EFFECTIVE DIELECTRIC RELAXATION TIMES FOR THE TWO DIMENSIONAL ROTATIONAL BROWNIAN MOTION IN *N*-FOLD COSINE POTENTIALS

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ABSTRACT

Effective eigenvalue method is applied to obtain closed form expressions for the effective relaxation times of the two dimensional rotational Brownian motion in N-fold Cosine potentials. The expressions obtained are valid for any potential of the form CosNθ.

INTRODUCTION

A comprehensive numerical study of the rotational Brownian motion of the two dimensional rotator in *N*-fold cosine potentials in both time and frequency domains has been given by Reid [1] with particular reference to the behaviour of the dielectric dispersion and absorption spectra. The analysis was based on the Fokker-Planck equation approach. Reid [1] compares the spectra computed from the model with those obtained from experimental observations of rotator-phase furan and CH_2Cl_2. There is reasonable agreement with experiment. Further he finds that, unlike the free rotator or the harmonic potential version, this model can reproduce both relaxation and resonant behaviour when inertial effects are included. This is due to the use of a periodic potential rather than a parabolic potential. Such a potential allows the flipping of rotators to neighbouring wells, thus permitting both relaxation and oscillatory behaviour [1] in the same model. Such a model has also been studied (also in the non-inertial limit) by Lauritzen and Zwanzig [2] in connection with site models of dielectric relaxation in molecular crystals.

In this paper the effective eigenvalue method is applied to this model to obtain general longitudinal and transverse relaxation times in the non-inertial limit. We shall consider the rotational Brownian motion of a two dimensional rotator with dipole moment μ in the *N*-fold cosine potential

$$V(\theta) = -V_o \cos N\theta \tag{1}$$

in the context of the Langevin equation. θ is the angle between the dipole vector μ and the z-axis. (See Figure 1)

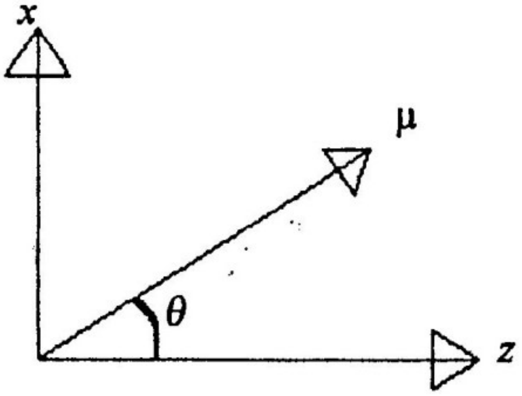

Figure. 1

The quantities of interest are the longitudinal and transverse effective relaxation times $\tau_{||}$ and $\tau_{\perp}$ respectively.

THE LANGEVIN EQUATION FOR ROTATION IN TWO DIMENSIONS: APPLICATION TO THE DIELECTRIC RELAXATION OF AN ASSEMBLY OF TWO DIMENSIONAL ROTATORS

The Langevin equation for a dipole μ to rotate about an axis normal to the xy plane is [1,3]

$$I\ddot{\theta}(t)+\varsigma\dot{\theta}(t)+NV_{0}\sin N\theta(t)+\mu(t)F(t)\sin\theta(t)=\lambda(t) \qquad (2)$$

In Eq. (2), I is the moment of inertia of the rotator about the axis of rotation, θ is the angle the rotator makes with the direction of the driving field $F(t)$, $\varsigma(\dot{\theta})$ and $\lambda(t)$ are the frictional and white noise torques due to the Brownian motion. It is assumed that the random torque $\lambda(t)$ has the property

$$\overline{\lambda(t)} = 0, \quad \overline{\lambda(t)\lambda(t')} = 2\varsigma kT\delta(t-t') \tag{3}$$

kT is the thermal energy with k the Boltzmann constant and T the absolute temperature. The overbar indicates statistical average. $\delta(t)$ is the Dirac delta function

$$\delta(t-t') = \begin{cases} \infty \; if \; t = t' \\ 0 \; otherwise \end{cases} \tag{4}$$

In order to specialise Eq. (2) to a step-on field we write

$$\mathbf{F}(t) = \mathbf{F}_0 U(t) \tag{5}$$

where $U(t)$ is the unit step function and $\mathbf{F}_o$ is its amplitude. We require to calculate, for this model, the statistical averages $\langle \mu \cos\theta \rangle$ and $\langle \mu \sin\theta \rangle$ when the inertial effects are ignored.

The problem which presents itself when treating the model using the Langevin equation in the form of Eq. (2) is that it is not apparent how that equation may be linearized to yield the solution for small $\mu F_0 / kT$. This difficulty may be circumvented by rewriting Eq. (2) as an equation of motion for instantaneous dipole moment

$$p = \mu \cos\theta \tag{6}$$

so that

$$\dot{\theta} = -\dot{p}(\mu^2 - p^2)^{-\frac{1}{2}} = -\dot{p}(\mu \sin\theta)^{-1} \tag{7}$$

and

$$\ddot{\theta} = -\ddot{p}(\mu \sin\theta)^{-1} - \dot{\theta}^2 \; p(\mu \sin\theta)^{-1} \tag{8}$$

The Langevin equation (2) with the field $\mathbf{F}$ applied along the z-axis and this change of variable becomes

$$I\frac{d^2}{dt^2}\cos\theta(t)+\varsigma\frac{d}{dt}\cos\theta(t)+I\dot{\theta}^2(t)\cos\theta(t)+\frac{NV_o}{2}[\cos(N+1)\theta(t)-\cos(N-1)\theta(t)]$$

$$=\mu F_o U(t)(1-\cos^2\theta(t))-\sin\theta(t)\lambda(t) \tag{9}$$

which is the Langevin equation for the motion of the instantaneous dipole moment. To solve it we first form its statistical average over a large number of rotators to obtain

$$I\frac{d^2}{dt^2}\langle\cos\theta\rangle+\varsigma\frac{d}{dt}\langle\cos\theta\rangle+\left\langle I\dot{\theta}^2\cos\theta\right\rangle+\frac{NV_o}{2}[\langle\cos(N+1)\theta\rangle-\langle\cos(N-1)\theta\rangle]$$

$$=\mu F_o U(t)(1-\left\langle\cos^2\theta\right\rangle) \tag{10}$$

We remark that $\theta(t)$ in Eq. (9) and θ in Eq. (10) have different meanings. $\theta(t)$ in Eq. (9) is a stochastic variable while in Eq. (10) θ is the sharp (definite) value $\theta(t)=\theta$ at time t. (Instead of using different symbols for the two quantities we have distinguished the sharp values at time t from the stochastic variables by deleting the time argument). However the quantity θ is itself a random variable which must be averaged over an ensemble of rotators. The symbol $\langle\ \rangle$ means such an ensemble average. We also note that Eq. (10) may be written as

$$I\frac{d^2}{dt^2}\langle\cos\theta\rangle+\varsigma\frac{d}{dt}\langle\cos\theta\rangle+\left\langle I\dot{\theta}^2\cos\theta\right\rangle+\frac{NV_o}{2}[\langle\cos(N+1)\theta\rangle-\langle\cos(N-1)\theta\rangle]$$

$$=\frac{1}{2}\mu F_o U(t)(1-\langle\cos 2\theta\rangle) \tag{11}$$

We note that when the field $\mathbf{F}$ is applied along the x-axis the quantity of interest $q=\mu\sin\theta(t)$ obeys the similar equation

$$I\frac{d^2}{dt^2}\langle\sin\theta\rangle+\varsigma\frac{d}{dt}\langle\sin\theta\rangle+\left\langle I\dot{\theta}^2\sin\theta\right\rangle+\frac{NV_o}{2}[\langle\sin(N+1)\theta\rangle-\langle\sin(N-1)\theta\rangle]$$

$$=\mu F_o U(t)(1-\left\langle\sin^2\theta\right\rangle) \tag{12}$$

The remaining terms in Eqs. (11) and (12) which cause difficulty are

$$\langle I\dot{\theta}^2 \sin\theta\rangle \text{ and } \langle I\dot{\theta}^2 \cos\theta\rangle \qquad (13)$$

Since the non-inertial response (Debye theory) pertains to the situation where

$$t >> I/\varsigma \qquad (14)$$

which implicitly means [4] that a Maxwellian distribution of angular velocities has been achieved, we may now write

$$\langle I\dot{\theta}^2 \cos\theta\rangle = kT\langle\cos\theta\rangle \qquad (15)$$

and

$$\langle I\dot{\theta}^2 \sin\theta\rangle = kT\langle\sin\theta\rangle \qquad (16)$$

since the orientation and the angular velocity variables, when equilibrium of the angular velocities has been reached, are decoupled from each other, as far as the time behaviour of the orientations is concerned [5]. In the non-inertial limit we set

$$I\langle\ddot{p}\rangle = 0 \qquad (17)$$

in Eqs. (11) and (12), so that finally

$$\frac{d}{dt}\langle\cos\theta\rangle + \frac{kT}{\varsigma}\langle\cos\theta\rangle = \frac{NV_o}{2\varsigma}[\langle\cos(N-1)\theta\rangle - \langle\cos(N+1)\theta\rangle]$$
$$+\frac{1}{2\varsigma}\mu F_o U(t)(1-\langle\cos 2\theta\rangle) \qquad (18)$$

and

$$\frac{d}{dt}\langle\sin\theta\rangle + \frac{kT}{\varsigma}\langle\sin\theta\rangle = \frac{NV_o}{2\varsigma}[\langle\sin(N-1)\theta\rangle - \langle\sin(N+1)\theta\rangle]$$
$$+\frac{1}{\varsigma}\mu F_o U(t)(1-\langle\sin^2\theta\rangle) \qquad (19)$$

GENERAL EXPRESSIONS FOR THE LONGITUDINAL AND TRANSVERSE EFFECTIVE RELAXATION TIMES

Eqs. (18) and (19) are the first terms in the infinite hierarchy of differential-difference equations, which describe the ensemble averages $\langle\cos n\theta\rangle$ and $\langle\sin n\theta\rangle$. We have mentioned in the previous chapter that the standard approach to the calculation of the longitudinal and transverse relaxation times is accomplished by rewriting the infinite hierarchy as a set of ordinary differential equations of the form

$$\dot{\mathbf{X}} = \mathbf{AX} + \mathbf{BU}(t) \tag{20}$$

where $\mathbf{A}$ is the transition matrix and $\mathbf{B}$ is the driving force matrix, and truncating at a given size of $\mathbf{A}$. The longest relaxation time is then the reciprocal of the lowest root of the characteristic equation

$$\det\{s\mathbf{I} - \mathbf{A}\} = 0 \tag{21}$$

where s denotes the complex frequency.

The disadvantage of this method is that it is in general, impossible to obtain a closed form expression for the longest relaxation time. This difficulty may be circumvented by means of the effective eigenvalue method.

We first consider the parallel equation of motion, namely Eq. (18) and recall that the field F_0 has been applied for a long time and that we are only interested in the response linear in $\mathbf{F}$. We therefore assume that in Eq. (18)

$$\langle\cos n\theta\rangle = \langle\cos n\theta\rangle_{eq} + \langle\cos n\theta\rangle_1 \tag{22}$$

where the subscript eq denotes the equilibrium ensemble average in the absence of a perturbing constant field $\mathbf{F}$ and the subscript 1 denotes the portion of the ensemble average which is linear in $\mathbf{F}$. On substituting this equation into Eq. (18) we find that $\langle\cos n\theta\rangle_1$ satisfies

$$\frac{d}{dt}\langle\cos\theta\rangle_1 + \frac{kT}{\varsigma}\langle\cos\theta\rangle_1 = \frac{NV_o}{2\varsigma}[\langle\cos(N-1)\theta\rangle_1 - \langle\cos(N+1)\theta\rangle_1]$$

$$+\frac{1}{2\varsigma}\mu F_o U(t)(1-\langle\cos 2\theta\rangle_0) \tag{23}$$

In the last term of Eq. (23), the ensemble average is taken as that in the absence of **F**. This is because this term is multiplied by $F_0 U$ thus making it comparable to the other terms in the equation.

Eq. (23) represents a recurrence relation driven by a forcing function, namely the $U(t)$ term. In order to determine the effective eigenvalues we consider the unforced equation, namely

$$\frac{d}{dt}\langle\cos\theta\rangle_1 + \frac{kT}{\varsigma}\langle\cos\theta\rangle_1 = \frac{NV_0}{2\varsigma}[\langle\cos(N-1)\theta\rangle_1 - \langle\cos(N+1)\theta\rangle_1]$$

Following the discussions of Coffey et. al. [6] the effective relaxation time is defined as

$$\tau_{ef} = \frac{1}{\lambda_{ef}} \tag{24}$$

where

$$\lambda_{ef} = -\frac{\left\langle\dot{A}(0)\right\rangle}{\langle A(0)\rangle} \tag{25}$$

is the effective eigenvalue. $A(t)$ is any given quantity.

Whence the effective eigenvalue method leads to

$$\lambda_{ef}^{||} = -\frac{\frac{d}{dt}\langle\cos\theta\rangle_1}{\langle\cos\theta\rangle_1}$$

$$= \frac{\frac{kT}{\varsigma}\langle\cos\ \theta\rangle_1 + \frac{NV_0}{2\varsigma}\left[\langle\cos(N+1)\theta\rangle_1 - \langle\cos(N-1)\theta\rangle_1\right]}{\langle\cos\ \theta\rangle_1} \tag{26}$$

We now have at $t = 0$

$$\langle\cos\ \theta\rangle_1 = \langle\cos\ \theta\rangle_0 - \langle\cos\ \theta\rangle_{eq} \tag{27}$$

At equilibrium

$$\langle\cos\theta\rangle_{eq} = \frac{\int_0^{2\pi}\cos\theta e^{(V_o\cos N\theta + \mu F_o\cos\theta)/kT}d\theta}{\int_0^{2\pi}e^{(V_o\cos N\theta + \mu F_0\cos\theta)/kT}d\theta}$$

$$\cong \frac{\int_o^{2\pi}\cos\theta e^{(V_o\cos\theta)/kT}\left[1 + \frac{\mu F_0}{kT}\cos\theta + 0(\frac{\mu F_0}{kT})^2\right]d\theta}{\int_0^{2\pi}e^{(V_o\cos N\theta)/kT}\left[1 + \frac{\mu F_0}{kT}\cos\theta + 0(\frac{\mu F_0}{kT})^2\right]d\theta}$$

$$= \frac{\langle \cos\theta\rangle_0 + \frac{\mu F_0}{kT}\langle \cos^2\theta\rangle_0}{1+\frac{\mu F_0}{kT}\langle \cos\theta\rangle_0} \tag{28}$$

On using the approximation $(1+x)^{-1} \cong 1 - x + O(x^2)$ for the linear response we get

$$\langle \cos\theta\rangle_{eq} \cong \langle \cos\theta\rangle_0 + \frac{\mu F_0}{kT}\left| \langle \cos^2\theta\rangle_0 - \langle \cos\theta\rangle_0^2 \right|$$

$$= \langle \cos\theta\rangle_0 + \frac{\mu F_0}{kT}\left| 1 + \langle \cos 2\theta\rangle_0 - 2\langle \cos\theta\rangle_0^2 \right|. \tag{29}$$

Further at $t = 0$

$$\begin{aligned} &\frac{NV_o}{2}[\langle\cos(N+1)\theta\rangle_1 - \langle\cos(N-1)\theta\rangle_1] \\ &= \frac{NV_o}{2}[\langle\cos(N+1)\theta\rangle_0 - \langle\cos(N-1)\theta\rangle_0] - \frac{NV_o}{2}[\langle\cos(N+1)\theta\rangle_{eq} - \langle\cos(N-1)\theta\rangle_{eq}] \\ &= -NV_0[\langle\sin N\theta \sin\theta\rangle_0 - \langle\sin N\theta\sin\theta\rangle_{eq}] \end{aligned} \tag{30}$$

At equilibrium we have

$$NV_0\langle \sin N\theta \sin\theta\rangle = NV_0 \frac{\int_0^{2\pi} \sin N\theta \sin\theta\, e^{(V_o \cos N\theta + \mu F_o \cos\theta)/kT}\, d\theta}{\int_0^{2\pi} e^{(V_o \cos N\theta + \mu F_o \cos\theta)/kT}\, d\theta}$$

$$\cong NV_0 \frac{\int_0^{2\pi} \sin N\theta \sin\theta e^{(V_o \cos N\theta)/kT}[1+\frac{\mu F_o}{kT}\cos\theta + O(\frac{\mu F_o}{kT})^2]d\theta}{\int_0^{2\pi} e^{(V_o \cos N\theta)/kT}[1+\frac{\mu F_o}{kT}\cos\theta + O(\frac{\mu F_o}{kT})^2]d\theta}$$

$$= \frac{NV_0\left[\langle \sin N\theta \sin\theta\rangle_0 + \frac{\mu F_o}{kT}\langle \sin N\theta \sin\theta\cos\theta\rangle_0\right]}{[1+\frac{\mu F_o}{kT}\langle\cos\theta\rangle_0]}$$

$$\cong NV_0\langle \sin N\theta \sin\theta\rangle_0 + \frac{NV_0\mu F_o}{kT}\left\langle \sin N\theta \sin\theta(\cos\theta - \langle\cos\theta\rangle_0)\right\rangle_0 \qquad (31)$$

The last term on the right hand side of Eq. (31) can be simplified as follows:

$$\frac{NV_0}{kT}\langle \sin N\theta \sin\theta(\cos\theta - \langle\cos\theta\rangle_0)\rangle = \frac{\mu F_0}{2kT}\langle(\sin 2\theta - 2\sin\theta\langle\cos\theta\rangle_0)\frac{\partial}{\partial\theta}V(\theta)\rangle_0 .$$

Now

$$\left\langle \sin 2\theta \frac{\partial}{\partial\theta}V(\theta)\right\rangle_0 = \frac{\int_0^{2\pi} \sin 2\theta \frac{\partial}{\partial\theta}V(\theta)e^{(V_0 \cos N\theta)/kT}d\theta}{\int_0^{2\pi} e^{(V_0 \cos N\theta)/kT}d\theta}$$

$$= kT\frac{\int_0^{2\pi} \sin 2\theta d e^{(V_0 \cos N\theta)/kT})}{\int_0^{2\pi} e^{(V_0 \cos N\theta)/kT}d\theta}$$

$$= \frac{kT\sin 2\theta e^{(V_0\cos N\theta)/kT}\Big|_0^{2\pi} + \frac{kT}{2}\int_0^{2\pi}\cos 2\theta e^{(V_0\cos N\theta)/kT})d\theta}{\int_0^{2\pi} e^{(V_0\cos N\theta)/kT}d\theta}$$

$$= \frac{kT}{2}\langle\cos 2\theta\rangle_0 \tag{32}$$

Similarly

$$\langle 2\sin\theta\langle\cos\theta\rangle_0 \frac{\partial}{\partial\theta}V(\theta)\rangle_0 = 2kT\,\langle\cos\theta\rangle_0^2.$$

Thus taking account of Eqs. (29)-(32) we obtain

$$\lambda_{ef}^{||} = \frac{kT}{\varsigma} - \frac{2kT}{\varsigma}\frac{\langle\cos 2\theta\rangle_0 - \langle\cos\theta\rangle_0^2}{1+\langle\cos 2\theta\rangle_0 - 2\langle\cos\theta\rangle_0}$$

$$= \frac{kT}{\varsigma}\frac{1-\langle\cos 2\theta\rangle_0}{1+\langle\cos 2\theta\rangle_0 - 2\langle\cos\theta\rangle_0^2} \tag{33}$$

so that the effective longitudinal relaxation time $\tau_{ef}^{||} = \left(\lambda_{ef}^{||}\right)^{-1}$ is given by

$$\tau_{ef}^{||} = \tau_D \frac{1+\langle\cos 2\theta\rangle_0 - 2\langle\cos\theta\rangle_0^2}{1-\langle\cos 2\theta\rangle_0} \tag{34}$$

where

$$\tau_D = \frac{\varsigma}{kT} \tag{35}$$

is the Debye relaxation time for planar rotators [3].

In order to calculate the transverse relaxation time $\tau_{\perp}$ we consider the same problem as above but this time the step change in the field is applied parallel to the x-axis so that we need to determine the behaviour of $\langle \mu_x \rangle$. We assume as before that

$$\langle \sin n\theta \rangle = \langle \sin n\theta \rangle_{eq} + \langle \sin n\theta \rangle_1$$

which leads to the linearized equation for $\langle \sin \theta \rangle_1$, i.e.

$$\frac{d}{dt}\langle \sin \theta \rangle_1 + \frac{kT}{\varsigma}\langle \sin \theta \rangle_1 = \frac{NV_0}{2\varsigma}\left[\langle \sin(N-1)\theta \rangle_1 - \langle \sin(N+1)\theta \rangle_1\right]$$

$$+\frac{\mu}{\varsigma}F_0 U(t)\left|1 - \langle \sin^2 \theta \rangle_0\right|. \tag{36}$$

Likewise, the eigenvalue equation is

$$\lambda_{ef}^{\perp} = \frac{\frac{kT}{\varsigma}\langle \sin \theta \rangle_1 + \frac{NV_0}{2\varsigma}\left[\langle \sin(N+1)\theta \rangle_1 - \langle \sin(N-1)\theta \rangle_1\right]}{\langle \sin \theta \rangle_1} \tag{37}$$

Noting that

$$\langle \sin \theta \rangle_0 = \frac{\int_0^{2\pi} \sin \theta e^{(V_0 \cos N\theta + \mu F_0 \cos \theta)/kT} d\theta}{\int_0^{2\pi} e^{(V_0 \cos N\theta + \mu F_0 \cos \theta)/kT} d\theta} = 0 \tag{38}$$

we obtain in the linear approximation of $\mu F_0 / kT$ that at $t = 0$

$$\langle \sin \theta \rangle_1 = -\langle \sin \theta \rangle_{eq} = -\frac{\mu F_0}{2kT}\left(1 - \langle \cos 2\theta \rangle_0\right) \tag{39}$$

and similarly

$$\frac{NV_0}{2\varsigma}\left[\langle\sin(N+1)\theta\rangle_1 - \langle\sin(N-1)\theta\rangle_1\right] = -\frac{\mu F_0}{\varsigma}\langle\cos 2\theta\rangle_0. \tag{40}$$

Thus

$$\lambda_{ef}^{\perp} = \frac{kT}{\varsigma}\frac{1+\langle\cos 2\theta\rangle_0}{1-\langle\cos 2\theta\rangle_0} \tag{41}$$

so that the effective transverse relaxation time is given by

$$\tau_{ef}^{\perp} = \tau_D \frac{1-\langle\cos 2\theta\rangle_0}{1+\langle\cos 2\theta\rangle_0}. \tag{42}$$

Eqs. (34) and (42) are the general formulae for the effective relaxation times in N-fold cosine potential. They will hold for any potential of the form $\cos N\theta$.

CONCLUSIONS

The purpose of this paper was to demonstrate how the effective eigenvalue method allied with the Langevin equation may be applied with much success to the Two-Dimensional rotational Brownian motion in N-fold cosine potential. The most noteworthy feature of the method is that it yields closed form expressions which in many cases may accurately describe the low frequency relaxation behaviour of the system in question.

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