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The itinerant oscillator model II analysis for dielectric relaxation and incoherent neutron scattering from atoms

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A model of brownian motion in a fluid or disordered solid is developed whereby cooperative motions are accounted for in the shell of nearest neighbours of a given molecule. This is mathematically tractable for the angular fluctuations in a plane of a dipole vector embedded in the asymmetric top. The Fokker–Planck–Kramers equations of motion are developed from the initial stochastic differential equations and full solutions derived in terms of multivariate probability density functions. An integro-differential representation of the same system is solved in terms of a generalized Fokker–Planck equation derived by Davies and Evans [24] and valid for a column vector of n linearly independent dynamical variables.

1. INTRODUCTION

In a recent series of articles [1–6], a model of the dynamical behaviour of a molecule in a fluid which embodies the suggestion that a typical molecule of the fluid is capable of vibration about a temporary equilibrium position [7, 8] has been developed from the original attempt at a quantitative treatment of this idea by Hill [9], Sears [10], Wyllie [11] and Larkin *et al.* [12]. The essence of the idea embodied in the model (termed an itinerant oscillator) is that a molecule may undergo rotational or translational harmonic oscillations in a potential well (caused by its cage of nearest neighbours), which itself undergoes rotational or translational brownian motion. The treatment of the model described in [1–6] explicitly assumes that the only damping and collisional forces (torques) acting on the vibrating particle representing the molecule are those which arise from the brownian movement of the cage. Here we seek, following Larkin *et al.* [12], to consider the case in which the damping and collisional forces (torques) *act on both the molecule and the cage*. We start by considering the two-dimensional rotator version of the model which is appropriate to the theory of dielectric relaxation [13] and depolarized Rayleigh scattering. It is assumed that the system consisting of the vibrating central molecule together with its cage of neighbours may be represented by an annulus which is free to rotate

about a central axis perpendicular to itself ; concentric and co-planar with the annulus is a disc which is free to rotate about the same central axis. (The words disc and annulus are used only as a convenient schematic description of the model ; *the theory will apply to a body of arbitrary shape provided its dipole is constrained to rotate in a plane.*) The analysis which follows has been detailed in [3] and here we use the notation of that paper.

When steady conditions have been reached, the equations of motion are

$$I_1\ddot{\psi}(t)+I_1\beta_1\dot{\psi}(t)-I_2\omega_0{}^2[\theta(t)-\psi(t)]=I_1\dot{W}(t) \tag{1}$$

and

$$I_2\ddot{\theta}(t)+I_2\beta_2\dot{\theta}(t)+I_2\omega_0{}^2[\theta(t)-\psi(t)]=I_2\dot{W}(t). \tag{2}$$

In equations (1) and (2), $\beta_1=\zeta_1/I_1$ and $\beta_2=\zeta_2/I_2$ refer to functions on the annulus and disc respectively, and ω_0 is the natural angular frequency of oscillation of the disc when the annulus is held stationary. (This is taken as the far-infra-red peak frequency.) We have also assumed in writing equations (1) and (2) that the random couples λ_1 and λ_2 may be represented by Wiener processes.

We now write equations (1) and (2) in the matrix form

$$\dot{\boldsymbol{X}}(t)=\boldsymbol{A}\boldsymbol{X}(t)+\boldsymbol{B}\dot{\boldsymbol{W}}(t), \tag{3}$$

where

$$\boldsymbol{A}=\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -\omega_0{}^2 & \omega_0{}^2 & \beta_2 & 0 \\ \Omega_0{}^2 & -\Omega_0{}^2 & 0 & -\beta_1 \end{bmatrix}, \quad \boldsymbol{B}=\begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}, \tag{4}$$

$$\boldsymbol{X}=\begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{bmatrix}=\begin{bmatrix} \theta \\ \psi \\ \dot{\theta} \\ \dot{\psi} \end{bmatrix}, \tag{5}$$

and

$$\Omega_0{}^2=\frac{I_2}{I_1}\omega_0{}^2.$$

One may calculate, from the stationary solution of equation (3), the averages $\langle\dot{\theta}(0)\dot{\theta}(t)\rangle$ and $\langle\cos\theta(0)\cos\theta(t)\rangle_0$ (where zero denotes the time at which the applied field is removed), and hence the complex polarizability [14, 15].

One should note that, since the differences of the Wiener processes form a gaussian process, and since $\theta(0)$ and $\theta(t)$ satisfy equation (1), the average $\langle\cos\theta(0)\cos\theta(t)\rangle$ may be written (for details see Coffey and Morita [16] as

$$\langle\cos\theta(0)\cos\theta(t)\rangle=\tfrac{1}{2}\exp\left[-\frac{\langle(\Delta\theta)^2\rangle}{2}\right], \tag{6}$$

where

$$\Delta\theta=[\theta(t)-\theta(0)]. \tag{7}$$

2. Calculation of the orientational autocorrelation functions

The solution [17] of equation (3) is discussed [1–6] elsewhere for $\beta_2=0$. Here, we calculate making use of the properties of the Wiener process) the averages $\langle\Delta\theta\rangle_0$, $\langle\dot{\theta}(0)\dot{\theta}(t)\rangle$ and $\langle\cos\theta(0)\cos\theta(t)\rangle_0$. This proceeds exactly as in [8], and we quote the results for the model at hand. After considerable algebra, we find that

$$\langle(\Delta\theta)\rangle_0=0, \tag{8}$$

$$\langle\dot{\theta}(0)\dot{\theta}(t)\rangle_0=\mathscr{L}^{-1}\left\{\frac{k_BT}{I_2}\frac{s(s+\beta_1)+\Omega_0{}^2}{F(s)}\right\} \tag{9}$$

and

$$\langle(\Delta\theta)^2\rangle_0=\mathscr{L}^{-1}\left\{\frac{2k_BT}{I_2}\frac{s(s+\beta_1)+\Omega_0{}^2}{s^2F(s)}\right\}, \tag{10}$$

and, on using equation (6),

$$\langle\cos\theta(0)\cos\theta(t)\rangle_0=\tfrac{1}{2}\exp\left[-\tfrac{1}{2}\langle(\Delta\theta)^2\rangle_0\right]$$

$$=\tfrac{1}{2}\exp\left[-\int_0^t(t-u)\langle\dot{\theta}(0)\dot{\theta}(u)\rangle_0\,du\right]. \tag{11}$$

On evaluating the inverse Laplace transform indicated in equation (9), we find the angular velocity autocorrelation function to be

$$\phi(t)=\frac{\langle\dot{\theta}(0)\dot{\theta}(t)\rangle_0}{\langle\dot{\theta}^2(0)\rangle}=\frac{1}{1+\Gamma}$$

$$\times\left\{\left[\cos\omega_1t+\frac{(\sigma_1+\Gamma\sigma_2)}{\omega_1}\sin\omega_1t\right]\exp(-\sigma_1t)+\Gamma\exp(-\sigma_2t)\right\}, \tag{12}$$

where

$$\Gamma=-\frac{2\sigma_1(\sigma_1{}^2+\omega_1{}^2)}{\sigma_2(3\sigma_1{}^2-\sigma_2{}^2-\omega_1{}^2)}. \tag{13}$$

The quantities σ_1, σ_2 and ω_1 are defined by the equations

$$\lambda_1=\sigma_1+i\omega_1 \quad \lambda_2=\sigma_1-i\omega_1 \quad \text{and} \quad \lambda_3=\sigma_2, \tag{14}$$

where λ_i are the non-zero roots of the characteristic equation

$$sF(s)=s[s^3+s^2(\beta_1+\beta_2)+(\omega_0{}^2+\Omega_0{}^2+\beta_1\beta_2)s+\beta_1\omega_0{}^2+\beta_2\Omega_0{}^2]=0 \tag{15}$$

of the differential equations (1) and (2). We have assumed in calculating the inverse transform that the motion is lightly damped so that two of the λ_is are complex. The method of dealing with the case in which the λ_is may have any value is described by Coffey and Evans [6]. On substituting equation (12) into equation (11), we find that

$$\langle\cos\theta(0)\cos\theta(t)\rangle_0=\tfrac{1}{2}\exp(-y(t)), \tag{16}$$

where $y(t)$ is given by

$$y(t)=\frac{1}{1+\Gamma}\frac{kT}{I_2}\left\{\left[\frac{2\sigma_1\sigma_2+\Gamma(\sigma_1^2+\sigma_2^2+\omega_1^2)}{\sigma_2(\sigma_1^2+\omega_1^2)}\right]t\right.$$
$$-\left(\frac{\Gamma}{\sigma_2^2}+\frac{3\sigma_1^2+2\sigma_1\sigma_2\Gamma-\omega_1^2}{(\sigma_1^2+\omega_1^2)^2}\right)+\left(\frac{3\sigma_1^2+2\sigma_1\sigma_2\Gamma-\omega_1^2}{(\sigma_1^2+\omega_1^2)^2}\right)$$
$$\times\left(\cos\omega_1 t+\frac{[\sigma_1^3-3\sigma_1\omega_1^2+\sigma_2\Gamma(\sigma_1^2-\omega_1^2)]}{\omega_1(3\sigma_1^2+2\sigma_1\sigma_2\Gamma-\omega_1^2)}\sin\omega_1 t\right)$$
$$\left.\times\exp(-\sigma_1 t)+\frac{\Gamma}{\sigma_2^2}\exp(-\sigma_2 t)\right\}. \tag{17}$$

Note that equations (12) and (17) are identical in form to the corresponding equations for the case in which the damping and random torques acting on the dipole are ignored. Thus the two versions of the model differ from each other *only by virtue of their characteristic equation.* The orientational autocorrelation functions $\rho_n(t)$, defined by

$$\rho_n(t)=(\langle\cos n\theta(0)\cos n\theta(t)\rangle_0/\cos^2 n\theta(0)),\quad n=1,2,\ldots$$

are given, from equation (11), by

$$\rho_n(t)=\exp\left[-n^2\frac{\langle(\Delta\theta)^2\rangle_0}{2}\right]=\exp[-n^2 y(t)]. \tag{18}$$

The complex polarizability, $\alpha_\mu(\omega)$, may now be found by Fourier transformation; in practice, however, a numerical integration is preferable. It suffices to say that the general behvaiour of the integral is similar to that for the case in which the damping torque on the dipole is set equal to zero. The general effect of including the damping on the dipole is simply to broaden the high-frequency resonance absorption peak. We now proceed to describe the translational version of the model which was first formulated by Sears [10].

3. The translational itinerant oscillator II

Here it is assumed that the motion of the cage of neighbours of an atom or molecule may be represented by the translational brownian motion of a particle of mass m. The position of m relative to the origin at time t is denoted by a coordinate $\mathbf{r}(t)$. The vibrating atom or molecule is represented by a second particle of mass M whose position relative to the origin at time t is $\mathbf{R}(t)$. This particle is attracted towards the cage by a restoring force which is proportional to the difference $[\mathbf{R}(t)-\mathbf{r}(t)]$. Thus the equations of motion of the dynamical system comprising m and M are

$$m\ddot{\mathbf{r}}(t)+m\beta_1\dot{\mathbf{r}}(t)-M\omega_0^2[\mathbf{R}(t)-\mathbf{r}(t)]=m\dot{\mathbf{W}}_1(t) \tag{19}$$

and

$$M\ddot{\mathbf{R}}(t)+M\beta_2\dot{\mathbf{R}}_2(t)+M\omega_0^2[\mathbf{R}(t)-\mathbf{r}(t)]=M\dot{\mathbf{W}}_2(t). \tag{20}$$

Here $m\beta_1\dot{\mathbf{r}}(t)$ and $M\beta_2\dot{\mathbf{R}}_2(t)$ are the frictional forces acting on m and M respectively, $M\omega_0^2$ is the spring constant, and $m\dot{\mathbf{W}}_1(t)$ and $M\dot{\mathbf{W}}_2(t)$ are the forces acting on m and M due to random collisions where, again, $\mathbf{W}_1$ and $\mathbf{W}_2$ are Wiener

processes. Our object here is to calculate from equations (19) and (20) the autocorrelation function $C_v(t)$ of the velocity of the particle, given by

$$C_v(t)=\frac{\langle\dot{\mathbf{R}}(0)\cdot\dot{\mathbf{R}}(t)\rangle}{\langle\dot{R}^2(0)\rangle}, \tag{21}$$

and the self van Hove probability density function $G_s(\mathbf{R}, t)$, which is the probability per unit volume of finding the particle at a position $\mathbf{R}$ at time t, given that it was initially ($t=0$) at the origin. The significance of $G_s(\mathbf{R}, t)$ lies in the result that the *Fourier transform*

$$\int\int G_s(\mathbf{R}, t)\exp[i(\mathbf{K}\cdot\mathbf{r}-\omega t)]\,d^3\mathbf{r}\,dt=\Gamma_s(\mathbf{K}, \omega) \tag{22}$$

essentially gives, in the classical limit, the incoherent cross-section for the scattering of neutrons by a monatomic liquid. In equation (22), the scattering vector is defined by

$$\mathbf{K}=\mathbf{k}-\mathbf{k}_0, \tag{23}$$

where $\mathbf{k}$ and $\mathbf{k}_0$ are the wavenumbers of the incident and scattered neutrons respectively. The functions $C_v(t)$ and $G_s(\mathbf{R}_1 t)$ may be readily calculated from the results of §§ (1) and (2), starting from the general solution of the differential equation (3), where this time the matrix $\boldsymbol{X}$ is given by

$$\boldsymbol{X}=\begin{bmatrix}X_1\\X_2\\X_3\\X_4\end{bmatrix}=\begin{bmatrix}R_i\\r_i\\\dot{R}_i\\\dot{r}_i\end{bmatrix},\quad i=1,2,3. \tag{24}$$

One finds results for $C_v(t)$ formally identical with equation (12).

The van Hove function $G_s(\mathbf{R}, t)$ is, as we have seen, the probability density function of the random variable $\mathbf{R}(t)$. This probability density function is gaussian because equations (23) and (24) are linear and because $\mathbf{W}_1$ and $\mathbf{W}_2$ are gaussian processes. Thus $G_s(\mathbf{R}, t)$ has the general form

$$G_s(\mathbf{R}, t)=\left\{\frac{3}{2\pi\langle|\mathbf{R}(t)-\langle\mathbf{R}(t)\rangle|^2\rangle}\right\}^{3/2}\exp\left[-\frac{3|\mathbf{R}(t)-\langle\mathbf{R}(t)\rangle|^2}{2\langle|\mathbf{R}(t)-\langle\mathbf{R}(t)\rangle|^2\rangle}\right]. \tag{25}$$

If we now assume, following Chandrasekhar's discussion of the brownian motion of a free particle [22], that the random variable $\mathbf{R}(t)$ has initially a Maxwell–Boltzmann distribution, equation (25) may be simplified as

$$G_s(\mathbf{R}, t)=\left[\frac{3}{2\pi\langle|\Delta\mathbf{R}|^2\rangle}\right]^{3/2}\exp\left[-\tfrac{3}{2}\frac{|\Delta\mathbf{R}|^2}{\langle|\Delta\mathbf{R}|^2\rangle}\right], \tag{26}$$

where

$$\Delta\mathbf{R}=\mathbf{R}(t)-\mathbf{R}_0$$

and $\mathbf{R}_0$ denotes the value of $\mathbf{R}(t)$ at time $t=0$. The assumption that $\mathbf{R}_0$ has a Maxwell–Boltzmann distribution immediately allows us to make use of the fact that

$$\langle|\Delta\mathbf{R}|^2\rangle=2\int_0^t(t-u)\langle\mathbf{R}_0\cdot\mathbf{R}(u)\rangle\,du \tag{27}$$

and so we find that $\langle|\Delta\mathbf{R}|^2\rangle$ is given by an equation which is formally identical with equation (17) for $y(t)$ provided I_2 is replaced by $M/6$.

One may also write the intermediate scattering function, defined by

$$F_s(\mathbf{K}, t) = \exp i\mathbf{K} \cdot (\mathbf{R}(t) - \mathbf{R}_0)\rangle \tag{28}$$

since, for a gaussian process [20],

$$F_s(\mathbf{K}, t) = \exp\left(-\frac{K^2}{6}\langle|\Delta\mathbf{R}|^2\rangle\right). \tag{29}$$

There is a curious analogy between equations (29) and (16) in that they are identical for $K^2 = 1$. This analogy holds good for several different models for incoherent scattering and dielectric relaxation [23]; however, there is no particular physical significance in this—it is simply a consequence of the gaussian probability density function underlying both relaxation processes.

4. The Kramers equation for the itinerant oscillator

So far we have indicated how the various ensemble averages and probability density functions appropriate to dielectric relaxation and incoherent neutron scattering may be computed by using a method based on the direct solution of the equations of motion of the oscillator. In this section we show one way of proceeding to the calculation of these averages by constructing a partial differential equation (the Kramers equation) for the evolution, in phase space, of the probability density function underlying the model [22]. The method is sufficiently well illustrated by considering the version of the Kramers equation appropriate to the two-dimensional rotator form of the model.

We start by writing the equations of motion in the matrix form :

$$d\begin{bmatrix}\theta(t)\\ \psi(t)\\ \dot\theta(t)\\ \dot\psi(t)\end{bmatrix} = \begin{bmatrix}\dot\theta(t)\\ \dot\psi(t)\\ -\beta_2\dot\theta(t) - \omega_0^2(\theta-\psi)\\ -\beta_1\dot\psi(t) + \Omega_0^2(\theta-\psi)\end{bmatrix} dt + \begin{bmatrix}0\\ 0\\ dW_\theta\\ dW_\psi\end{bmatrix}, \tag{30}$$

which in turn may be written in the general form

$$d\begin{bmatrix}X_1\\ X_2\\ X_3\\ X_4\end{bmatrix} = \begin{bmatrix}g_1\\ g_2\\ g_3\\ g_4\end{bmatrix} dt + \begin{bmatrix}0&0&0&0\\ 0&0&0&0\\ 0&0&1&0\\ 0&0&0&1\end{bmatrix}\begin{bmatrix}dW_1\\ dW_2\\ dW_3\\ dW_4\end{bmatrix}$$

or, in an obvious notation,

$$d\boldsymbol{X}(t) = \boldsymbol{g}(t, \boldsymbol{X})\, dt + \boldsymbol{C}\, d\boldsymbol{W}(t), \tag{31}$$

where $\boldsymbol{X}(t)$ is a vector in $\mathbb{R}^4$.

(Note that the symbols dW_θ and dW_ψ are used here instead of 1 and 2 in order to avoid confusion in the following calculation).

The Chapman–Kolmogorov equation associated with the stochastic differential equation (31) is

$$f(\boldsymbol{X}, t+\delta t) = \int_{\mathbb{R}^4} f(\boldsymbol{X}, t+\delta t|\boldsymbol{X}', t) f(\boldsymbol{X}', t)\, d\boldsymbol{X}',$$

where f denotes the probability density function in the configuration–angular-velocity space $\mathbb{R}^4$. On writing

$$\boldsymbol{Z} = \boldsymbol{X} - \boldsymbol{X}' \quad \text{and} \quad \boldsymbol{X}' = \boldsymbol{X}(t+\delta t),$$

and defining a function q by means of the equation

$$f(\boldsymbol{X}, t+\delta t|\boldsymbol{X}', t) = q(\boldsymbol{Z}, \delta t|\boldsymbol{X} - \boldsymbol{Z}, t),$$

we have

$$f(\boldsymbol{X}, t+\delta t|\boldsymbol{X}', t) = \int_{\mathbb{R}^4} q(\boldsymbol{Z}, \delta t|\boldsymbol{X} - \boldsymbol{Z}, t) f(\boldsymbol{X} - \boldsymbol{Z}, t)\, d\boldsymbol{Z}. \tag{32}$$

We now *assume* that we may approximate the integrand in equation (32) by the first few terms of a Taylor series about the point $\boldsymbol{Z} = \boldsymbol{X}$; to this end, we define

$$h(\boldsymbol{X} - \boldsymbol{Z}, t, \boldsymbol{Z}, \delta t) = q(\boldsymbol{Z}, \delta t|\boldsymbol{X} - \boldsymbol{Z}, t) f(\boldsymbol{X} - \boldsymbol{Z}, t) = h(\boldsymbol{X} - \boldsymbol{Z}),$$

say, for simplicity.

Clearly,

$$h(\boldsymbol{X} - \boldsymbol{Z}) = \exp(-\boldsymbol{Z} \cdot \nabla_{\boldsymbol{X}}) h(\boldsymbol{X}), \tag{33}$$

where $\boldsymbol{Z} \cdot \nabla_{\boldsymbol{X}}$ stands for the operator

$$Z_1\frac{\partial}{\partial X_1} + \ldots + Z_4\frac{\partial}{\partial X_4},$$

thus

$$\exp[-\boldsymbol{Z} \cdot \nabla_{\boldsymbol{X}}(\cdot)] = 1 - \sum_{l=1}^{4} Z_l \frac{\partial(\cdot)}{\partial X_l} + \frac{1}{2!}\sum_{l=1}^{4}\sum_{m=1}^{4} Z_l Z_m \frac{\partial^2(\cdot)}{\partial X_l \partial X_m}.$$

From these results,

$$f(\boldsymbol{X}, t+\delta t) = \int_{\mathbb{R}^4} h(X_1 \ldots X_4)\, d\boldsymbol{Z} - \sum_{l=1}^{4}\int_{\mathbb{R}^4} Z_l \frac{\partial}{\partial X_l}[h(X_1 \ldots X_4)]\, d\boldsymbol{Z} + \frac{1}{2!}\sum_{l=1}^{4}\sum_{m=1}^{4}\int_{\mathbb{R}^4} Z_l Z_m \frac{\partial^2 h(X_1 \ldots X_4)}{\partial X_l \partial X_m}\, d\boldsymbol{Z}.$$

Assuming that the order of differentiation and integration may be interchanged in this equation, we have, on substituting for h from equation (33),

$$\begin{aligned} f(\boldsymbol{X}, t+\delta t) &= \int_{\mathbb{R}^4} q(Z_1 \ldots Z_4, \delta t|X_1 \ldots X_4, t) f(X_1 \ldots X_4, t)\, d\boldsymbol{Z} \\ &\quad - \sum_{l=1}^{4}\frac{\partial}{\partial X_l}\left[\int_{\mathbb{R}^4} Z_l q(Z_1 \ldots Z_4, \delta t|X_1 \ldots X_4, t) f(X_1 \ldots X_4, t)\, d\boldsymbol{Z}\right] \\ &\quad + \frac{1}{2!}\sum_{m=1}^{4}\sum_{l=1}^{4}\frac{\partial^2}{\partial X_l \partial X_m}\left[\int_{\mathbb{R}^4} Z_l Z_m q(Z_1 \ldots Z_4, \delta t|X_1 \ldots X_4, t) \right. \\ &\quad \left. \times (X_1 \ldots X_4, t)\, d\boldsymbol{Z}\right]. \end{aligned} \tag{34}$$

Now,

$$f(X_1 \dots X_4, t+\delta t) = f(X_1 \dots X_4, t) + \delta t \frac{\partial f}{\partial t} + O(\delta t)^2 + \dots,$$

whence, with equation (34), on remembering that q is a probability density function,

$$\left.\begin{aligned} &\int_{\mathbb{R}^4} q\, dz = 1 \\ &\langle Z_l \rangle = \int_{\mathbb{R}^4} Z_l q(\boldsymbol{Z}, \delta t/X, t) dZ \\ &\delta t \frac{\partial f}{\partial t} = -\sum_{l=1}^{4} \frac{\partial}{\partial X_l} [\langle Z_l(\boldsymbol{X}, \delta t, t)\rangle f(\boldsymbol{X}, t)] \\ &\qquad + \frac{1}{2!} \sum_{l=1}^{4} \sum_{m=1}^{4} \frac{\partial^2}{\partial X_l \partial X_m} [\langle Z_l Z_m(\boldsymbol{X}, \delta t, t)\rangle f(\boldsymbol{X}, t)]. \end{aligned}\right\} \quad (35)$$

The task that now remains is to determine the averages $\langle Z_l \rangle$ and $\langle Z_l Z_m \rangle$ or, more precisely,

$$\left.\begin{aligned} &\lim_{\delta t \to 0} \left[\frac{\langle Z_l(\boldsymbol{X}, \delta t, t)\rangle}{\delta t}\right] \\ &\lim_{\delta t \to 0} \left[\frac{\langle Z_l Z_m(\boldsymbol{X}, \delta t, t)\rangle}{\delta t}\right]. \end{aligned}\right\} \quad (36)$$

To do this we return to our initial stochastic differential equation (31), which may be written, on integrating between t and $t+\delta t$, as

$$\boldsymbol{X}(t+\delta t) - \boldsymbol{X}(t) = \int_t^{t+\delta t} \boldsymbol{g}(t', \boldsymbol{X}(t'))\, dt' + \int_t^{t+\delta t} \boldsymbol{C}\, d\boldsymbol{W}(t').$$

If we now approximate the first integral on the right-hand side of this equation by $g(t, \boldsymbol{X}(t))\delta t$, we find that the equation becomes

$$\boldsymbol{X}(t+\delta t) - \boldsymbol{X}(t) = \boldsymbol{g}(t, \boldsymbol{X}(t))\delta t + \boldsymbol{C}\boldsymbol{\xi}(\delta t).$$

However,

$$\boldsymbol{X}(t+\delta t) - \boldsymbol{X}(t) = \boldsymbol{Z}$$

by our earlier definition of $\boldsymbol{Z}$, so that

$$\boldsymbol{Z} = \boldsymbol{g}(t, \boldsymbol{X}(t))\delta t + \boldsymbol{C}\boldsymbol{\xi}(\delta t). \quad (37)$$

From the properties of $\boldsymbol{\xi}$, it follows that

$$\langle \boldsymbol{Z} \rangle = g(t, \boldsymbol{X}(t))\delta t$$

and

$$\lim_{\delta t \to 0} \frac{\langle Z_l(\delta t, \boldsymbol{X}, t)\rangle}{\delta t} = g_l(\boldsymbol{X}, t). \quad (38)$$

Writing the formal solution of equation (3) in terms of its separate components, we have

$$\left.\begin{aligned} &Z_l = g_l(t, \boldsymbol{X}(t))\delta t, && l = 1, 2 \\ &Z_l = g_l(t, \boldsymbol{X}(t))\delta t + \xi_l(\delta t), && l = 3, 4. \end{aligned}\right\} \quad (39)$$

Let us now take two distinct components, l and m, where $l = 3, 4$ and $m = 3, 4$. Thus, on multiplying these together, we have

$$Z_l Z_m = g_l g_m (\delta t)^2 + g_l \xi_m (\delta t)\delta t + g_m \xi_l (\delta t)\delta t + \xi_l \xi_m.$$

On ignoring terms $O(\delta t)^2$ and remembering that

$$\langle \xi_l(\delta t)\rangle = \langle \xi_m(\delta t)\rangle = 0,$$

we have, on taking mean values,

$$\lim_{\delta t \to 0} \frac{\langle Z_l Z_m \rangle}{\delta t} = \lim_{\delta t \to 0} \frac{\langle \xi_m(\delta t)\xi_l(\delta t)\rangle}{\delta t}.$$

and again, by the properties of the Wiener process,

$$\lim_{\delta t \to 0} \frac{\langle \xi_l(\delta t)\xi_m(\delta t)\rangle}{\delta t} = C_l^2\, \delta_{mn}, \quad (40)$$

where δ_{mn} is the Kronecker delta. Thus our differential equation (35) is reduced to

$$\frac{\partial f}{\partial t}(\boldsymbol{X}, t) = -\sum_{l=1}^{4} \frac{\partial}{\partial X_l}(g_l(\boldsymbol{X}, t) f(X, t)) + \frac{1}{2!} \sum_{l=3}^{4} \sum_{l=3}^{4} C_l^2\, \delta_{mn} \frac{\partial^2}{\partial X_l \partial X_m} f(\boldsymbol{X}, t). \quad (41)$$

On substituting for the various g_ls in equation (41) from equations (39), we find finally that f satisfies the equation

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \theta}(\dot\theta f) + \frac{\partial}{\partial \psi}(\dot\psi f) - \frac{\partial}{\partial \dot\theta}(\omega_0^2(\theta - \psi) f) - \frac{\partial}{\partial \dot\psi}(\Omega_0^2(\theta - \psi) f) = \beta_2 \frac{\partial}{\partial \dot\theta}(\dot\theta f) + \beta_1 \frac{\partial}{\partial \dot\psi}(\dot\psi f) + \beta_2 \frac{kT}{I_2} \frac{\partial^2 f}{\partial \dot\theta^2} + \beta_1 \frac{kT}{I_1} \frac{\partial^2 f}{\partial \dot\psi^2}, \quad (42)$$

where the constants C_l^2 have been replaced by $\beta_1 kT/I_1$ and $\beta_2 kT/I_2$. The values of these constants are determined from the fact that

$$f(\theta, \psi, \dot\theta, \dot\psi, 0) = A \exp\left\{-\frac{1}{2kT}[I_1 \dot\psi^2 + I_2 \dot\theta^2 + I_2 \omega_0^2 (\theta - \psi)^2]\right\}$$

(where A is a given constant), must be the equilibrium solution of equation (42).

The Kramers equation in $\mathbb{R}^{12}$ for the translational version of the model has the same general form as equation (42). One finds that $f = f(\mathbf{r}, \mathbf{R}, \dot{\mathbf{r}}, \dot{\mathbf{R}}, t)$ satisfies

$$\frac{\partial f}{\partial t} + (\dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} + \dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}}) f - \nabla_{\dot{\mathbf{R}}} \cdot [\omega_0^2(\mathbf{R} - \mathbf{r}) f] - \nabla_{\dot{\mathbf{r}}} \cdot [\Omega_0^2(\mathbf{r} - \mathbf{R}) f] = \beta_2 \nabla_{\dot{\mathbf{r}}} \cdot (\dot{\mathbf{r}} f) + \beta_1 \nabla_{\dot{\mathbf{R}}} \cdot (\dot{\mathbf{R}} f) + \beta_1 \frac{kT}{m} \nabla_{\dot{\mathbf{r}}}^2 f + \beta_2 \frac{kT}{M} \nabla_{\dot{\mathbf{R}}}^2 f. \quad (43)$$

5. Integro-differential representation of the itinerant oscillator: translation

In this section we note that the set of equations (19) and (20) can be written as a special case of the general matrix equation [21, 24]

$$\mathbf{A}(t) = -\int_0^t \boldsymbol{\Phi}_{\mathbf{A}}(t-\tau)\dot{\mathbf{A}}(\tau)\,d\tau + \boldsymbol{F}_{\mathbf{A}}(t), \tag{44}$$

where

$$\mathbf{A}(t) = \begin{bmatrix} \dot{\mathbf{R}}(t) \\ \dot{\boldsymbol{r}}(t) \end{bmatrix}, \quad \boldsymbol{\Phi}_{\mathbf{A}}(t) = \begin{bmatrix} \beta_2\delta(t) + \omega_0^2 & -\omega_0^2 \\ -\Omega_0^2 & \beta_1\delta(t) + \Omega_0^2 \end{bmatrix}$$

and

$$\boldsymbol{F}_{\mathbf{A}}(t) = \begin{bmatrix} \mathbf{W}_2(t) \\ \mathbf{W}_1(t) \end{bmatrix}.$$

Here $\delta(t)$ is a delta function, and $\Omega_0^2 = M\omega_0^2/m$. The diffusion equation corresponding to equation (44) has recently been found to be [24]

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \mathbf{A}} \cdot (C_{\mathbf{A}} C_{\mathbf{A}}^{-1}\,\mathbf{A} f) + \tfrac{1}{2}\frac{\partial}{\partial \mathbf{A}} \cdot \left[C_{\mathbf{A}} \frac{d}{dt} (\boldsymbol{M}_0^{-1}) C_{\mathbf{A}}^{\mathrm{T}} \frac{df}{d\mathbf{A}} \right]. \tag{45}$$

Here $\mathbf{A}(t)$ is a column vector of n linearly independent dynamic variables, the probability density function for which is f, and $\mathbf{A}^{\mathrm{T}}(t)$ is the row vector corresponding to $\mathbf{A}(t)$. In addition,

$$\mathbf{M}_0 = \mathbf{C}_{\mathbf{A}}^{\mathrm{T}}\,\mathbf{V}^{-1}\,\mathbf{C}_{\mathbf{A}},$$

where

$$\mathbf{V}(t) = \langle \mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(0)\rangle - \mathbf{C}_{\mathbf{A}}(t)\langle \mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(0)\rangle \mathbf{C}_{\mathbf{A}}^{\mathrm{T}}(t)$$

and

$$\mathbf{C}_{\mathbf{A}}(t) = \langle \mathbf{A}(t)\mathbf{A}^{\mathrm{T}}(0)\rangle \langle \mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(0)\rangle^{-1}.$$

The probability density function f may now be written as

$$f(\mathbf{A}(t),\ \mathbf{A}(0),\ t) = (2\pi)^{-n/2}(\det \mathbf{V}(t))^{-1/2}$$
$$\times \exp\left[-\tfrac{1}{2}(\mathbf{A}(t) - \mathbf{C}_{\mathbf{A}}(t)\mathbf{A}(0))^{\mathrm{T}}\,\mathbf{V}^{-1}(t)(\mathbf{A}(t) - \mathbf{C}_{\mathbf{A}}(t)\mathbf{A}(0))\right]. \tag{46}$$

Writing $\mathbf{A}(t)$ as

$$\begin{bmatrix} \mathbf{R}(t) \\ \boldsymbol{r}(t) \\ \dot{\mathbf{R}}(t) \\ \dot{\boldsymbol{r}}(t) \end{bmatrix},$$

equation (44) reduces in our case to one of the form of equation (3), and equation (45) to one of the form of equation (43). The relevant form of f may be evaluated from the equivalent of equation (46).

Rotation

Due to the condition imposed by the equilibrium solution of equation (42), the evaluation of a probability density function such as $f(\theta, \psi, \dot{\theta}, \dot{\psi}, t)$ is greatly complicated. However, we note that the restricted probability density function for θ in the range $(-\pi, \pi)$ is that of a wrapped normal distribution which may be approximated [24] by the von Mises distribution

$$f(\theta(t),\ \theta(0),\ \dot{\theta}(0),\ t)$$
$$\doteq [2\pi I_0(\alpha(t))]^{-1} \exp\left[\alpha(t)\cos\left(\theta(t) - \theta(0) - X_J(t)\dot{\theta}(0)\right)\right]. \tag{47}$$

Here the function $\alpha(t)$ can be found at any specific time t by numerically solving the equation

$$\frac{I_1(\alpha(t))}{I_0(\alpha(t))} = \exp\left[-\frac{kT}{I}\left(\int_0^t X_J(\tau)\,d\tau - \frac{X_J^2(t)}{2}\right)\right],$$

where I_0 and I_1 are the modified Bessel functions of zeroth and first order respectively, and

$$X_J(t) = \int \langle \dot{\theta}(\tau)\dot{\theta}(0)\rangle\,d\tau.$$

The functions $f(\theta(t), \theta(0), \dot{\theta}(0), t)$ are symmetric about $\theta(0)$, eventually dying down to a flat distribution as $t \to \infty$. The similarity in shape to gaussian distributions [25] disappears as time increases.

6. Dipole–dipole coupling

In this section we note finally that equations (1) and (2), besides having the kinematic meaning ascribed to them earlier, are formally identical [26] with those needed in two dimensions to account for the electrostatic dipole–dipole interaction between a pair of dipoles undergoing brownian motion in a plane. The electrical torque between the dipoles is of the form

$$\gamma(\theta(t) - \psi(t))$$

and inertial effects are accounted for, this giving rise in principle to a spread of Debye times (as observed) at kilohertz frequencies and also a broad librational band. In general the torque will be of the form

$$\gamma \sin(\theta(t) - \psi(t)),$$

making equations (1) and (2) non-linear differential stochastic equations, which would be soluble numerically in the Kramers–Fokker–Planck form such as that of equation (42).

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