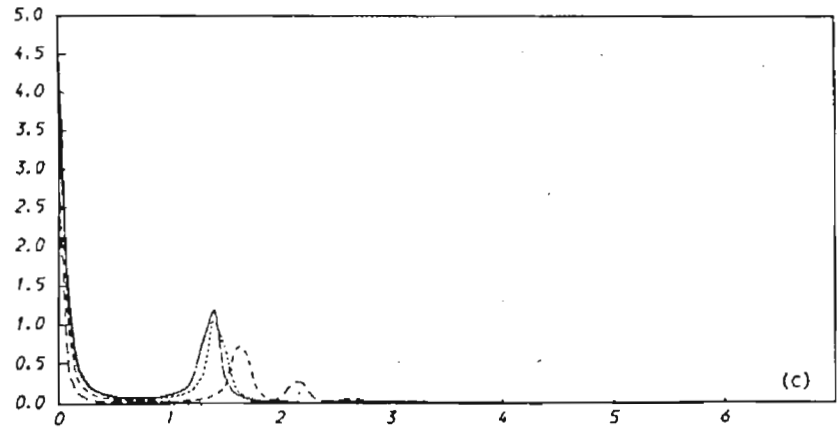
- - - - - - = 0.05, d = 1.00

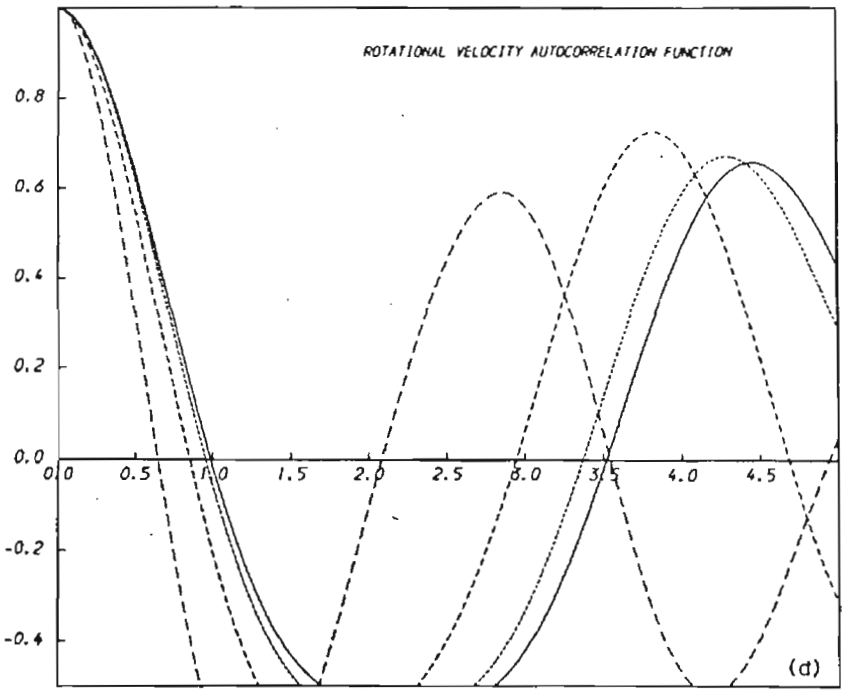
- - - - - = 0.05, d=2.00

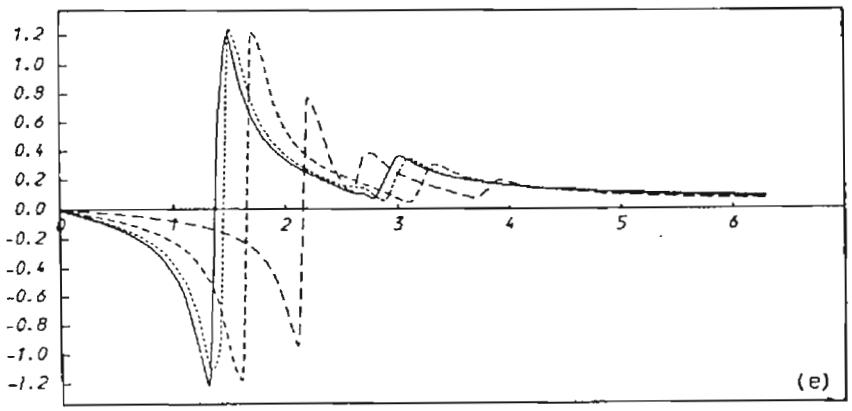
b) and c). Real and imaginary parts of the angular velocity spectrum Abscissa in reduced frequency units

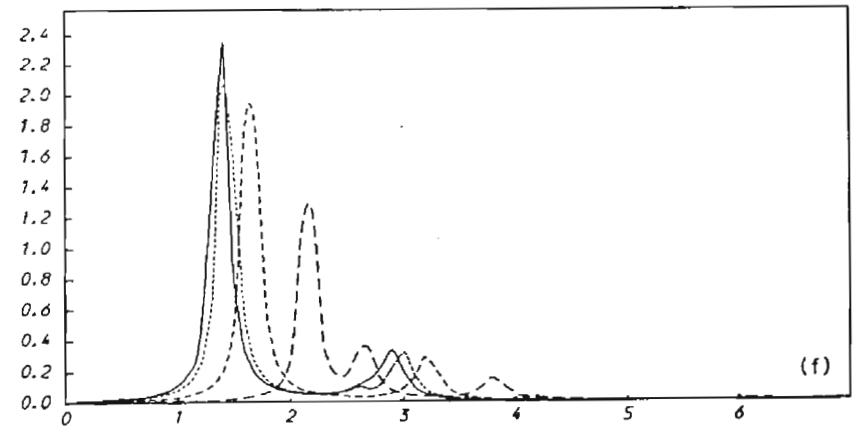
d) rotational velocity autocorrelation function, the second derivative of the orientational autocorrelation function.


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6
(b)


5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
(c)


ROTATIONAL VELOCITY AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
(d)





e) and f). Far infra-red dispersion and power absorption coefficient respectively. Note the multiple peak structure reminiscent of lattice librations in the solid state.

g) $\langle \cos\theta(t)\cos\theta(0) \rangle$

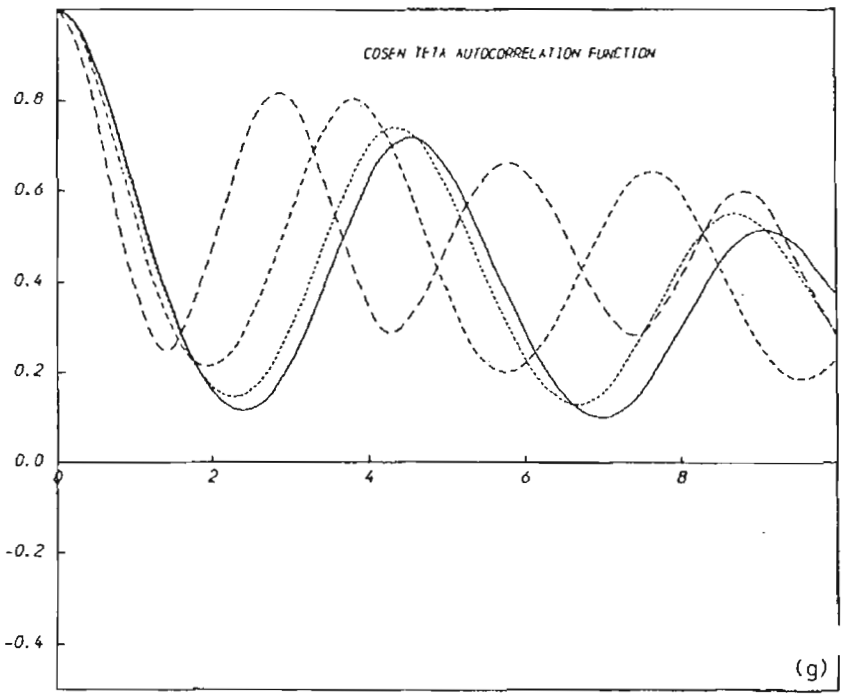
h)and i). Fourier transform components of g)

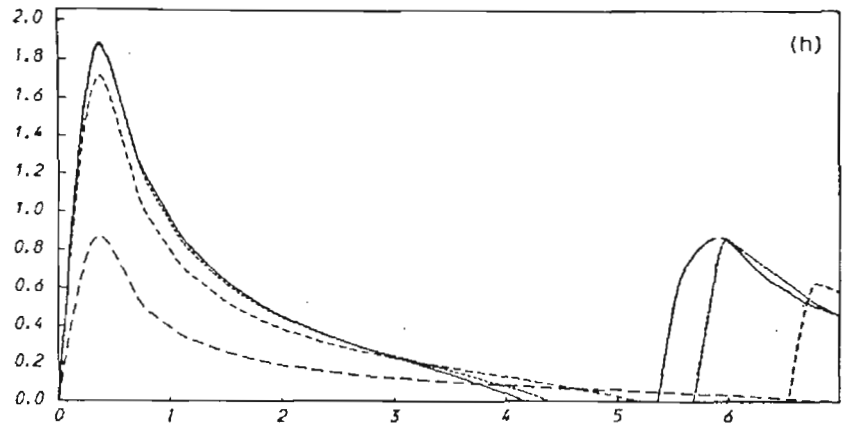
j) $\langle \cos 2\theta(t)\cos 2\theta(0) \rangle$

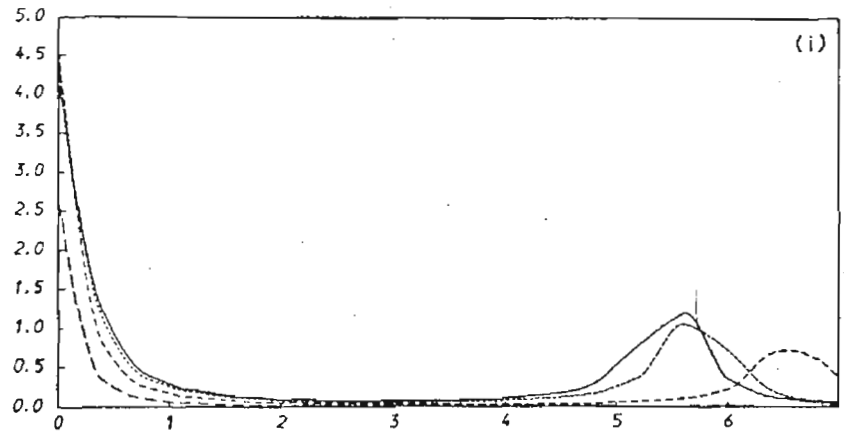
k) and l). Fourier transform components of j).

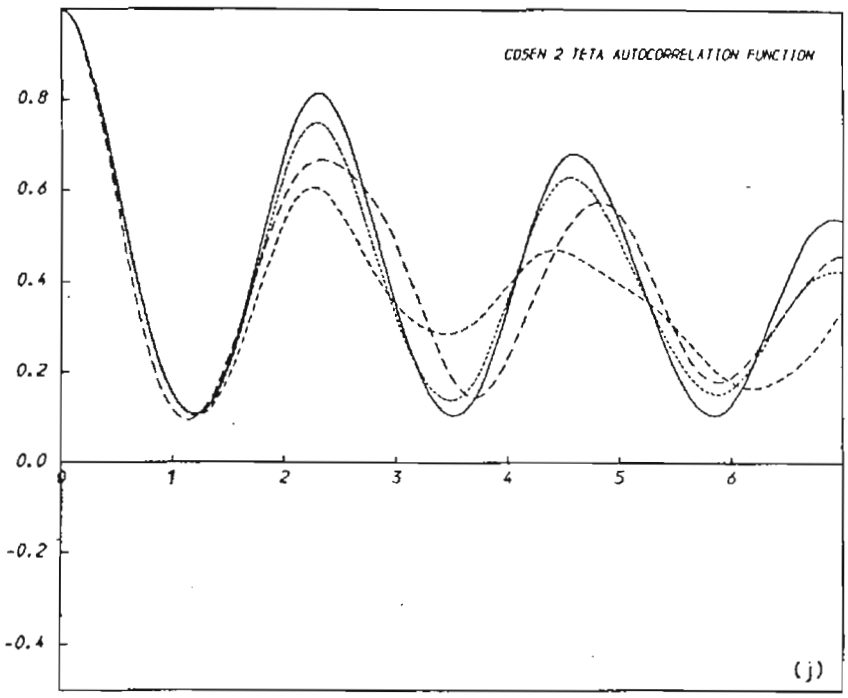
m) $\langle \cos 3\theta(t)\cos 3\theta(o) \rangle$

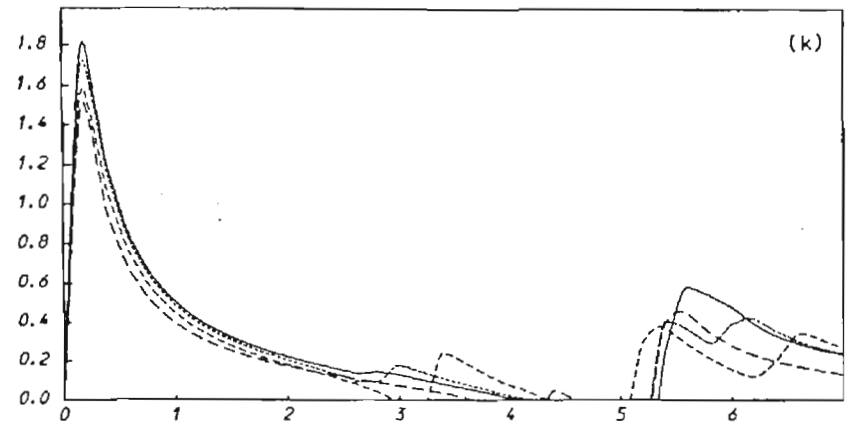
n) and o). Fourier transform components of m).

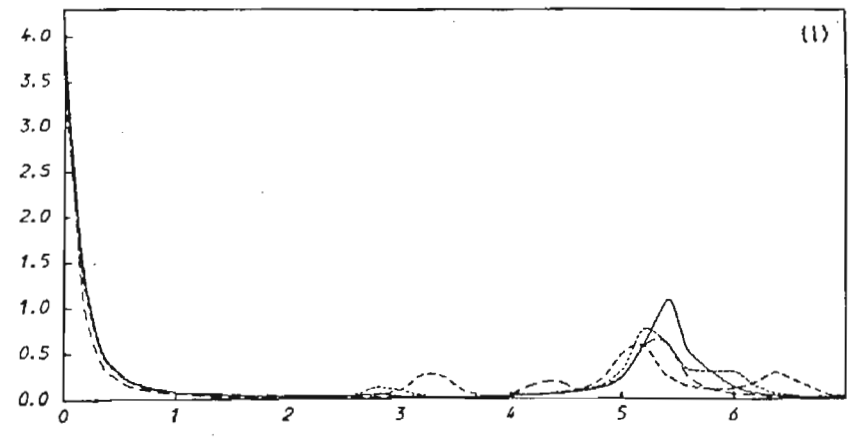

COSEN TETA AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0
2
4
6
8
(g)

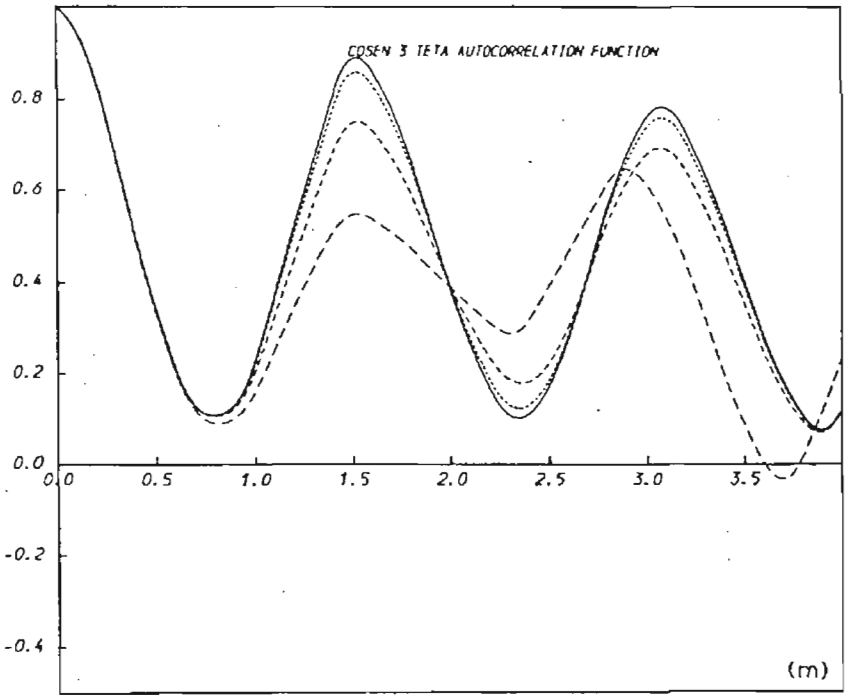

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6
(h)

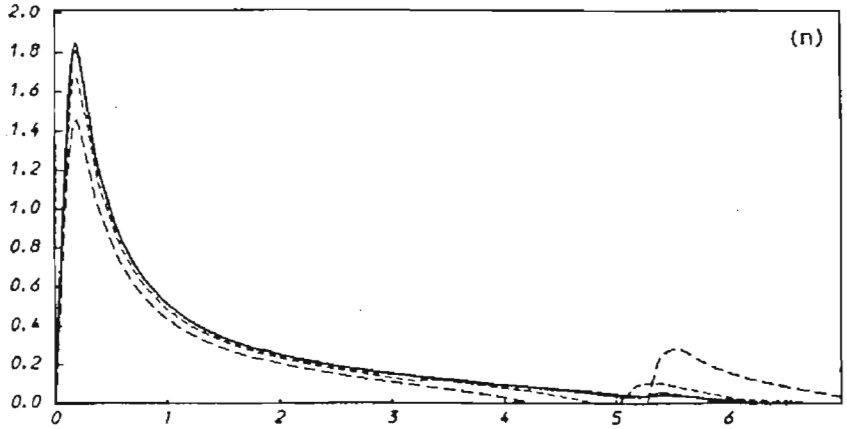

5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
(i)


COSEN 2 TETA AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0
1
2
3
4
5
6
(j)


1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6
(k)


4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
(l)


COSEN 3 TETA AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
(m)


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6
(n)

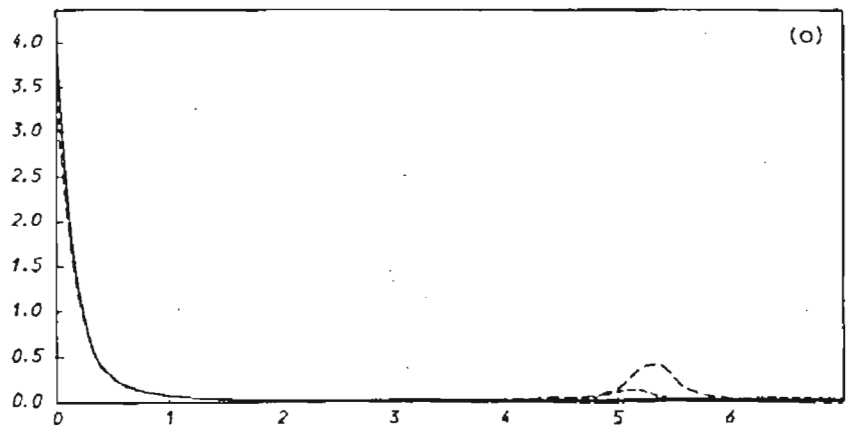

4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
(o)

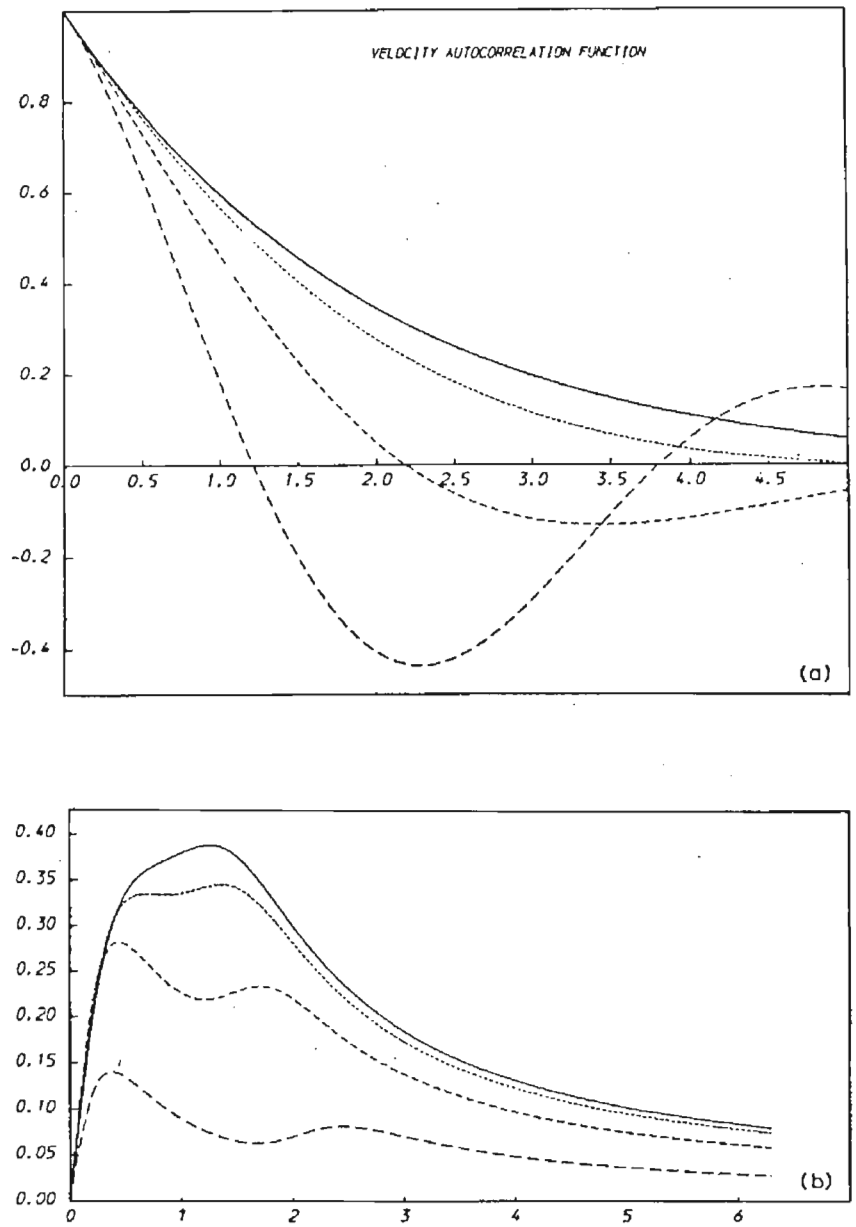
FIGURE 2 Intermediate damping, as for figure 1.

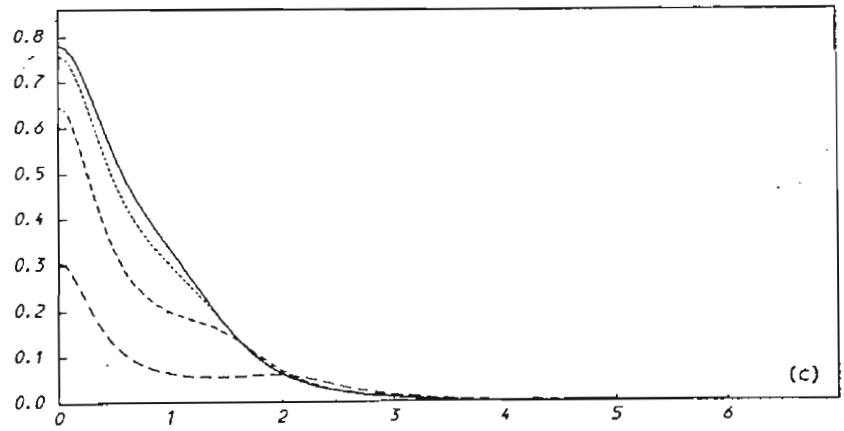
$\beta = 0.5$ $d = 0.25$

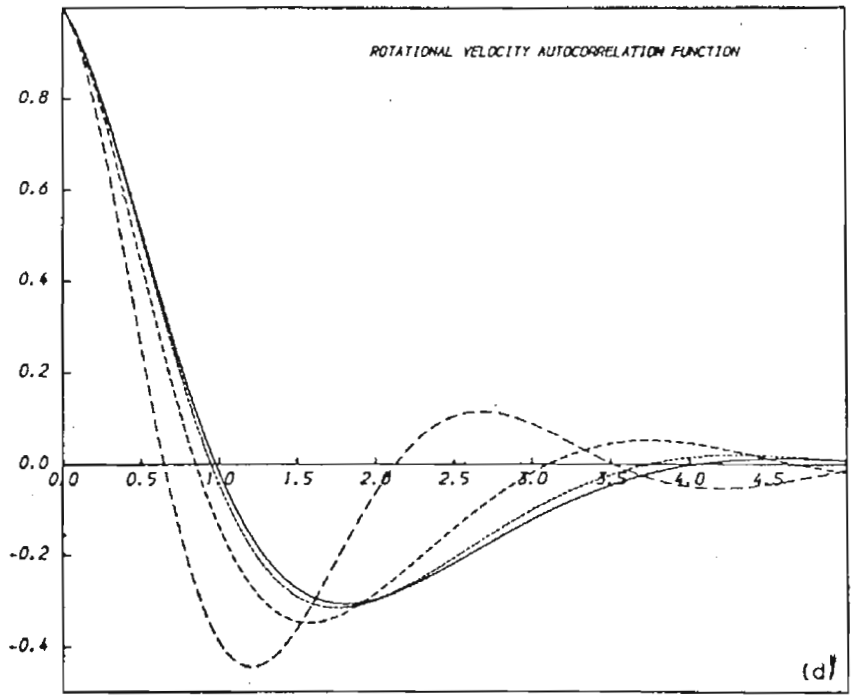
$d = 0.5$

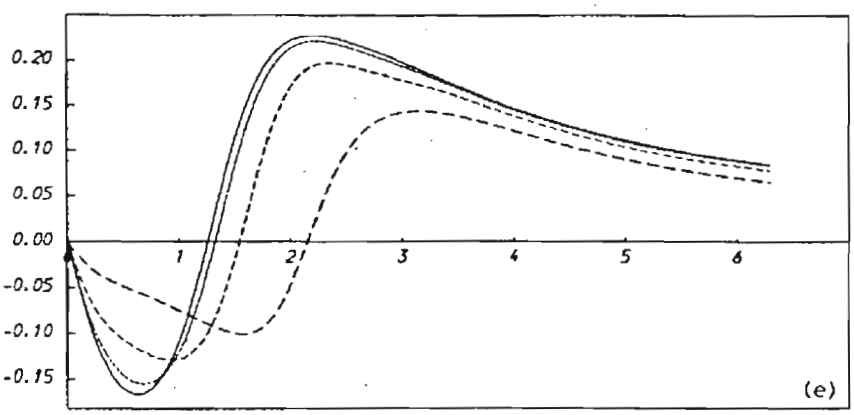
$d = 1.0$

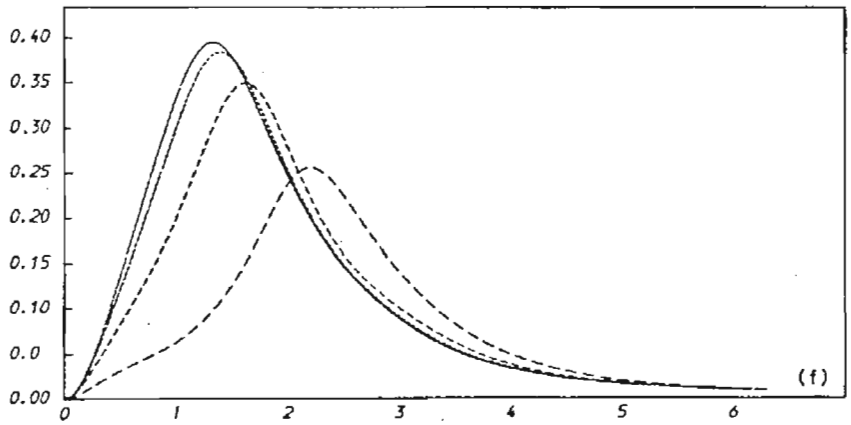
$d = 2.0$

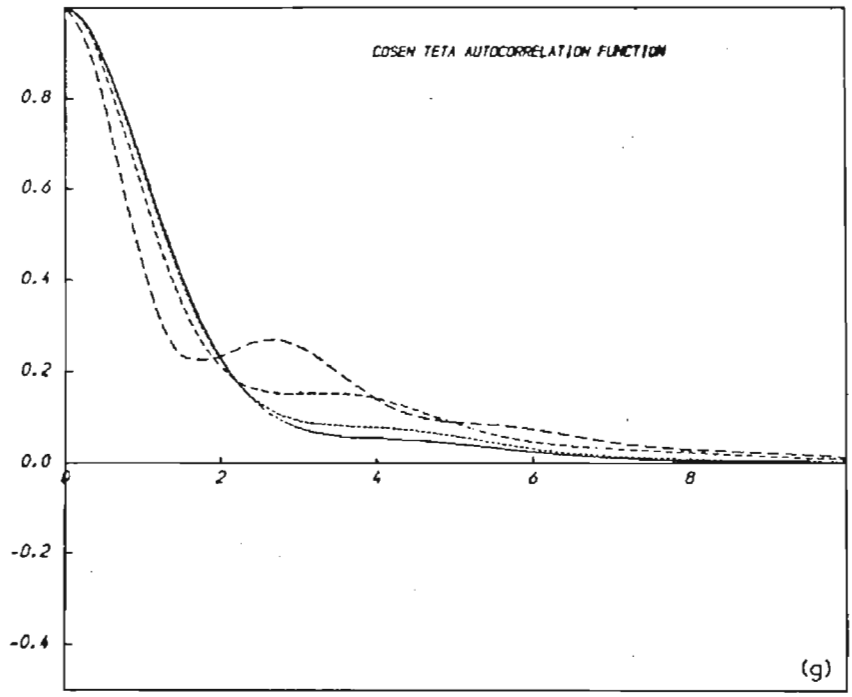


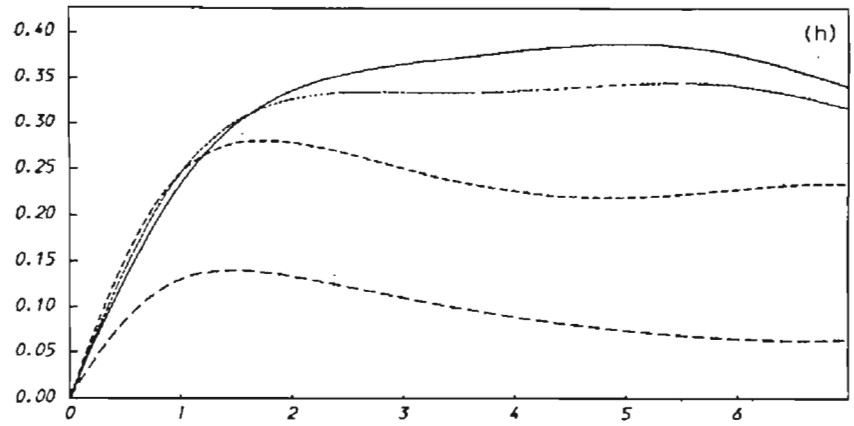

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6
(c)

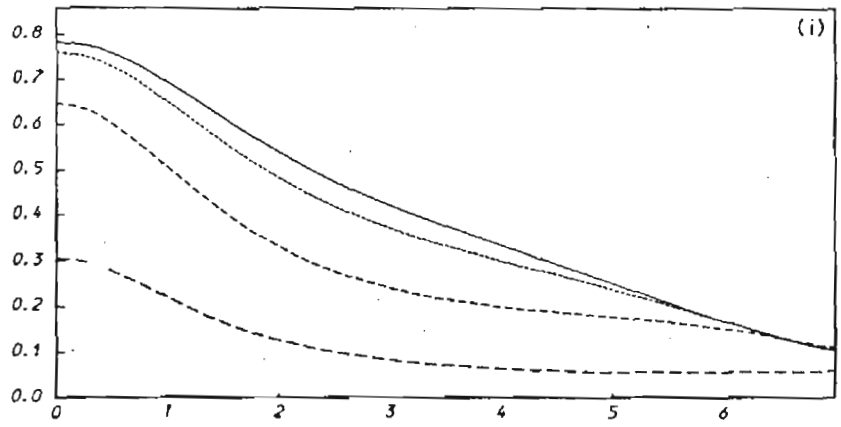

ROTATIONAL VELOCITY AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
(d)

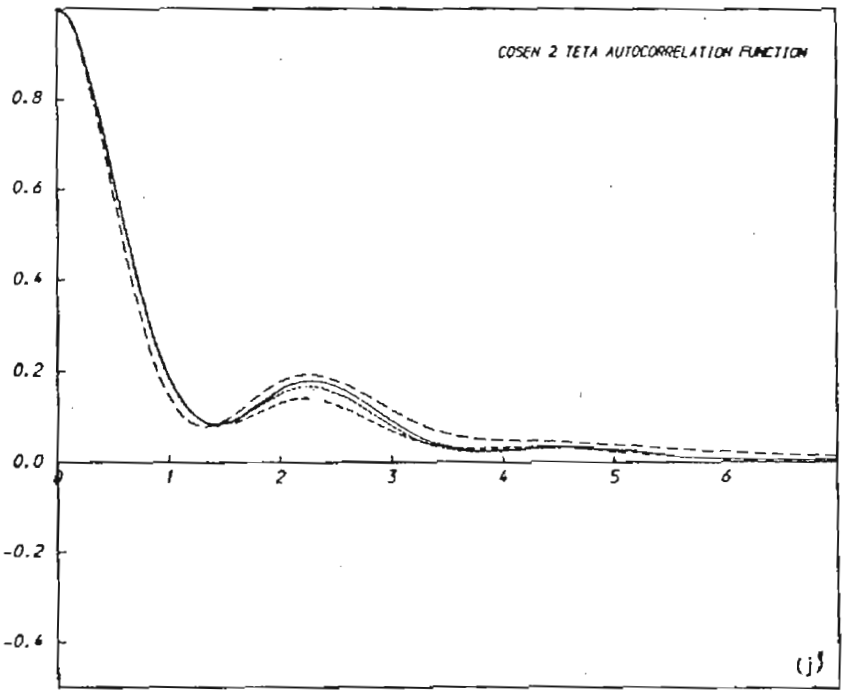

0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
1
2
3
4
5
6
(e)

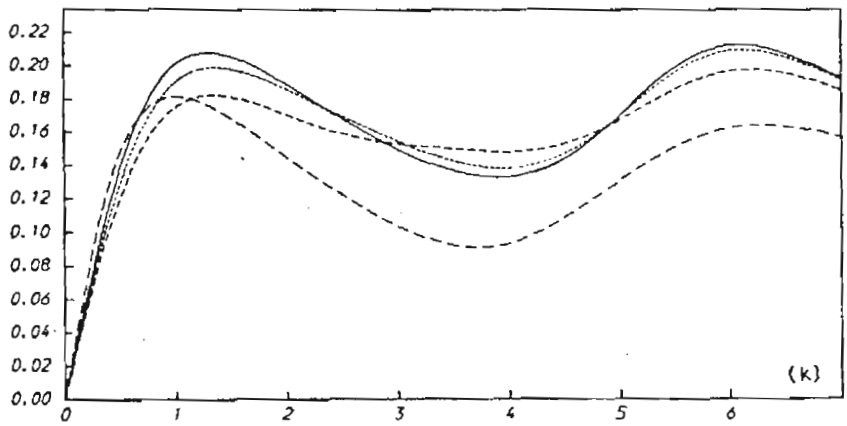

0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.0
0.00
0
1
2
3
4
5
6
(f)

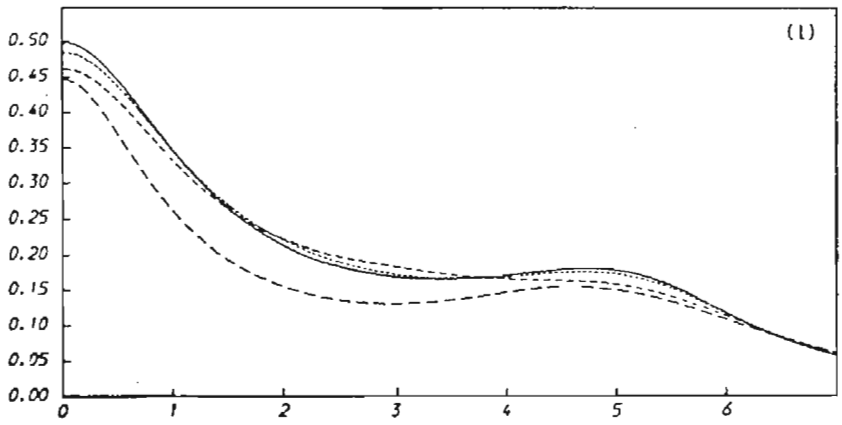

COSEN TETA AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0
2
4
6
8
(g)

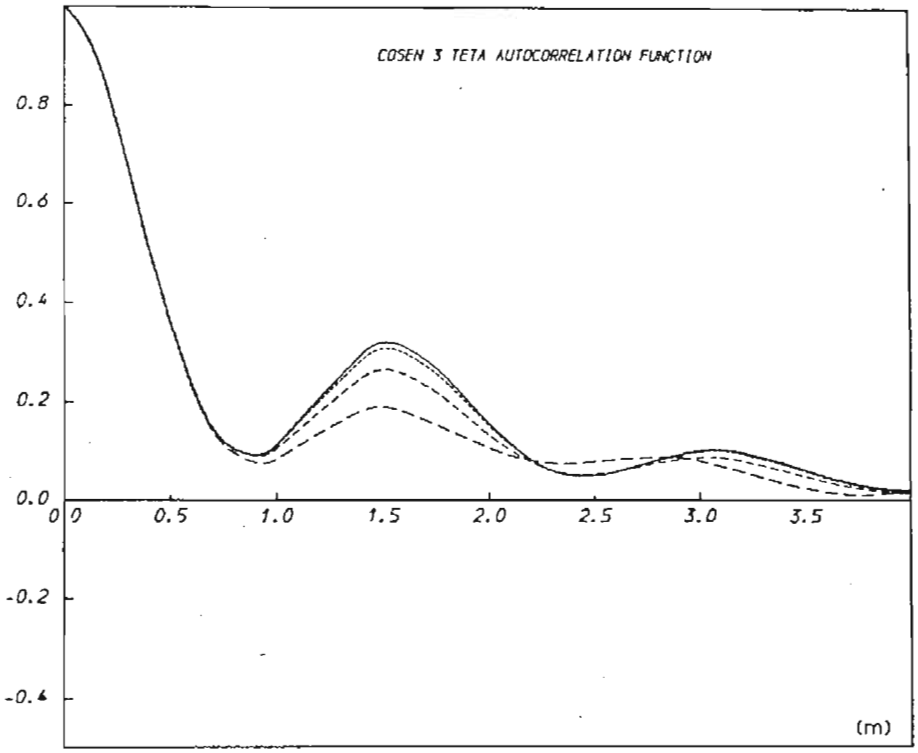

0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
(h)

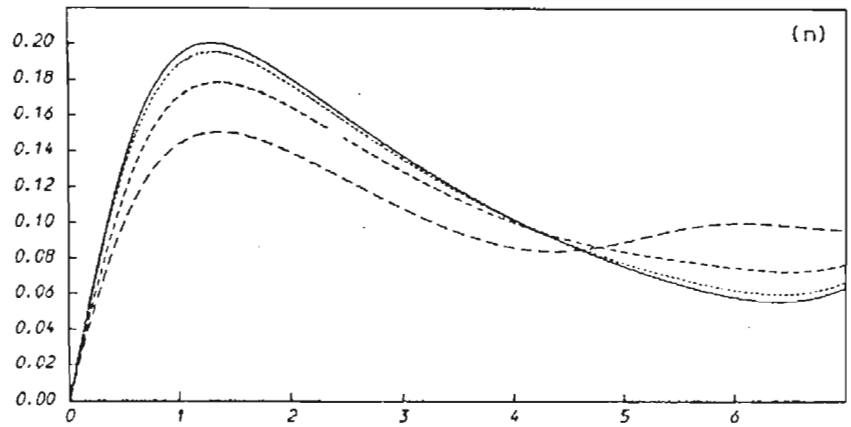

(i)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6

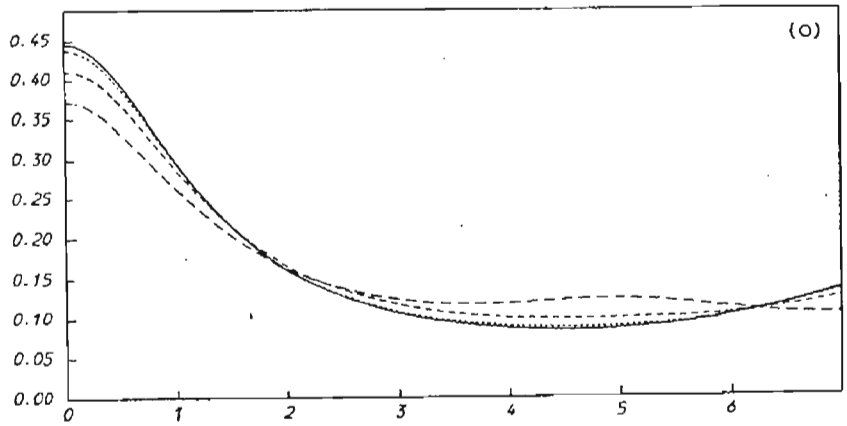

COSEN 2 TETA AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0
1
2
3
4
5
6
(j)


0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
1
2
3
4
5
6
(k)


(l)
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6


COSEN 3 TETA AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
(m)


(n)
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
1
2
3
4
5
6

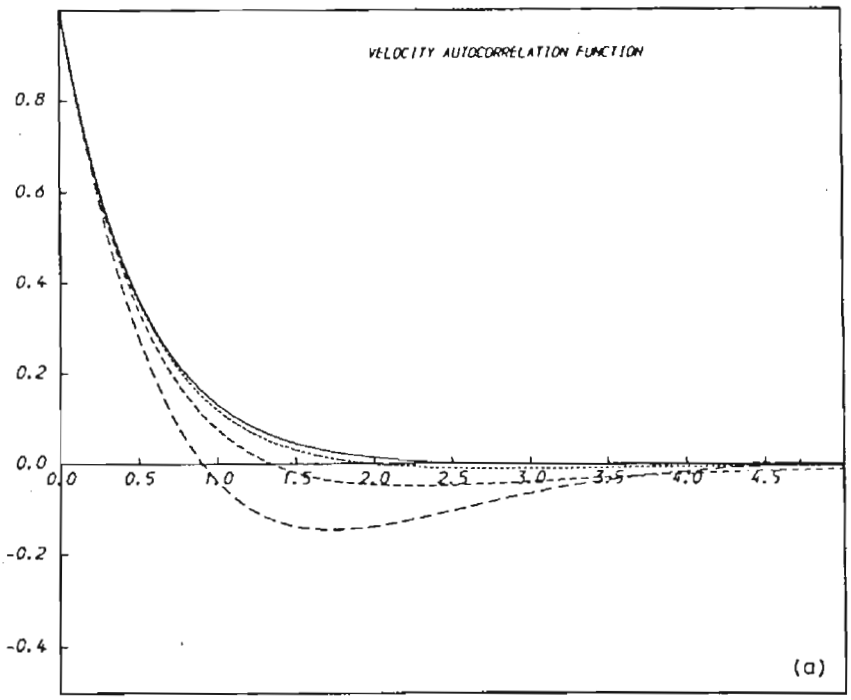


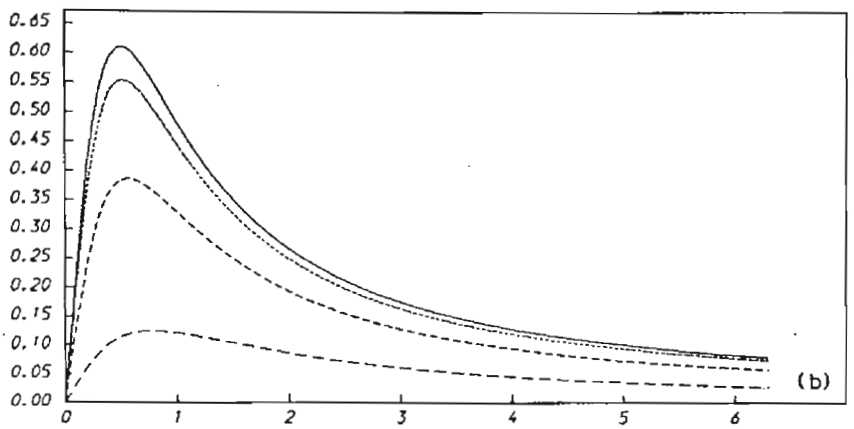
delta function off-diagonal elements. The initial behaviour of the velocity or angular velocity correlation function from this model is also $1 - \beta_2 t + O(t^2)$, i.e. only in the case $\beta_2 = o$ do we recover the correct initial behaviour. This is when the model reduces to the version first derived in Mori continued fraction form by Evans [8(1)].

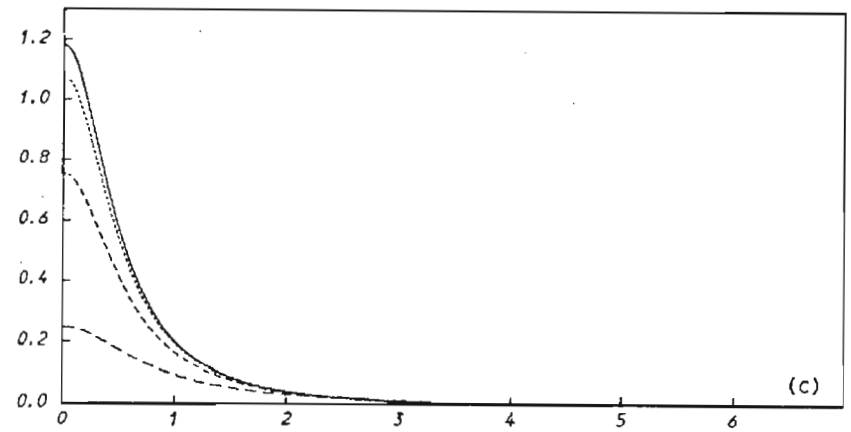
Both the models considered here are therefore fundamentally flawed except in the case $\beta_2 = o$ for the second. It is surprising therefore that the Kramers/Fokker/Planck equation on which they are based continues to be used uncritically in much of the physical literature [7] as the starting point for the description of phenomena connected with, for example, Josephson tunnelling, superconduction and second-order phase loop analysis in laser technology.

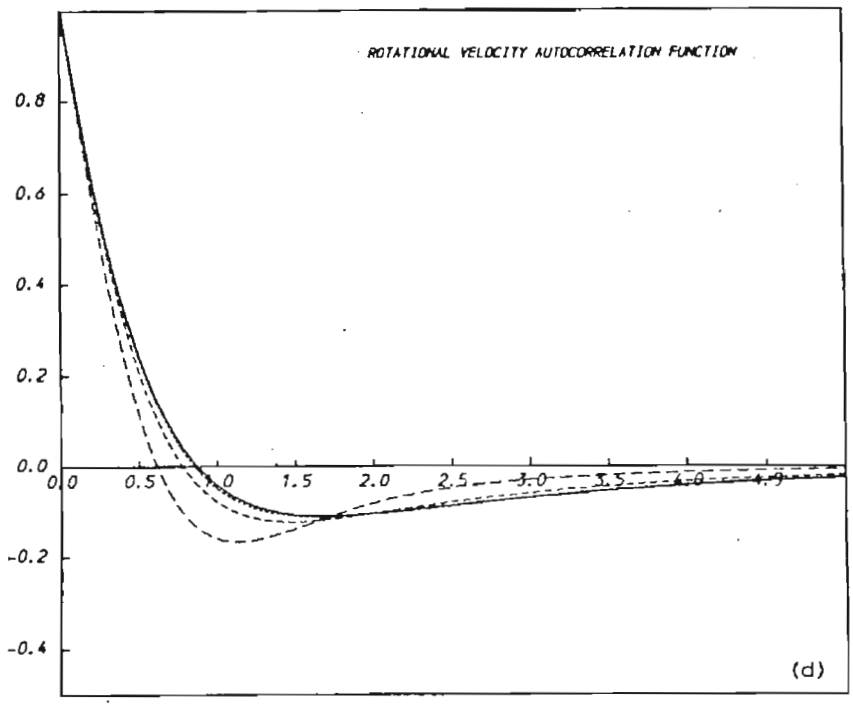
We have already revealed the mathematical limitations of the Kramers equations, but in physical terms the most incisive experimental technique in this context is that of zero-THz spectroscopy of ultra-viscous and vitreous media [10]. In terms of dielectric loss the spectrum of low temperature viscous molecular solutions peaks three times (α, β and γ) over a very wide range of about twelve decades of frequency. At room temperatures the viscosity and spectral features are drastically altered. Evans equations describe the spectral features in the latter case fairly satisfactorily, but fail at high viscosities (as described elsewhere [10]) because only two loss peaks can be produced theoretically. With the more complicated case $\beta_2 \neq o$ the situation is improved by virtue of the fact that the theoretical γ peak may

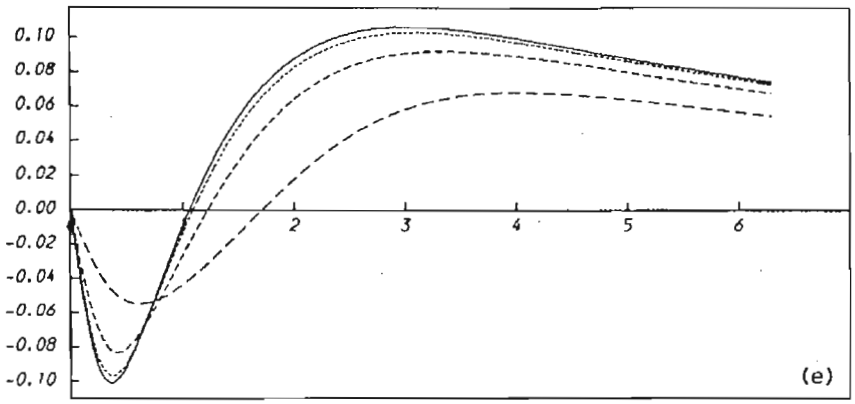
FIGURE 3 Heavily damped case, as for figure 1. $\beta = 2.0$ $d = 0.25$ $d = 0.50$ $d = 1.00$ $d = 2.00$

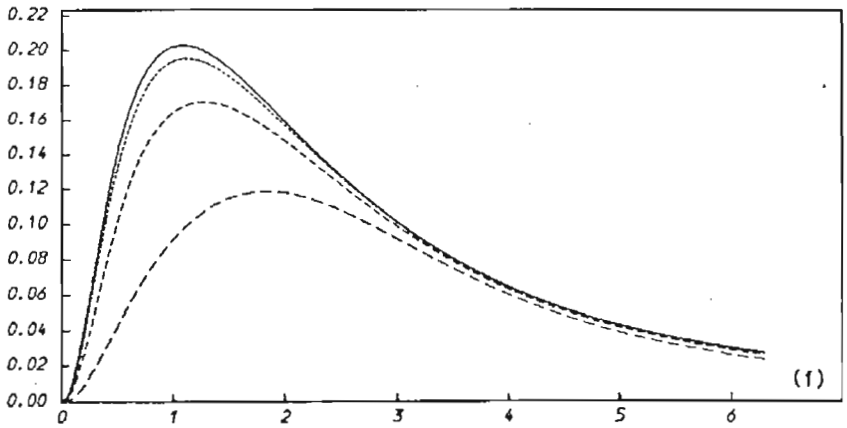


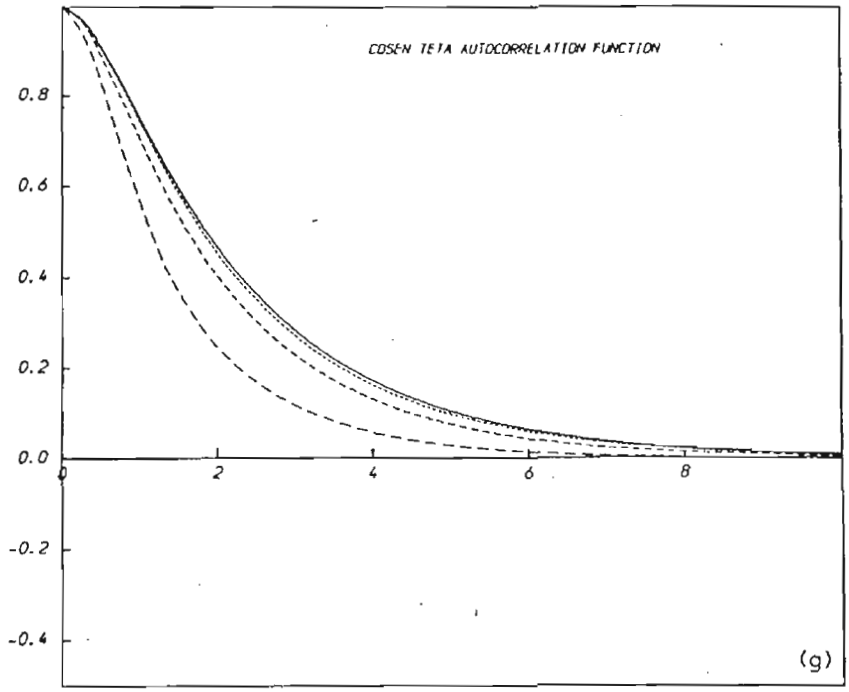


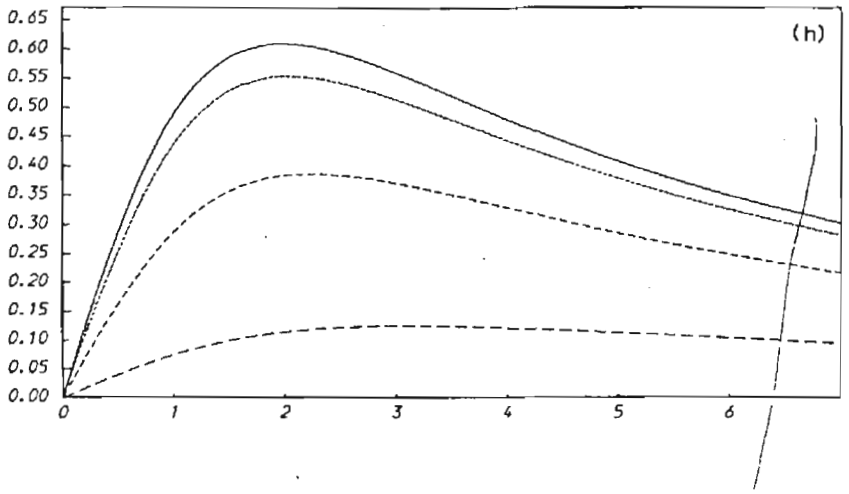


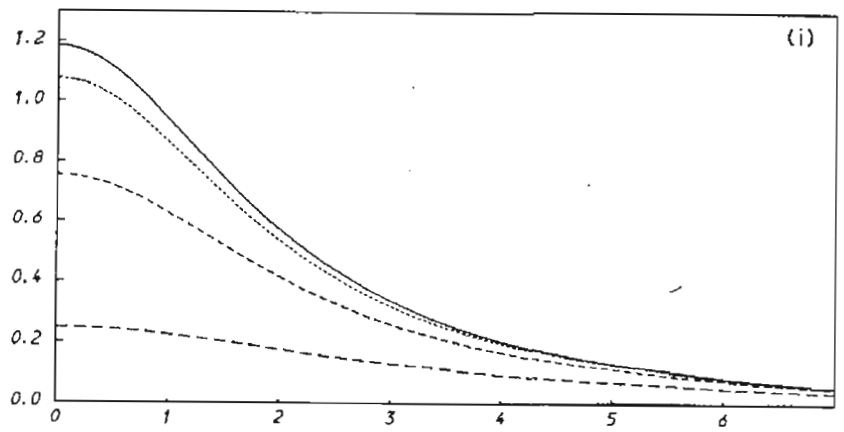

ROTATIONAL VELOCITY AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
(d)

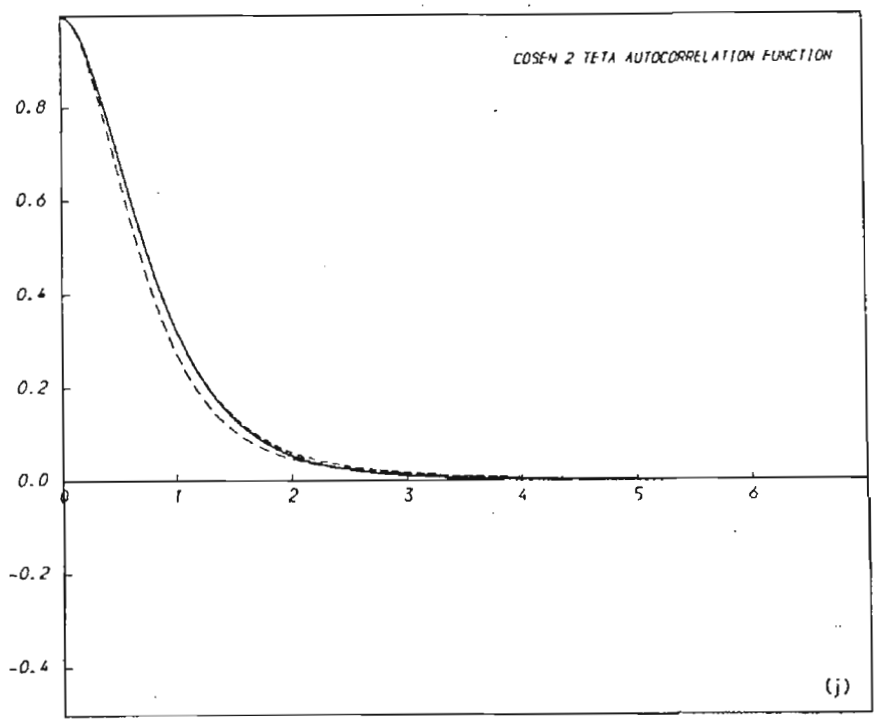

0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
2
3
4
5
6
(e)

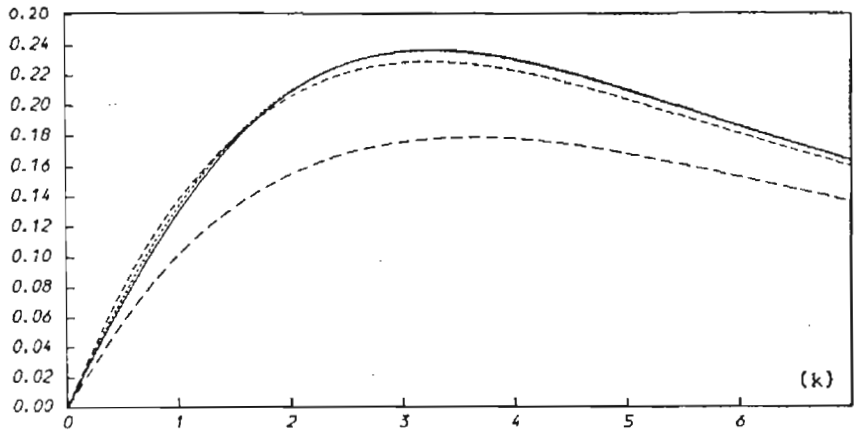

0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
1
2
3
4
5
6
(f)

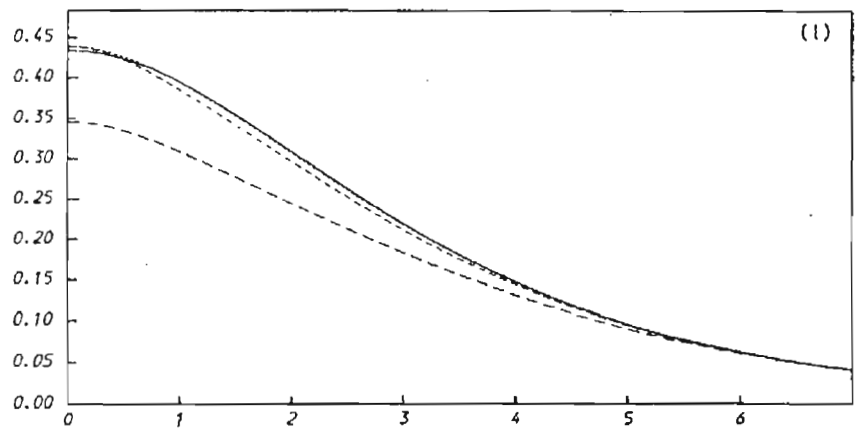

COSEN TETA AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0
2
4
6
8
(g)

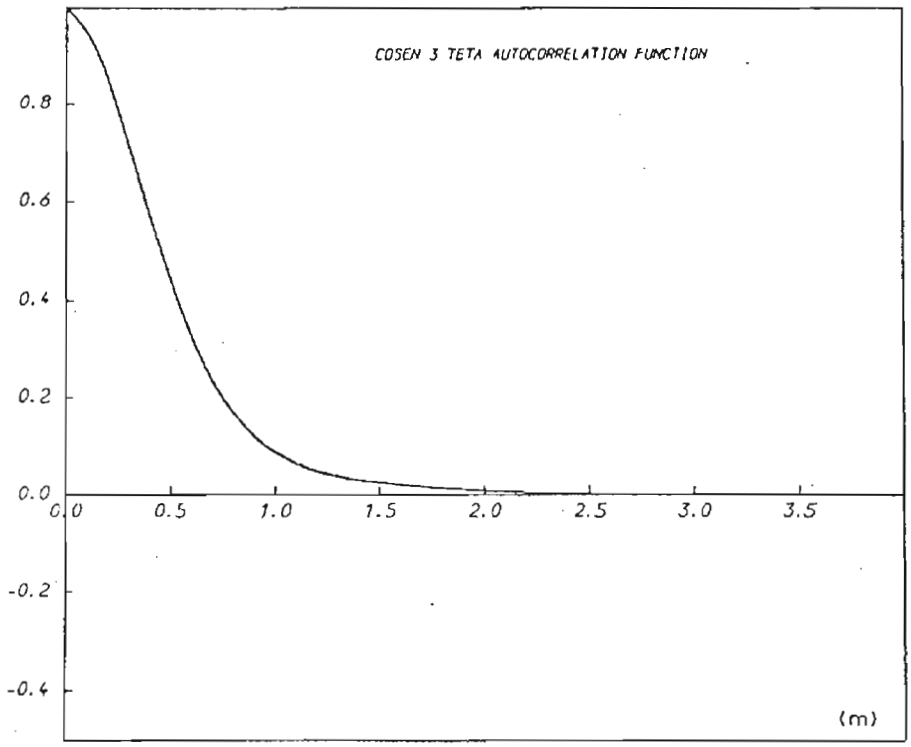

0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
(h)

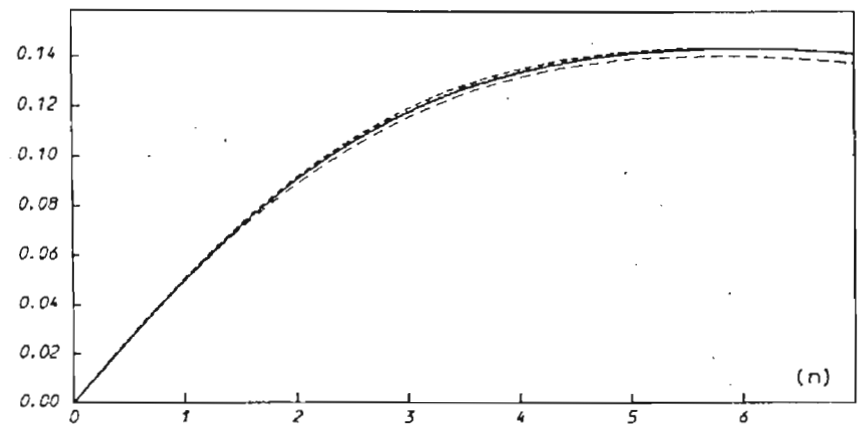

1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6
(i)

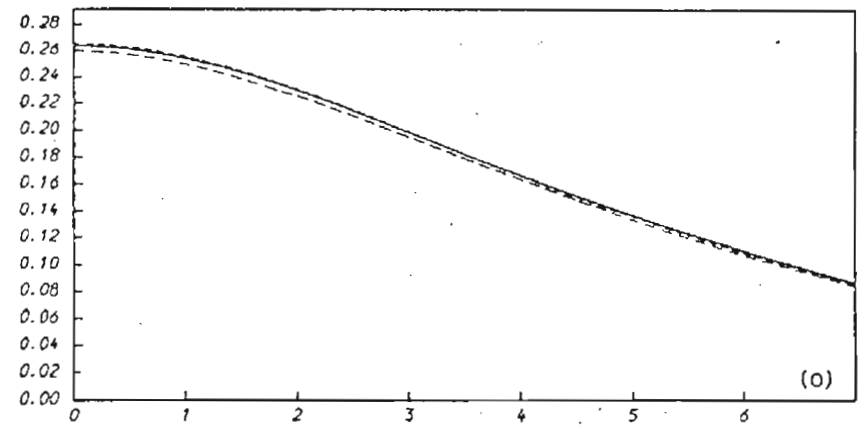

COSEN 2 TETA AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0
1
2
3
4
5
6
(j)


0.20
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
1
2
3
4
5
6
(k)


0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
(l)


COSEN 3 TETA AUTOCORRELATION FUNCTION
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
(m)


0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
1
2
3
4
5
6
(n)


0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
1
2
3
4
5
6
(o)

now be broadened, but at extreme high frequencies (around 200 cm^{-1}) the mathematical flaw at $t \to o$ manifests itself in a theoretical return to transparency which is far too slow.

To emphasize in detail the shortcomings of both models the most useful technique is to use the far infra-red power absorption coefficient ($\alpha(\omega)$/ neper cm^{-1}) of dipolar molecular liquids and solutions. This is sometimes known as the Poley absorption [1-5], but should always be considered as a version of the dielectric loss weighted by a multiplication by the angular frequency (rad sec^{-1}) and division by $n(\omega)$ the refractive index. The far infra-red range is the extreme high frequency limit of a spectrum extending to static whose shape represents a molecular dynamical evolution extending from ps onwards.

In conclusion, therefore, we see clearly by numerical analysis that the form of potential used in FPK equations is irrelevant in the description of zero-THz spectra when the underlying mathematical structure is imperfect (i.e. based on naive concepts of the molecular dynamics). The Kramers Fokker-Planck equation of the type considered here succeeds in describing results in other branches of physics only because the data available on these phenomena do not cover a wide enough range of conditions.

Suggested improvements may be listed as follows:

(i) The Fokker-Planck-Kramers equations should be given a memory function other than a delta function. This would rectify the incorrect behaviour as $t \to o$.

(ii) Increased effots should be made to coordinate the research in fields where these equations are used as starting points with the results of molecular dynamics simulations and broad-band spectroscopy.

(iii) Until memory and inertial effects are involved properly these equations cannot be useful in discriminating between forms of the inter-molecular potential. Only then will it be possible to progress from such crudities as harmonic cosine forms, chosen only for reasons of analytical tractability.

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