Proc. R. Soc. Lond. A **410**, 61–88 (1987)
Printed in Great Britain

On the role of inertial effects and dipole–dipole coupling in the theory of the Debye and far-infrared absorption of polar fluids

By W. T. Coffey[1], P. M. Corcoran[1]† and M. W. Evans[2]‡

[1] *School of Engineering, Department of Microelectronics and Electrical Engineering, Trinity College, Dublin 2, Republic of Ireland*

[2] *Department of Physics, University College of Swansea, Singleton Park, Swansea SA2 8PP, U.K.*

(*Communicated by F. J. M. Farley, F.R.S. – Received 8 April 1986*)

The theory of dielectric relaxation of an assembly of molecules containing rotating polar groups, originally developed by Budó, is extended to include inertial effects. It is shown that the inclusion of these effects gives rise to a resonance absorption in the far infrared band of frequencies. To obtain analytical formulae for the polarizability and the absorption coefficient the system is first treated in the harmonic approximation. Nonlinear effects are then taken account of by using the averaging method of Krylov and Bogoliubov. Inclusion of these effects indicates that the frequency of maximum far-infrared power absorption should decrease as the temperature increases in qualitative agreement with experimental findings. Also the nonlinear effects cause the angular-velocity correlation functions to become less oscillatory as temperature is increased. The present treatment gives rise to equations that in the harmonic approximation are formally similar to those of the itinerant oscillator model.

1. Introduction

Some years ago Calderwood and one of us (Calderwood & Coffey 1977) made calculations on 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. The essence of the model (which is now called the itinerant oscillator (IO) model after earlier work of Hill (1963), Sears (1965) and Wyllie (1971)) is that a molecule may undergo rotational or translational oscillations in a potential well caused by its nearest neighbours, while the potential well undergoes Brownian motion. The model is also related to a treatment, given originally by Budó (1949) for the dielectric relaxation of molecules containing rotating polar groups. In the original treatment of Calderwood & Coffey (1977) and in subsequent work (e.g. Coffey & Evans 1978) it was not possible to give explicit expressions for the various correlation functions of the model. These were expressed only in terms of the roots of the characteristic equation or secular

† Present address: Department of Electronic Engineering, University College Galway, Republic of Ireland.

‡ Present address: IBM, Neighborhood Road, Kingston, New York 12401, U.S.A.

determinant of the system of equations describing the model. It is the purpose of this paper to show how explicit expressions for all the relevant correlation functions may be obtained in the general case where the masses or inertias of the molecules are not equal. The corresponding results when the two molecules are equal in all respects have already been given in closed form (Coffey 1985).

We shall frame our discussion in terms of the Budó (1949) treatment of dielectric relaxation. (The translational case of interest in the context of thermal neutron scattering merely requires that we replace the moments of inertia by the masses of the molecules and the angular variables by their Cartesian equivalents.) Thus we suppose that a typical molecule contains two dipoles, each constrained to rotate about a central axis normal to the plane of rotation. The angle of dipole one, which is of moment of inertia I_1 and dipole moment $\boldsymbol{\mu}_1$ (relative to the direction of a steady electric field $\boldsymbol{E}$) is ϕ_1 and the angle of dipole two, of dipole moment $\boldsymbol{\mu}_2$ and moment of inertia I_2, is ϕ_2. The potential energy of dipole interaction is $V(\phi_1-\phi_2)$. Each of the dipoles is subject to a random torque $\lambda_i(t)$ and a viscous drag torque $\zeta_i\,\dot{\phi}_i(t)$ arising from the Brownian movement of the surroundings. At a time $t=0$ the steady field $\boldsymbol{E}$ is switched off and thus the system relaxes to a new equilibrium state in the absence of the field. We wish to calculate how the mean dipole moment

$$\begin{aligned} M(t) &= \langle(\boldsymbol{m}(0)\cdot\boldsymbol{e})\,(\boldsymbol{m}(t)\cdot\boldsymbol{e})\rangle_0 \\ &= \langle(\mu_1\cos\phi_1(0)+\mu_2\cos\phi_2(0))\,(\mu_1\cos\phi_1(t)+\mu_2\cos\phi_2(t))\rangle_0, \end{aligned}$$

of the system varies as a function of time after the switching off of the field. The subscript '0' denotes that the ensemble average is to be evaluated in the absence of the field $\boldsymbol{E}$. Having calculated $M(t)$ one may determine the complex polarizability $\alpha(\omega)$ and thus the absorption coefficient from linear-response theory (Scaife 1971) via the formula

$$\alpha(\omega) = \alpha'(\omega) - \mathrm{i}\alpha''(\omega) = \frac{1}{kT}\left[M(0) - \mathrm{i}\omega\int_0^\infty M(t)\,\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}t\right].$$

The absorption coefficient $\mathscr{A}(\omega)$ (Np cm^{-1}†) is then given by

$$c\mathscr{A}(\omega) \approx \omega\epsilon''(\omega) \approx \omega\alpha''(\omega),$$

where $\epsilon(\omega)$ is the complex permittivity ($\epsilon''(\omega) \propto \alpha''(\omega)$ because for a dilute solution $\epsilon(\omega)+2 \approx 3$; c is the velocity of light).

The other correlation functions that we would like to calculate besides those of orientation are the angular-velocity auto- and cross-correlation functions. These are of interest because (*a*) they may be directly constructed by using molecular dynamics simulations and (*b*) they yield, albeit indirectly, the mean-square value of the angular displacements of the dipoles and are much easier to calculate than the displacements themselves. For example, one may show (details in Appendix A) that ($\mathscr{L}$ denotes the Laplace transform operator)

$$(1/s^2)\,\mathscr{L}\{\langle\dot{\phi}_i(0)\,\dot{\phi}_i(t)\rangle_0\} = (1/s^2)\,\mathscr{L}\{C_{\dot{\phi}_i}(t)\} = \tfrac{1}{2}\mathscr{L}\{\langle(\Delta\phi_i)^2\rangle_0\},$$

where

$$\Delta\phi_i = [\phi_i(t)-\phi_i(0)], \quad i = 1, 2$$

so that the Laplace transform of the mean-square angular displacement may be

† 1 Np = 8.68589 dB = 20 lg e.

directly calculated from the Laplace transform of the angular velocity correlation functions. Further, if we replace the Laplace variables by $i\omega$ in $\mathscr{L}\{C_{\dot{\phi}_i}(t)\}$ we obtain the one-sided Fourier transform of $C_{\dot{\phi}_i}(t)$ that yields the dynamic mobility. This is of particular interest in the application of the model to incoherent scattering of slow neutrons where the ϕs are replaced by their translational equivalents†.

2. Equations of motion of the system

The equations of motion before the field has been removed are

$$I_1\ddot{\phi}_1+\zeta_1\dot{\phi}_1+V'(\phi_1-\phi_2)+\mu_1 E\sin\phi_1 = \lambda_1(t), \tag{1}$$

$$I_2\ddot{\phi}_2+\zeta_2\dot{\phi}_2-V'(\phi_1-\phi_2)+\mu_2 E\sin\phi_2 = \lambda_2(t). \tag{2}$$

In general for dipole–dipole coupling

$$V(\phi_1-\phi_2) = -2V_0\cos(\phi_1-\phi_2), \tag{3}$$

where $4V_0$, the difference between the potential energies in the equal and opposite directions of the moments $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$ is a measure of the interaction between the groups. The case in which the potential has its minimum in the same direction as that of the moments $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ is called, following Budó, the *cis* case while if the potential has its minimum in the opposite direction to that of the moments it is termed the *trans* case. We follow Budó by always measuring from the position in which the potential has its minimum value. Results for the *trans* case may be obtained from those of the *cis* case by writing $\boldsymbol{\mu}_2 = -\boldsymbol{\mu}_2$ in the *cis* formulae. The primes denote differentiation of V with respect to its argument so that $V'(\phi_1-\phi_2) = 2V_0\sin(\phi_1-\phi_2)$.

In writing down these equations we note that the only dipole–dipole coupling that is taken account of is that between *pairs* of dipoles. If this is not done we are forced to deal with the many-body problem.

Let us now suppose that the steady field, $\boldsymbol{E}$, is switched off at time $t = 0$. It is implicitly assumed that $\boldsymbol{E}$ has been applied for a long time so that equilibrium conditions have been attained. Thus (1) and (2) become ($t > 0$)

$$I_1\ddot{\phi}_1+\zeta_1\dot{\phi}_1+V'(\phi_1-\phi_2) = \lambda_1(t), \tag{4}$$

$$I_2\ddot{\phi}_2+\zeta_2\dot{\phi}_2-V'(\phi_1-\phi_2) = \lambda_2(t). \tag{5}$$

Equations (4) and (5) describe a type of coupled pendulum. One would in general, therefore, expect two normal modes of oscillation of the system. In order to find these modes it is convenient to introduce

$$\chi = \frac{I_1\phi_1+I_2\phi_2}{I_1+I_2}, \tag{6}$$

$$\eta = \tfrac{1}{2}(\phi_1-\phi_2). \tag{7}$$

χ therefore yields the motion of the sum angle mode and η gives the relative motion of the two dipoles. Adding (4) and (5) yields

$$\frac{I_1\ddot{\phi}_1+I_2\ddot{\phi}_2}{I_1+I_2}+\frac{\zeta_1\dot{\phi}_1+\zeta_2\dot{\phi}_2}{I_1+I_2} = \frac{\lambda_1+\lambda_2}{I_1+I_2}. \tag{8}$$

† The concept of vibration about a temporary equilibrium position (termed libration) is mentioned by Frenkel (1946) and Fröhlich (1949).

If
$$\zeta_1/\zeta_2 = I_1/I_2, \tag{9}$$
that is,
$$\beta = \zeta_1/I_1 = \zeta_2/I_2, \tag{10}$$
then (8) may be written
$$(I_1+I_2)\ddot{\chi}+(I_1+I_2)\beta\dot{\chi} = \lambda_1+\lambda_2, \tag{11}$$
whereas by subtraction
$$\eta = \tfrac{1}{2}(\phi_1-\phi_2) \quad (V(2\eta) = -2V_0\cos 2\eta)$$
satisfies
$$\ddot{\eta}+\beta\dot{\eta}+V_0(1/I_1+1/I_2)\sin 2\eta = \tfrac{1}{2}(\lambda_1/I_1-\lambda_2/I_2). \tag{12}$$

Thus we see that for these values of the friction coefficients the motion of the system may be decomposed into the motion of a rotator in a $\cos 2\eta$ potential and the motion of a *free* rotator of moment of inertia I_1+I_2 and friction constant per unit rotational mass β. This factorization makes for great simplification of subsequent calculations because χ and η, *unlike* ϕ_1 and ϕ_2 are *independent* random variables. It also allows the time behaviour of all the correlation functions in the small oscillation approximation to be found in closed form. The normal modes of the system consist of one of infinitely low frequency that is the one of the χ variable, yielding Debye-type behaviour whereas the other is that of the η variable of frequency
$$\omega_0 = \sqrt{[2V_0(1/I_1+1/I_2)]}. \tag{13}$$

The quantity $(1/I_1+1/I_2)$ is the reciprocal of the reduced moment of inertia that plays the role of the reduced mass in the two-body problem of mechanics. It is convenient to write (13) as
$$\omega_0 = \sqrt{(2V_0/J)}, \tag{14}$$
where
$$J = I_1 I_2/(I_1+I_2). \tag{15}$$

Equation (13) may be found either directly from the equations of motion or by writing down the Hamiltonian for the undamped motion of the system. For convenience and in order to avoid confusion later we deduce ω_0 from the Hamiltonian. We have, in terms of the original variables ϕ_1, ϕ_2,
$$H = \tfrac{1}{2}I_1\dot{\phi}_1^2+\tfrac{1}{2}I_2\dot{\phi}_2^2+V(\phi_1-\phi_2), \tag{16}$$
which in terms of the new variables becomes in the small oscillation approximation
$$H = \tfrac{1}{2}(I_1+I_2)\dot{\chi}^2+2I_1I_2/(I_1+I_2)\dot{\eta}^2-2V_0(1-2\eta^2). \tag{17}$$
Differentiating with respect to time we then find, because χ and η are uncoupled,
$$(I_1+I_2)\ddot{\chi} = 0, \tag{18}$$
$$\ddot{\eta}+(2V_0/J)\eta = 0. \tag{19}$$
so that η executes simple harmonic motion of angular frequency given by (13). Finally, we note that in the original work of Calderwood & Coffey (1977), ϕ_1 would correspond to θ and ϕ_2 to ψ in their calculation. Also $\zeta_1 = \lambda_1 = 0$.

3. Calculation of the angular velocity correlation functions

We shall first treat the angular velocity autocorrelation functions

$$C_{11} = \langle \dot{\phi}_1(0)\,\dot{\phi}_1(t)\rangle_0, \tag{20}$$

$$C_{22} = \langle \dot{\phi}_2(0)\,\dot{\phi}_2(t)\rangle_0 \tag{21}$$

and the angular-velocity cross-correlation function

$$C_{12} = C_{21} = \langle \dot{\phi}_1(0)\,\dot{\phi}_2(t)\rangle_0 \tag{22}$$

as they are easier to calculate than the orientational correlation functions. Again the '0' subscript on the averaging brackets indicates that the ensemble-average is taken in the absence of the applied field, E. In terms of our χ and η variables C_{11} becomes

$$\begin{aligned} C_{11} &= \langle [\dot{\chi}(0) + a_1\,\dot{\eta}(0)]\,[\dot{\chi}(t) + a_1\,\dot{\eta}(t)]\rangle_0 \\ &= \langle \dot{\chi}(0)\,\dot{\chi}(0)\rangle_0 + a_1\langle \dot{\eta}(0)\,\dot{\chi}(t)\rangle_0 \\ &\quad + a_1\langle \dot{\chi}(0)\,\dot{\eta}(t)\rangle_0 + a_1^2\langle \dot{\eta}(0)\,\dot{\eta}(t)\rangle_0, \end{aligned} \tag{23}$$

where

$$a_1 = \frac{2I_2}{I_1+I_2}, \quad a_2 = \frac{2I_1}{I_1+I_2}, \quad \left.\begin{array}{l} 0 \leqslant a_1 \leqslant 2, \\ 0 \leqslant a_2 \leqslant 2. \end{array}\right\} \tag{24}$$

Now χ and η are independent random variables whence

$$\langle \dot{\chi}(0)\,\dot{\eta}(t)\rangle_0 = \langle \dot{\chi}(0)\rangle_0\,\langle \dot{\eta}(t)\rangle_0 = 0, \tag{25}$$

$$C_{11} = \langle \dot{\chi}(0)\,\dot{\chi}(t)\rangle_0 + a_1^2\langle \dot{\eta}(0)\,\dot{\eta}(t)\rangle_0 \tag{26}$$

and in exactly the same way

$$C_{22} = \langle \dot{\chi}(0)\,\dot{\chi}(t)\rangle_0 + a_2^2\langle \dot{\eta}(0)\,\dot{\eta}(t)\rangle_0 \tag{27}$$

and

$$C_{12} = \langle \dot{\chi}(0)\,\dot{\chi}(t)\rangle_0 - a_1\,a_2\langle \dot{\eta}(0)\,\dot{\eta}(t)\rangle_0. \tag{28}$$

These foregoing results are perfectly general and hold no matter what the form of the potential, V, the only restrictive condition being the one $\zeta_1/I_1 = \zeta_2/I_2$. The χ correlation function may be written down immediately from the known results for the disc model (Coffey *et al.* 1984, pages 90 *et seq*). The χ angular-velocity correlation function is then (where t means $|t|$ from now on)

$$\langle \dot{\chi}(0)\,\dot{\chi}(t)\rangle_0 = \langle \dot{\chi}^2\rangle_0\,\mathrm{e}^{-\beta t}. \tag{29}$$

The average $\langle \dot{\chi}^2\rangle_0$ is found by inspection of the Hamiltonian, (17) above. We must have (from the equipartition theorem)

$$\tfrac{1}{2}(I_1+I_2)\,\langle \dot{\chi}^2\rangle_0 = \tfrac{1}{2}kT. \tag{30}$$

Thus

$$\langle \dot{\chi}(0)\,\dot{\chi}(t)\rangle_0 = [kT/(I_1+I_2)]\,\mathrm{e}^{-\beta t}. \tag{31}$$

The η correlation function on the other hand can only be found in closed form in the small oscillation approximation. The results for this correlation function in the small oscillation approximation may be written down immediately from the results of Calderwood *et al.* (1976) given in Coffey *et al.* (1984, page 98) in the underdamped case. We note from this that

$$\langle \dot{\eta}(0)\,\dot{\eta}(t)\rangle_0 = \langle \dot{\eta}^2\rangle_0\, e^{-\beta t/2}\,(\cos\omega_1 t - (\beta/2\omega_1)\sin\omega_1 t). \tag{32}$$

In order to write down the value of $\langle \dot{\eta}^2\rangle_0$ we refer again to (17). Because χ, η are independent we must have by the equipartition theorem

$$\tfrac{1}{2}[4I_1 I_2/(I_1+I_2)]\langle \dot{\eta}^2\rangle_0 = \tfrac{1}{2}kT. \tag{33}$$

Thus

$$\langle \dot{\eta}^2\rangle_0 = kT(I_1+I_2)/4I_1 I_2. \tag{34}$$

We now substitute all these results into (26)–(28) and find that

$$C_{11} = \langle \dot{\phi}_1(0)\,\dot{\phi}_1(t)\rangle_0 = \frac{kT}{I_1+I_2}\left[e^{-\beta t} + \frac{I_2}{I_1}\,e^{-\frac{1}{2}\beta t}\left(\cos\omega_1 t - \frac{\beta}{2\omega_1}\sin\omega_1 t\right)\right], \tag{35}$$

$$C_{22} = \langle \dot{\phi}_2(0)\,\dot{\phi}_2(t)\rangle_0 = \frac{kT}{I_1+I_2}\left[e^{-\beta t} + \frac{I_1}{I_2}\,e^{-\frac{1}{2}\beta t}\left(\cos\omega_1 t - \frac{\beta}{2\omega_1}\sin\omega_1 t\right)\right], \tag{36}$$

$$C_{12} = \langle \dot{\phi}_1(0)\,\dot{\phi}_2(t)\rangle_0 = \frac{kT}{I_1+I_2}\left[e^{-\beta t} - e^{-\frac{1}{2}\beta t}\left(\cos\omega_1 t - \frac{\beta}{2\omega_1}\sin\omega_1 t\right)\right]. \tag{37}$$

We note that C_{11} and C_{22} are oscillatory functions of time. The cross correlation function may also be an oscillatory function of time, but, unlike the autocorrelation function, will pass through a maximum before decaying to zero. The angular frequency of oscillation, of these correlation functions is given by

$$\omega_1 = \sqrt{(2V_0/J - \beta^2/4)}, \tag{38}$$

where J is the reduced moment of inertia

$$J = I_1 I_2/(I_1+I_2). \tag{39}$$

In conclusion to this section we note that the reduction of the problem of the dielectric relaxation of two coupled dipoles to the solution of the free rotator and the pendulum problem was first given by Schröer for the special case $I_1 = I_2$. (W. Schröer personal communication 1981, see also Coffey *et al.* 1982*b*; Risken & Vollmer 1982).

4. Fourier transforms of the velocity correlation functions

The Fourier transforms of the C_{ij} essentially give the frequency dependence of the mobilities of the system. This is of particular interest in the theory of thermal neutron scattering Sears (1965). The Fourier transform of C_{11} is

$$\begin{aligned}\mathscr{F}\{\langle \dot{\phi}_1(0)\,\dot{\phi}_1(t)\rangle_0\} &= \mu'_{11}(\omega) - i\mu''_{11}(\omega)\\ &= \frac{kT}{I_1+I_2}\left\{\frac{\beta - i\omega}{\beta^2+\omega^2} + \frac{I_2}{I_1}\,\frac{i\omega[(\omega_0^2-\omega^2) - i\omega\beta]}{(\omega_0^2-\omega^2)^2+\omega^2\beta^2}\right\}.\end{aligned} \tag{40}$$

$$\mathscr{F}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_2(t)\rangle_0\} = \mu'_{22}(\omega) - \mathrm{i}\mu''_{22}(\omega)$$
$$= \frac{kT}{I_1+I_2}\left\{\frac{\beta-\mathrm{i}\omega}{\beta^2+\omega^2} + \frac{I_1}{I_2}\,\frac{\mathrm{i}\omega[(\omega_0^2-\omega^2)-\mathrm{i}\omega\beta]}{(\omega_0^2-\omega^2)^2+\omega^2\beta^2}\right\}, \quad (41)$$

$$\mathscr{F}\{\langle\dot{\phi}_1(0)\,\dot{\phi}_2(t)\rangle_0\} = \mu'_{12}(\omega) - \mathrm{i}\mu''_{12}(\omega)$$
$$= \frac{kT}{I_1+I_2}\left\{\frac{\beta-\mathrm{i}\omega}{\beta^2+\omega^2} - \frac{\mathrm{i}\omega[(\omega_0^2-\omega^2)-\mathrm{i}\omega\beta]}{(\omega_0^2-\omega^2)^2+\omega^2\beta^2}\right\}. \quad (42)$$

In the application to thermal neutron scattering it is assumed that the rotational quantities I_1 and I_2, ϕ_1 and ϕ_2, etc., are replaced by their translational equivalents. In the itinerant oscillator model of Sears (1965), m_1 corresponds to the mass of the encaged particle whereas m_2 is the mass of the cage of neighbours. Before leaving this part of the calculation we note that C_{11} at an initial time $t = 0$ has the value kT/I_1 whereas C_{22} has the value kT/I_2. It is therefore convenient when plotting the autocorrelation functions C_{11} and C_{22} to normalize them by these initial values. The cross-correlation function, C_{12} on the other hand, has initial value zero as it must have.

The spectra of the various mobilities are of interest in that they consist in each case of a pure Lorentzian superimposed on which is a high-frequency resonance absorption. In each case this resonance absorption will pass through a maximum that depends on ω_0 and β. The sharpness of this high-frequency maximum depends on the value of the Q-factor of system. Because the η part of the response is that of a harmonic oscillator one may immediately write down the Q-factor. It is simply

$$Q = \frac{\omega_0}{\beta} = \sqrt{(2V_0/J\beta^2)}. \quad (43)$$

Thus the sharpness of the high-frequency absorption depends on the potential strength, the friction coefficient and the reduced moment of inertia. This simple expression for the factors on which the sharpness of the resonance depends is a direct consequence of the factorization of the system in χ and η variables.

5. Orientational correlation functions

To calculate these we make use of a theorem concerning characteristic functions of Gaussian random variables (Cramér 1970)

$$\langle\exp\mathrm{i}X\rangle = \exp[\mathrm{i}\langle X\rangle - \tfrac{1}{2}\langle X^2\rangle]. \quad (44)$$

Because the noise torques λ_1 and λ_2 acting on the system have Gaussian distributions and because the equations of motion of η in the harmonic approximation are linear, then η will be a Gaussian random variable (linear transformations of Gaussian random variables are themselves Gaussian) and χ is automatically a Gaussian random variable because the equation of motion of χ contains no external torques apart from those due to Brownian movement.

Returning now to our original variables ϕ_1 and ϕ_2, we wish to calculate the mean dipole moment $M(t)$ following the removal of the external field at $t = 0$. We have, by definition

$$\begin{aligned} M(t) &= \langle (\boldsymbol{m}(0)\cdot\boldsymbol{e})\,(\boldsymbol{m}(t)\cdot\boldsymbol{e})\rangle_0 \\ &= \langle[\mu_1 \cos\phi_1(0)+\mu_2\cos\phi_2(0)]\,[\mu_1\cos\phi_1(t)+\mu_2\cos\phi_2(t)]\rangle_0 \\ &= \mu_1^2\langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0+2\mu_1\mu_2\langle\cos\phi_1(0)\cos\phi_2(t)\rangle_0 \\ &\quad+\mu_2^2\langle\cos\phi_2(0)\cos\phi_2(t)\rangle_0. \end{aligned} \tag{45}$$

We now write (45) in terms of the independent random variables χ and η.

$$\begin{aligned} M(t) &= \langle\cos\chi(0)\cos\chi(t)\rangle_0\{\mu_1^2[\langle\cos a_1\eta(0)\cos a_1\eta(t)\rangle_0 \\ &\quad+\langle\sin a_1\eta(0)\sin a_1\eta(t)\rangle_0] \\ &\quad+2\mu_1\mu_2[\langle\cos a_1\eta(0)\cos a_2\eta(t)\rangle_0 \\ &\quad-\langle\sin a_1\eta(0)\sin a_2\eta(t)\rangle_0] \\ &\quad+\mu_2^2[\langle\cos a_2\eta(0)\cos a_2\eta(t)\rangle_0+\langle\sin a_2\eta(0)\sin a_2\eta(t)\rangle_0]\}. \end{aligned} \tag{46}$$

In writing (46) we have made use of the fact that χ and η are independent random variables thus averages like

$$\langle\cos\chi(0)\cos\chi(t)\cos a_1\eta(0)\cos a_1\eta(t)\rangle_0 \tag{47}$$

may be written

$$\langle\cos\chi(0)\cos\chi(t)\rangle_0\langle\cos a_1\eta(0)\cos a_1\eta(t)\rangle_0 \tag{48}$$

while averages like

$$\langle\cos\chi(0)\sin\chi(t)\cos a_1\eta(0)\sin a_1\eta(t)\rangle_0 \tag{49}$$

all vanish. We have also used the fact that for the freely rotating disc

$$\langle\cos\chi(0)\cos\chi(t)\rangle_0=\langle\sin\chi(0)\sin\chi(t)\rangle_0.$$

In (46) the terms prefixed by μ_1^2 and μ_2^2 are the autocorrelation functions whereas the term $2\mu_1\mu_2$ is the cross-correlation function. We have written the formula for the *cis* case. Those of the *trans* case are found by writing $\mu_1 = -\mu_1$, thus the effect of going from *cis* to *trans* is simply to change the sign of the crosscorrelation function of the dipoles.

We now write (46) in a form where the Gaussian theorem given above may be used. We first define

$$\Delta\eta = \eta(t)-\eta(0) \tag{50}$$

and write

$$\begin{aligned} r_{11}(t) &= \langle\cos a_1\eta(0)\cos a_1\eta(t)\rangle_0+\langle\sin a_1\eta(0)\sin a_1\eta(t)\rangle_0 \\ &= \langle\cos a_1\eta(0)\cos[a_1\eta(0)+a_1\Delta\eta]\rangle_0 \\ &\quad+\langle\sin a_1\eta(0)\sin[a_1\eta(0)+a_1\Delta\eta]\rangle_0, \end{aligned} \tag{51}$$

which on use of the addition formula,

$$\cos[\tfrac{1}{2}(\alpha+\beta)]\cos[\tfrac{1}{2}(\alpha-\beta)]=\tfrac{1}{2}[\cos\alpha+\cos\beta], \tag{52}$$

becomes

$$r_{11}(t) = \langle \cos a_1\, \Delta\eta \rangle_0 \tag{53}$$

$$= \mathrm{Re}\,[\langle \exp \mathrm{i} a_1\, \Delta\eta \rangle_0]. \tag{54}$$

$\eta(t)$ and $\eta(0)$ are Gaussian random variables, therefore $\Delta\eta$ is a Gaussian random variable. We may now make use of (44) to write

$$r_{11}(t) = \mathrm{Re}\,\{\exp[\mathrm{i}a_1\langle\Delta\eta\rangle_0 - \tfrac{1}{2}a_1^2\langle(\Delta\eta)^2\rangle_0]\}. \tag{55}$$

According to Coffey *et al.* (1984, page 98)

$$\langle \eta(0) \rangle_0 = \langle \eta(t) \rangle_0.$$

Thus $\Delta\eta$ is a centred random variable whence

$$r_{11} = \exp[-\tfrac{1}{2}a_1^2\langle(\Delta\eta)^2\rangle_0]. \tag{56}$$

Thus we can write r_{11} by knowing $\langle(\Delta\eta)^2\rangle_0$ only. To use the results of Coffey *et al.* (1984) it is convenient to substitute for $\langle(\Delta\eta)^2\rangle_0$ so that (56) becomes

$$\exp\{-\tfrac{1}{2}a_1^2[\langle \eta^2(0) + \eta^2(t) - 2\eta(0)\,\eta(t)\rangle_0]\}$$
$$= \exp[-a_1^2\langle\eta^2(0)\rangle_0]\exp[a_1^2\langle\eta(0)\,\eta(t)\rangle_0] \tag{57}$$

because $\langle\eta^2(0)\rangle_0 = \langle\eta^2(t)\rangle_0$ by stationarity. Before explicitly writing down $\langle\eta(0)\,\eta(t)\rangle_0$ it will be convenient to evaluate the remainder of $\langle(\boldsymbol{m}(0)\cdot\boldsymbol{e})\,(\boldsymbol{m}(t)\cdot\boldsymbol{e})\rangle_0$. The term in that expression prefixed by μ_2^2 is

$$\langle \cos a_2\,\eta(0)\cos a_2\,\eta(t)\rangle_0 + \langle \sin a_2\,\eta(0)\sin a_2\,\eta(t)\rangle_0. \tag{58}$$

Equation (58) is evidently similar to (57). The only difference is that a_1 must now be replaced by a_2. This completes our discussion of the autocorrelation part of the mean dipole moment. The crosscorrelation function is the part prefixed by $\mu_1\mu_2$. This is

$$r_{12}(t) = \langle \cos a_1\,\eta(0)\cos a_2\,\eta(t)\rangle_0 - \langle \sin a_1\,\eta(0)\sin a_2\,\eta(t)\rangle_0. \tag{59}$$

As before, we introduce the variable $\Delta\eta$ and use the addition formulae. This leads, in exactly the same way as before, to

$$r_{12}(t) = \langle\cos[a_1\,\eta(0) + a_2\,\eta(t)]\rangle_0 = \exp\{-\tfrac{1}{2}\langle[a_1\,\eta(0) + a_2\,\eta(t)]^2\rangle_0\} \tag{60}$$

On expanding the argument of the exponential we find that

$$r_{12}(t) = \exp[-\tfrac{1}{2}(a_1^2 + a_2^2)\langle\eta^2(0)\rangle_0]\exp[-a_1 a_2\langle\eta(0)\,\eta(t)\rangle_0]. \tag{61}$$

We may now write down the complete expression for the mean dipole moment as

$$\langle(\boldsymbol{m}(0)\cdot\boldsymbol{e})\,(\boldsymbol{m}(t)\cdot\boldsymbol{e})\rangle_0 = C_\chi(t)\,\{\mu_1^2\exp(-a_1^2\langle\eta^2\rangle_0)\exp(a_1^2\langle\eta(0)\,\eta(t)\rangle_0)$$
$$+ 2\mu_1\mu_2\exp[-\tfrac{1}{2}(a_1^2 + a_2^2)\langle\eta^2\rangle_0]\exp(-a_1 a_2\langle\eta(0)\,\eta(t)\rangle_0)$$
$$+ \mu_2^2\exp(-a_2^2\langle\eta^2\rangle_0)\exp(a_2^2\langle\eta(0)\,\eta(t)\rangle_0)\}. \tag{62}$$

$C_\chi(t)$ is the autocorrelation function $\langle\cos\chi(0)\cos\chi(t)\rangle_0$ of the disc model. From Coffey *et al.* (1984, page 90 *et seq.*) the value of this is

$$\tfrac{1}{2}\exp\left[-\frac{kT}{(I_1+I_2)\,\beta^2}(\beta t - 1 + \mathrm{e}^{-\beta t})\right]. \tag{63}$$

It is interesting to mention the particular case where the two dipoles are equal in all respects. One then finds that

$$\langle (\boldsymbol{m}(0)\cdot\boldsymbol{e})\,(\boldsymbol{m}(t)\cdot\boldsymbol{e})\rangle_0 = 4\mu^2 C_\chi(t)\exp\left[-\langle\eta^2\rangle_0\right]\cosh\langle\eta(0)\,\eta(t)\rangle_0. \tag{64}$$

This is the result for the *cis* case $\mu_1 = \mu_2 = \mu$. The result for the *trans* case where $\mu_1 = -\mu_2$ is

$$\langle (\boldsymbol{m}(0)\cdot\boldsymbol{e})\,(\boldsymbol{m}(t)\cdot\boldsymbol{e})\rangle_0 = 4\mu^2 C_\chi(t)\exp\left[-\langle\eta^2\rangle_0\right]\sinh\langle\eta(0)\,\eta(t)\rangle_0.\dagger \tag{65}$$

We now return to the evaluation of $\langle\eta(0)\,\eta(t)\rangle_0$. We use the results of Coffey *et al.* (1984, page 98) in the underdamped case. Thus

$$\langle\eta(0)\,\eta(t)\rangle_0 = \gamma_1\, x(t), \tag{66}$$

where

$$x(t) = \exp\left(-\tfrac{1}{2}\beta t\right)\left(\cos\omega_1 t + \left(\tfrac{1}{2}\beta/\omega_1\right)\sin\omega_1 t\right) \tag{67}$$

and

$$\gamma_1 = \frac{\langle\dot\eta^2\rangle_0}{\omega_0^2} = \left[\left(\frac{I_1+I_2}{4I_1 I_2}\right)kT\right]\frac{J}{2V_0}. \tag{68}$$

Thus

$$\gamma_1 = kT/8V_0. \tag{69}$$

We may now write the complete expression for the mean dipole moment in closed form; that is,

$$\begin{aligned}\langle (\boldsymbol{m}(0)\cdot\boldsymbol{e})\,(\boldsymbol{m}(t)\cdot\boldsymbol{e})\rangle_0 = C_\chi(t)\,\{&\mu_1^2\exp\left[-a_1^2\gamma_1(1-x)\right]+\mu_2^2\exp\left[-a_2^2\gamma_1(1-x)\right]\\ &+2\mu_1\mu_2\exp\left[-\tfrac{1}{2}(a_1^2+a_2^2)\,\gamma_1\right]\exp\left[-a_1 a_2\gamma_1 x\right]\}.\end{aligned} \tag{70}$$

It is helpful to write down the mean square displacements of cage and particle in the translational problem. We essentially have to write $\langle(\Delta y_1)^2\rangle$ instead of $\langle(\Delta\phi_1)^2\rangle_0$. Also for translational motion

$$\langle(\Delta y_1^2)\rangle = \langle[y_1(t)-y_1(0)]^2\rangle. \tag{71}$$

We again introduce χ and η, where χ is defined as before with rotational quantities being replaced by the corresponding translational ones. χ in this case gives the motion of the centre of mass of the system whereas η gives the motion relative to the centre of mass. The fact that χ and η are independent random variables gives

$$\langle(\Delta y_1)^2\rangle = \langle(\Delta\chi)^2\rangle_0 + a_1^2\langle(\Delta\eta)^2\rangle_0. \tag{72}$$

In exactly the same way we find that

$$\langle(\Delta y_2)^2\rangle = \langle(\Delta\chi)^2\rangle_0 + a_2^2\langle(\Delta\eta)^2\rangle_0. \tag{73}$$

In the translational application $\langle(\Delta y_1)^2\rangle$ is the mean square displacement of the particle whereas $\langle(\Delta y_2)^2\rangle$ is the mean square displacement of the cage. Substituting for all the relevant quantities gives

$$\begin{aligned}\langle(\Delta y_1)^2\rangle = \frac{2kT}{(m_1+m_2)\,\beta^2}\left(\beta t - 1 + \mathrm{e}^{-\beta t}\right) + 2\left(\frac{kT}{8V_0}\right)\left(\frac{2m_2}{m_1+m_2}\right)^2\\ \times\left[1-\exp\left(-\frac{\beta t}{2}\right)\left(\cos\omega_1 t + \frac{\beta}{2\omega_1}\sin\omega_1 t\right)\right].\end{aligned} \tag{74}$$

† Note how the form of the η correlation function is very strangly affected by the configuration of the dipoles in the molecule.

$$\langle(\Delta y_2)^2\rangle = \frac{2kT}{(m_1+m_2)\,\beta^2}(\beta t-1+\mathrm{e}^{-\beta t})+2\left(\frac{kT}{8V_0}\right)\left(\frac{2m_1}{m_1+m_2}\right)^2$$
$$\times\left[1-\exp\left(-\tfrac{1}{2}\beta t\right)\left(\cos\omega_1 t+\frac{\beta}{2\omega_1}\sin\omega_1 t\right)\right], \quad (75)$$

$$\omega_0 = \sqrt{(2V_0/M)}, \quad (76)$$

$$M = m_1 m_2/(m_1+m_2). \quad (77)$$

The intermediate scattering function is essentially (Croxton 1974)

$$F_s(\boldsymbol{\kappa}, t) = \exp\left[-\frac{\kappa^2}{2}\langle(\Delta y_1)^2\rangle\right], \quad (78)$$

where $\boldsymbol{\kappa}$ is the scattering vector of the neutrons. The van Hove function may be immediately calculated from this result. It is worth noting that the Laplace transforms of these mean square displacements may be directly calculated from the Laplace transforms of the velocity correlation functions $\langle\dot{\chi}(0)\,\dot{\chi}(t)\rangle_0$ and $\langle\dot{\eta}(0)\,\dot{\eta}(t)\rangle_0$. This is a direct consequence of the theorem

$$\mathscr{L}\{\tfrac{1}{2}\langle(\Delta\eta)^2\rangle_0\} = \frac{1}{s^2}\mathscr{L}\{\langle\dot{\eta}(0)\,\dot{\eta}(t)\rangle_0\} \quad (79)$$

with a similar expression for $\mathscr{L}\{\frac{1}{2}\langle(\Delta\chi)^2\rangle_0\}$. This completes our study of the response of the model in the time domain.

6. Frequency response of the model

To compare the model with experimentally observed spectra it is useful to have formulae for the complex polarizability and by extension the absorption coefficient. The complex polarizability $\alpha(\omega) = \alpha'(\omega)-\mathrm{i}\alpha''(\omega)$ is calculated by using the linear response theory formula

$$\alpha(\omega) = -\frac{1}{kT}\int_0^\infty \frac{\mathrm{d}M}{\mathrm{d}t}\,\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}t, \quad (80)$$

which we shall use in the alternative form

$$\alpha(\omega) = \frac{1}{kT}\left[\alpha'(0)-\mathrm{i}\omega\int_0^\infty M(t)\,\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}t\right] \quad (81)$$

or if s denotes the complex frequency

$$\alpha(s) = \frac{1}{kT}\left[\alpha'(0)-s\int_0^\infty M(t)\,\mathrm{e}^{-st}\,\mathrm{d}t\right]. \quad (82)$$

Some difficulty is posed in evaluating (82) for the model because of the double transcendental nature of $M(t)$ as is evident on inspection of (70). A complete expression for $\alpha(\omega)$ may be obtained by expanding $M(t)$ in single transcendental functions as for the torsional oscillator model, Calderwood *et al.* (1976); Coffey *et al.* (1984, see page 100). The complete expression for $\alpha(\omega)$ is, however, very cumbersome (see Appendix B) and thus does not yield much insight into the behaviour of the model. In order to obtain exact results it is better to resort to numerical evaluation of (82). It should be noted that the χ part of the correlation functions does not give rise to this difficulty since the Laplace transform of C_χ may be expressed to any desired degree of accuracy by a continued fraction (Scaife 1971). With

$$\gamma = \frac{2kT}{(I_1+I_2)\,\beta^2} \tag{83}$$

$C_\chi(t)$ is of the form

$$\exp\left[-\tfrac{1}{2}\gamma y(t)\right] = \exp\left(\tfrac{1}{2}\gamma\right) \sum_{p=0}^{\infty} \frac{(-\frac{1}{2}\gamma)^p}{p!} \exp\left[-\left(\tfrac{1}{2}\gamma+p\right)\beta t\right]. \tag{84}$$

Now this function is closely approximated by (Coffey 1985)

$$(1-\tfrac{1}{2}\gamma)^{-1}\left[\exp\left(-\tfrac{1}{2}\gamma\beta t\right)-\tfrac{1}{2}\gamma\exp\left(-\beta t\right)\right] \tag{85}$$

for

$$\gamma \lesssim 0.05.$$

In what follows we shall assume that

$$C_\chi(t) \approx \tfrac{1}{2}(1-\tfrac{1}{2}\gamma)^{-1}\left[\exp\left(-\tfrac{1}{2}\gamma\beta t\right)-\tfrac{1}{2}\gamma\exp\left(-\beta t\right)\right] = h(t). \tag{86}$$

The polarizability arising from the χ portion of the response function alone when calculated from this formula is given by

$$\frac{\alpha(s)}{\alpha'(0)} = \frac{\frac{1}{2}\gamma\beta^2}{(s+\frac{1}{2}\gamma\beta)\,(s+\beta)} \approx \frac{\frac{1}{2}\gamma\beta^2}{(s^2+\beta s+\frac{1}{2}\gamma\beta^2)}. \tag{87}$$

This equation is similar in form to that obtained by Rocard in his 1933 discussion of inertial effects in the Debye theory of dielectric relaxation (Rocard 1933; McConnell 1980).

The η portion of the response is now treated by expanding the η part of (70) in powers of γ_1 and x. We then assume that γ_1^3, x^3 and higher powers of these quantities may be neglected. Thus we have

$$\begin{aligned} M(t) = h(t)\,\{&\mu_1^2[1-a_1^2\gamma_1(1-x)+\tfrac{1}{2}a_1^4\gamma_1^2(1-x)^2] \\ &+\mu_2^2[1-a_2^2\gamma_1(1-x)+\tfrac{1}{2}a_2^4\gamma_1^2(1-x)^2] \\ &+2\mu_1\mu_2[1-\tfrac{1}{2}\gamma_1(a_1^2+a_2^2+2a_1a_2x) \\ &+\tfrac{1}{8}\gamma_1^2(a_1^2+a_2^2+2a_1a_2x)^2]\}. \end{aligned} \tag{88}$$

An analytical expression for the complex polarizability is now obtained by substituting this approximate expression into (82). We shall now show how the computation of $\alpha(\omega)$ reduces to evaluating the integrals

$$A(s) = 1-s\int_0^\infty h\,\mathrm{e}^{-st}\,\mathrm{d}t, \tag{89}$$

$$B(s) = \int_0^\infty (1-x^2)\,h\,\mathrm{e}^{-st}\,\mathrm{d}t, \tag{90}$$

$$C(s) = 1-s\int_0^\infty hx\,\mathrm{e}^{-st}\,\mathrm{d}t. \tag{91}$$

These integrals may be readily evaluated from the results for $h = h(0) = 1$ by using the shifting theorem of the Laplace transformation, namely

$$\mathscr{L}\{e^{-at} f(t)\} = F(s+a),$$

where

$$\mathscr{L}\{f(t)\} = F(s). \tag{92}$$

We now show how $\alpha(s)$ may be arranged in terms of these integrals. We consider the components of α due to auto- and cross-correlation functions separately. As before, the results for the polarizability due to μ_2 can be found from those for μ_1 by simple interchange of subscripts. Considering the μ_1^2 term in (88) we arrange it to read as

$$h(t)\{\mu_1^2[(1-\Delta_1+\Delta_1^2)+(\Delta_1-\Delta_1^2)x-\tfrac{1}{2}\Delta_1^2(1-x^2)]\}, \tag{93}$$

where for notational convenience we have written

$$a_1^2\gamma_1 = \Delta_1. \tag{94}$$

Thus

$$\alpha_{\mu_1}(s) = \frac{\mu_1^2}{kT}\left\{\left[1-s(1+\Delta_1+\Delta_1^2)\int_0^\infty h\, e^{-st}\, dt\right]\right.$$
$$\left. + s\frac{\Delta_1^2}{2}\int_0^\infty h(1-x^2)\, e^{-st}\, dt + s(\Delta_1-\Delta_1^2)\int_0^\infty hx\, e^{-st}\, dt\right\}. \tag{95}$$

We now subtract $\Delta_1-\Delta_1^2$ from the leading term of this equation and add $(\Delta_1-\Delta_1^2)$ to the last term. It becomes

$$\alpha_{\mu_1}(s) = \frac{\mu_1^2}{kT}\left\{(1-\Delta_1+\Delta_1^2)\left[1-s\int_0^\infty h\, e^{-st}\, dt\right]\right.$$
$$\left. + \frac{\Delta_1^2 s}{2}\int_0^\infty h(1-x^2)\, e^{-st}\, dt + (\Delta_1-\Delta_1^2)\left[1-s\int_0^\infty hx\, e^{-st}\, dt\right]\right\}. \tag{96}$$

or

$$\alpha_{\mu_1}(s) = \frac{\mu_1^2}{kT}[(1-\Delta_1+\Delta_1^2)A(s)+\tfrac{1}{2}\Delta_1^2 sB(s)+(\Delta_1-\Delta_1^2)C(s)]. \tag{97}$$

In the same way

$$\alpha_{\mu_2}(s) = (\mu_2^2/kT)[(1-\Delta_2+\Delta_2^2)A(s)+\tfrac{1}{2}\Delta_2^2 sB(s)+(\Delta_2-\Delta_2^2)C(s)]. \tag{98}$$

This completes our analysis of the autocorrelation function contributions.

Returning to (88), picking off the $\mu_1\mu_2$ term and substituting that into the complex polarizability formula gives

$$\alpha_{\mu_1\mu_2}(s) = \frac{2\mu_1\mu_2}{kT}\left\{[1-\tfrac{1}{2}(a_1^2+a_2^2+2a_1a_2)\gamma_1+\tfrac{1}{8}(a_1^2+a_2^2+2a_1a_2)^2\gamma_1^2]\right.$$
$$\left. - s\int_0^\infty[1-\tfrac{1}{2}(a_1^2+a_2^2+2a_1a_2x)\gamma_1+\tfrac{1}{8}(a_1^2+a_2^2+2a_1a_2x)^2\gamma_1^2]\, h\, e^{-st}\, dt\right\} \tag{99}$$

that is,

$$\alpha_{\mu_1\mu_2}(s) = \frac{2\mu_1\mu_2}{kT}\Big\{[1-\tfrac{1}{2}(a_1^2+a_2^2)\gamma_1+\tfrac{1}{8}(a_1^2+a_2^2)^2\gamma_1^2$$
$$-a_1a_2\gamma_1+\tfrac{1}{2}a_1a_2(a_1^2+a_2^2)\gamma_1^2+\tfrac{1}{2}a_1^2a_2^2\gamma_1^2]$$
$$-s\int_0^\infty[1-\tfrac{1}{2}(a_1^2+a_2^2)\gamma_1+\tfrac{1}{8}(a_1^2+a_2^2)^2\gamma_1^2]\,e^{-st}h(t)\,dt$$
$$-s\int_0^\infty\left[-a_1a_2\gamma_1x+\frac{a_1a_2}{2}(a_1^2+a_2^2)\gamma_1^2x+\frac{a_1^2a_2^2}{2}\gamma_1^2x^2\right]h\,e^{-st}\,dt\Big\} \quad (100)$$

or

$$\alpha_{\mu_1\mu_2}(s) = \frac{2\mu_1\mu_2}{kT}\Big\{[1-\tfrac{1}{2}(a_1^2+a_2^2)\gamma_1+\tfrac{1}{8}(a_1^2+a_2^2)^2\gamma_1^2]\,A(s)$$
$$-\left[a_1a_2\gamma_1-\frac{a_1a_2}{2}(a_1^2+a_2^2)\gamma_1^2\right]C(s)+\tfrac{1}{2}(a_1^2a_2^2\gamma_1^2)\left[1-s\int_0^\infty x^2h\,e^{-st}\,dt\right]\Big\}. \quad (101)$$

Everything has now been expressed in terms of our standard integrals save the last term. By addition the last term in square brackets in (101) is

$$\left[1-s\int_0^\infty h\,e^{-st}\,dt+sB(s)\right]. \quad (102)$$

Substituting (102) into (101) and combining the terms together appropriately now yields

$$\alpha_{\mu_1\mu_2}(s) = \frac{2\mu_1\mu_2}{kT}\Big\{[1-\tfrac{1}{2}(a_1^2+a_2^2)\gamma_1+\tfrac{1}{8}(a_1^4+a_2^4+6a_1^2a_2^2)\gamma_1^2]\,A(s)$$
$$-\left[a_1a_2\gamma_1-\frac{a_1a_2}{2}(a_1^2+a_2^2)\gamma_1^2\right]C(s)+\tfrac{1}{2}a_1^2a_2^2\gamma_1^2\,sB(s)\Big\}. \quad (103)$$

The complete expression for the complex polarizability is then

$$\alpha(s) = \alpha_{\mu_1}(s)+\alpha_{\mu_2}(s)+\alpha_{\mu_1\mu_2}(s). \quad (104)$$

We note the particularly simple case where the two dipoles are equal in every respect. Here $a_1 = a_2$ so that $\Delta_1 = \Delta_2$

$$\alpha_c(s) = 2(\mu^2/kT)\,[2(1-\gamma_1+\gamma_1^2)\,A(s)+\gamma_1^2\,sB(s)]. \quad (105)$$

This is the result for equal dipoles for the *cis* case. For the *trans* case on the other hand the sign of the cross-correlation function is changed and the complex polarizability is simply

$$\alpha_t(s) = 4(\mu^2/kT)\,(\gamma_1-\gamma_1^2)\,C(s).$$

A seemingly strange consequence of this is that the polarizability for the *trans* case appears to possess no purely diffusional component. This is because we have ignored the effect of the finite height of the potential barrier. If this is taken account of there would be Debye relaxation due to crossings of the dipoles over potential hills. For further progress we require explicit expressions for the integrals $A(s)$, $B(s)$, $C(s)$. First we note that the complete expression for $\alpha(s)$ in terms of these integrals is given (after considerable algebra) by

$$\begin{aligned}\alpha(s) = {} & (1/kT)\{(\mu_1+\mu_2)^2-\gamma_1[(a_1\mu_1+a_2\mu_2)^2+2\mu_1\mu_2(a_1-a_2)^2] \\ & +\gamma_1^2[(a_1^2\mu_1+a_2^2\mu_2)^2+\tfrac{1}{4}(a_1^2-a_2^2)^2\mu_1\mu_2]\}\,A(s) \\ & +(\gamma_1^2/2kT)\,(\mu_1 a_1^2+\mu_2 a_2^2)^2\,sB(s) \\ & +(1/kT)\{\gamma_1(a_1\mu_1-a_2\mu_2)^2-\gamma_1^2[(a_1^2\mu_1-a_2^2\mu_2)^2-a_1a_2\mu_1\mu_2(a_1-a_2)^2]\}\,C(s).\end{aligned} \tag{106}$$

7. Evaluation of the integrals

The value of $A(s)$ is

$$\frac{\frac{1}{4}\gamma\beta^2}{(s+\frac{1}{2}\gamma\beta)\,(s+\beta)}. \tag{107}$$

Because $h(t)$ is a linear combination of exponentials the value of the parts $B(s)$ and $C(s)$ involving $x(t)$, namely

$$\int_0^\infty x^2 h\,\mathrm{e}^{-st}\,\mathrm{d}t \tag{108}$$

and

$$\int_0^\infty xh\,\mathrm{e}^{-st}\,\mathrm{d}t, \tag{109}$$

are best found by evaluating the integrals

$$\int_0^\infty x^2\,\mathrm{e}^{-st}\,\mathrm{d}t$$

and

$$\int_0^\infty x\,\mathrm{e}^{-st}\,\mathrm{d}t.$$

The shifting theorem is then used to work out the effect of multiplying them by $h(t)$. After lengthy algebra we find that

$$\begin{aligned}B(s) = \tfrac{1}{2}(1-\tfrac{1}{2}\gamma)^{-1}\Bigg\{ & \frac{2\omega_0^2[s+\beta(2+\frac{1}{2}\gamma)]}{(s+\frac{1}{2}\gamma\beta)\,[s+\beta(\frac{1}{2}\gamma+1)]\,[(s+\frac{1}{2}\gamma\beta)^2+2\beta(s+\frac{1}{2}\gamma\beta)+4\omega_0^2]} \\ & -\frac{\gamma}{2}\,\frac{2\omega_0^2(s+3\beta)}{(s+\beta)\,(s+2\beta)\,[(s+\beta)^2+2\beta(s+\beta)+4\omega_0^2]}\Bigg\}\end{aligned} \tag{110}$$

and

$$C(s) = \frac{1}{2}\left\{\frac{\begin{array}{r}s^2(\omega_0^2+\frac{1}{2}\gamma\beta^2)+s\{3\beta[\frac{1}{2}\beta^2\gamma(1+\frac{1}{2}\gamma)+\omega_0^2]+[\gamma\beta\omega_0^2-\frac{1}{2}\gamma^2\beta^3]\} \\ +[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2]\,(2\beta^2+\omega_0^2)\end{array}}{[(s+\frac{1}{2}\gamma\beta)^2+\beta(s+\frac{1}{2}\gamma\beta)+\omega_0^2]\,[(s+\beta)^2+\beta(s+\beta)+\omega_0^2]}\right\} \tag{111}$$

It is also of interest to consider the values of these integrals when $\gamma\beta$ goes to zero (i.e. the Debye time becomes very great). One finds that

$$B(s) = \frac{\omega_0^2(s+2\beta)}{s(s+\beta)\,(s^2+2\beta s+4\omega_0^2)} \tag{112}$$

and

$$C(s) = \frac{\omega_0^2}{2(s^2+\beta s+\omega_0^2)} \tag{113}$$

The high-frequency parts of the polarizabilities corresponding to *cis* and *trans* cases, respectively, are (with $\mu_1 = \mu_2$)

$$\frac{\mu^2}{kT}\frac{2\omega_0^2(s+2\beta)}{(s+\beta)(s^2+2\beta s+4\omega_0^2)}, \tag{114}$$

$$\frac{\mu^2}{kT}\frac{2\omega_0^2}{s^2+\beta s+\omega_0^2}. \tag{115}$$

When the dipoles are equal in all respects a striking fact is that the resonant frequency of (114) is of the order $2\omega_0$ whereas the resonant frequency of (115) is of order ω_0. Thus, as one would expect from physical reasoning, the far-infrared absorption is strongly affected by the configuration of the dipoles in the molecule. In order to proceed to the calculation of the absorption coefficient it is necessary to write the foregoing equations in the frequency domain with $s = \mathrm{i}\omega$ and then calculate the imaginary parts of the equations because the absorption coefficient, $\mathscr{A}(\omega)$ is proportional to $\omega\alpha''(\omega)$. We first write down the real and imaginary parts of the integrals $\mathrm{A}(s)$, $sB(s)$, $C(s)$, which separately constitute the polarizability. The function $\mathrm{A}(\omega)$ is

$$\mathrm{A}(\omega) = \frac{[\frac{1}{2}\gamma\beta^2-\omega^2-\mathrm{i}\omega\beta(1+\frac{1}{2}\gamma)]\frac{1}{4}\gamma\beta^2}{(\frac{1}{4}\gamma^2\beta^2+\omega^2)(\beta^2+\omega^2)} \tag{116}$$

The imaginary part of this when we define $\alpha(\omega)$ by $\alpha'(\omega)-\mathrm{i}\alpha''(\omega)$ so that $\mathrm{A}(\omega) = \mathrm{A}'(\omega)-\mathrm{i}\mathrm{A}''(\omega)$ is

$$\mathrm{A}''(\omega) = \frac{\omega\beta(1+\frac{1}{2}\gamma)\frac{1}{4}\gamma\beta^2}{(\frac{1}{4}\gamma^2\beta^2+\omega^2)(\beta^2+\omega^2)}. \tag{117}$$

We next consider $\mathrm{i}\omega B(\omega)$. The real and the imaginary parts of this function are (after considerable algebra, $\mathrm{i}\omega B(\omega) = \mathrm{i}\omega B'(\omega)+\omega B''(\omega)$),

$$\omega B''(\omega) =$$

$$\frac{\omega_0^2}{(1-\frac{1}{2}\gamma)}\left(\frac{\omega^2\{\beta^4\gamma(2+\frac{3}{2}\gamma+\frac{1}{4}\gamma^2)(1+\frac{1}{2}\gamma)^2-2\omega^2\beta^2(1-\frac{1}{4}\gamma^2)+[2\beta^2(1+\gamma+\frac{1}{8}\gamma^2)+\omega^2][4\omega_0^2-\omega^2+\beta^2\gamma(1+\frac{1}{4}\gamma)]\}}{(\frac{1}{4}\gamma^2\beta^2+\omega^2)[\beta^2(1+\frac{1}{2}\gamma)^2+\omega^2]\{[4\omega_0^2-\omega^2+\beta^2\gamma(1+\frac{1}{4}\gamma)]^2+4\omega^2\beta^2(1+\frac{1}{2}\gamma)^2\}}\right.$$
$$\left.-\omega^2\tfrac{1}{2}\gamma\frac{[24\beta^4+(7\beta^2+\omega^2)(4\omega_0^2-\omega^2+3\beta^2)]}{(\beta^2+\omega^2)(4\beta^2+\omega^2)[(4\omega_0^2-\omega^2+3\beta^2)^2+16\omega^2\beta^2]}\right). \tag{118}$$

$$\omega B'(\omega) =$$

$$\frac{\omega_0^2\omega}{(1-\frac{1}{2}\gamma)}\left(\frac{[\frac{1}{2}\gamma\beta^3(2+\frac{3}{2}\gamma+\frac{1}{4}\gamma^2)-\omega^2\beta(1-\frac{1}{2}\gamma)][4\omega_0^2-\omega^2+\beta^2\gamma(1+\frac{1}{4}\gamma)]-2\omega^2\beta(1+\frac{1}{2}\gamma)[2\beta^2(1+\gamma+\frac{1}{8}\gamma^2)+\omega^2]}{(\frac{1}{4}\gamma^2\beta^2+\omega^2)[\beta^2(1+\frac{1}{2}\gamma)^2+\omega^2]\{[4\omega_0^2-\omega^2+\beta^2\gamma(1+\frac{1}{4}\gamma)]^2+4\omega^2\beta^2(1+\frac{1}{2}\gamma)^2\}}\right.$$
$$\left.-\tfrac{1}{2}\gamma\frac{[6\beta^3(4\omega_0^2-\omega^2+3\beta^2)-4\omega^2\beta(7\beta^2+\omega^2)]}{(\beta^2+\omega^2)(4\beta^2+\omega^2)[(4\omega_0^2-\omega^2+3\beta^2)^2+16\omega^2\beta^2]}\right) \tag{119}$$

In the same way the real and imaginary parts of the function $C(\omega)$ are given by

$$C'(\omega) = \frac{1}{2}\biggl(\frac{\{[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2](2\beta^2+\omega_0^2)-\omega^2(\omega_0^2+\frac{1}{2}\gamma\beta^2)\}\{(2\beta^2+\omega_0^2-\omega^2)[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2-\omega^2]-3\omega^2\beta^2(1+\gamma)\}}{\{[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2-\omega^2]^2+\omega^2\beta^2(1+\gamma)^2\}[(2\beta^2+\omega_0^2-\omega^2)^2+9\omega^2\beta^2]}$$
$$+\frac{\omega^2\beta^2[\frac{1}{2}\gamma\beta^2(3+\frac{1}{2}\gamma)+\omega_0^2(3-\gamma)][(4+\gamma)(\omega_0^2-\omega^2)+2\beta^2(1+\frac{7}{4}\gamma+\frac{3}{8}\gamma^2)]}{\{[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2-\omega^2]^2+\omega^2\beta^2(1+\gamma)^2\}[(2\beta^2+\omega_0^2-\omega^2)^2+9\omega^2\beta^2]}\biggr).$$

$$C''(\omega) = \frac{\omega\beta}{2}\biggl(\frac{\{[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2](2\beta^2+\omega_0^2)-\omega^2(\omega_0^2+\frac{1}{2}\gamma\beta^2)\}[(4+\gamma)(\omega_0^2-\omega^2)+2\beta^2(1+\frac{7}{4}\gamma+\frac{3}{8}\gamma^2)]}{\{[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2-\omega^2]^2+\omega^2\beta^2(1+\gamma)^2\}[(2\beta^2+\omega_0^2-\omega^2)^2+9\omega^2\beta^2]}$$
$$+\frac{[\frac{1}{2}\gamma\beta^2(3+\frac{1}{2}\gamma)+\omega_0^2(3-\gamma)]\{(2\beta^2+\omega_0^2-\omega^2)[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2-\omega^2]-3\omega^2\beta^2(1+\gamma)\}}{\{[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2-\omega^2]^2+\omega^2\beta^2(1+\gamma)^2\}[(2\beta^2+\omega_0^2-\omega^2)^2+9\omega^2\beta^2]}\biggr); \tag{120}$$

respectively. Whence with (106):

$$\begin{aligned}\alpha'(\omega) = {} & (1/kT)\{(\mu_1+\mu_2)^2-\gamma_1[(a_1\mu_1+a_2\mu_2)^2+2\mu_1\mu_2(a_1-a_2)^2]+\gamma_1^2[(a_1^2\mu_1+a_2^2\mu_2)^2 \\ & +\tfrac{1}{4}(a_1^2-a_2^2)^2\mu_1\mu_2]\}A'(\omega)+(\gamma_1^2/2kT)(\mu_1a_1^2+\mu_2a_2^2)^2\omega B''(\omega) \\ & +(1/kT)\{\gamma_1(a_1\mu_1-a_2\mu_2)^2-\gamma_1^2[(a_1^2\mu_1-a_2^2\mu_2)^2-a_1a_2\mu_1\mu_2(a_1-a_2)^2]\}C'(\omega),\end{aligned}$$

$$\begin{aligned}\alpha''(\omega) = {} & (1/kT)\{(\mu_1+\mu_2)^2-\gamma_1[(a_1\mu_1+a_2\mu_2)^2+2\mu_1\mu_2(a_1-a_2)^2]+\gamma_1^2[(a_1^2\mu_1+a_2^2\mu_2)^2 \\ & +\tfrac{1}{4}(a_1^2-a_2^2)\mu_1\mu_2]\}A''(\omega)-(\gamma_1^2/2kT)(\mu_1a_1^2+\mu_2a_2^2)^2\omega B'(\omega) \\ & +(1/kT)\{\gamma_1(a_1\mu_1-a_2\mu_2)^2-\gamma_1^2[(a_1^2\mu_1-a_2^2\mu_2)^2-a_1a_2\mu_1\mu_2(a_1-a_2)^2]\}C''(\omega).\end{aligned} \tag{121}$$

We then find that the complete expression for the absorption coefficient

$$c^{-1}\mathscr{A}(\omega) = \omega\alpha''(\omega)$$

is (multiplied by c for convenience of notation)

$$\begin{aligned}c\mathscr{A}(\omega) = {} & (1/kT)\{(\mu_1+\mu_2)^2-\gamma_1[(a_1\mu_1+a_2\mu_2)^2+2\mu_1\mu_2(a_1-a_2)^2]+\gamma_1^2[(a_1^2\mu_1+a_2^2\mu_2)^2 \\ & +\tfrac{1}{4}(a_1^2-a_2^2)^2\mu_1\mu_2]\}\frac{\frac{1}{4}\gamma\beta^3(1+\frac{1}{2}\gamma)\omega^2}{(\frac{1}{4}\gamma^2\beta^2+\omega^2)(\beta^2+\omega^2)}-\frac{\gamma_1^2}{2kT}(\mu_1a_1^2+\mu_2a_2^2)^2\frac{\omega_0^2\omega^2}{(1-\frac{1}{2}\gamma)} \\ & \times\biggl(\frac{[\frac{1}{2}\gamma\beta^3(2+\frac{3}{2}\gamma+\frac{1}{4}\gamma^2)-\omega^2\beta(1-\frac{1}{2}\gamma)][4\omega_0^2-\omega^2+\beta^2\gamma(1+\frac{1}{4}\gamma)]-2\omega^2\beta(1+\frac{1}{2}\gamma)[2\beta^2(1+\gamma+\frac{1}{8}\gamma^2)+\omega^2]}{(\frac{1}{4}\gamma^2\beta^2+\omega^2)[\beta^2(1+\frac{1}{2}\gamma)^2+\omega^2]\{[4\omega_0^2-\omega^2+\beta^2\gamma(1+\frac{1}{4}\gamma)]^2+4\omega^2\beta^2(1+\frac{1}{2}\gamma)^2\}} \\ & -\tfrac{1}{2}\gamma\frac{[6\beta^3(4\omega_0^2-\omega^2+3\beta^2)-4\omega^2\beta(7\beta^2+\omega^2)]}{(\beta^2+\omega^2)(4\beta^2+\omega^2)[(4\omega_0^2-\omega^2+3\beta^2)^2+16\omega^2\beta^2]}\biggr) \\ & +\tfrac{1}{2}kT\{\gamma_1(a_1\mu_1-a_2\mu_2)^2-\gamma_1^2[(a_1^2\mu_1-a_2^2\mu_2)^2-a_1a_2(a_1-a_2)^2\mu_1\mu_2]\} \\ & \times\omega^2\beta\biggl(\frac{[\frac{1}{2}\gamma\beta^2(3+\frac{1}{2}\gamma)+\omega_0^2(3-\gamma)]\{(2\beta^2+\omega_0^2-\omega^2)[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2-\omega^2]-3\omega^2\beta^2(1+\gamma)\}}{\{[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2-\omega^2]^2+\omega^2\beta^2(1+\gamma)^2\}[(2\beta^2+\omega_0^2-\omega^2)^2+9\omega^2\beta^2]} \\ & +\frac{\{[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2](2\beta^2+\omega_0^2)-\omega^2(\omega_0^2+\frac{1}{2}\gamma\beta^2)\}[(4+\gamma)(\omega_0^2-\omega^2)+2\beta^2(1+\frac{7}{4}\gamma+\frac{3}{8}\gamma^2)]}{\{[\frac{1}{2}\gamma\beta^2(1+\frac{1}{2}\gamma)+\omega_0^2-\omega^2]^2+\omega^2\beta^2(1+\gamma)^2\}[(2\beta^2+\omega_0^2-\omega^2)^2+9\omega^2\beta^2]}\biggr).\end{aligned} \tag{122}$$

It is instructive to find the frequencies at which the various functions making up the absorption coefficient resonate. In order to reduce the amount of algebra we will simply consider in detail the function $sB(s)$. The behaviour of $C(s)$ may be inferred in the same manner. The function $A(s)$ is most significant in the microwave region and cannot resonate as it describes pure frictional relaxation. If we take

$$\lim_{\gamma\to 0} \mathrm{Im}\,[\mathrm{i}\omega B(\omega)] = \frac{\omega_0^2\,\omega\beta}{\beta^2+\omega^2}\left[\frac{\omega^2+4(\beta^2+\omega_0^2)}{(4\omega_0^2-\omega^2)^2+4\omega^2\beta^2}\right] \tag{123}$$

then this function should provide quite a close approximation to the high-frequency part of $\mathrm{i}\omega B(\omega)$ because the terms in γ should all be small. The absorption coefficient corresponding to this is then proportional to

$$\frac{\omega_0^2\,\omega^2\beta^2}{\beta^2+\omega^2}\left[\frac{\omega^2+4(\beta^2+\omega_0^2)}{(4\omega_0^2-\omega^2)^2+4\omega^2\beta^2}\right] = F(\omega). \tag{124}$$

For frequencies $\omega > \beta$ which condition is satisfied in the FIR region, $\omega^2(\beta^2+\omega^2)^{-1}$ is almost constant. Thus

$$F(\omega) \approx \omega_0^2\,\beta\left[\frac{\omega^2+4(\beta^2+\omega_0^2)}{(4\omega_0^2-\omega^2)^2+4\omega^2\beta^2}\right]. \tag{125}$$

To find the frequency of maximum power absorption ω_{m1} one must differentiate the denominator of (125) and then set the resulting expression equal to zero. One then finds that

$$\omega_{m1} = 2\omega_0\sqrt{(1-\beta^2/2\omega_0^2)}, \tag{126}$$

which by the binomial theorem is approximately

$$2\omega_0(1-\beta^2/4\omega_0^2).$$

This shows how the frequency of maximum power absorption is affected by the friction. The general conclusion is that the resonant frequency of the $B(\omega)$ part of the response is of order $2\omega_0$. The analysis for the $C(\omega)$ integral follows exactly as in the preceding case. One finds that the frequency of maximum power absorption is approximately that of the ω_0 mode of the system so that

$$\omega_{m2} = \sqrt{(\omega_0^2-\tfrac{1}{2}\beta^2)} \approx \omega_0(1-\beta^2/4\omega_0^2) \approx \omega_0. \tag{127}$$

We note that numerical Fourier transformation of $\dot{M}(t)$ with the fast Fourier transform algorithm also shows the presence of these maxima at the high frequency end of the spectrum. The numerical transformation also indicates that the maximum at the fundamental frequency ω_0 is far more pronounced than that at $2\omega_0$ and that there are subsidiary maxima at the higher harmonic frequencies but these are almost imperceptible for typical values of the molecular parameters I_1, I_2, β, etc. These harmonics are a direct consequence of the double transcendental nature of $M(t)$ (see B 4).

These analytical formulae for the spectrum have been obtained on the assumption that the correlation functions making up $M(t)$ in (62) may be expanded in powers of γ_1 and that only terms in γ_1 and γ_1^2 are retained in the expansion. The reason for doing this is to avoid the difficulties associated with integrating the double transcendental functions in (62). If the damping in the system were zero it would be possible to express the double transcendental functions in (62) as a Fourier series, the coefficients of which are the Bessel functions of imaginary argument. The series could then be integrated term by term to yield a complete expression for the polarizability. Unfortunately, it is not apparent how this may be done when damping is present. (It is, however, always possible to express $\alpha(\omega)$ as a triple sum, see Appendix B.) In view of these difficulties, it is best to resort to a numerical method such as the fast Fourier transform (applied to (62) and (80)) to find an expression for the polarizability in the general case when γ_1 is not necessarily small. This is the most practical way of proceeding when comparing the model spectra with experimental ones.

We further remark that our analysis so far has taken no account of the non-harmonic nature of the equations of motion of the dipoles. The effects of anharmonicity should be noticeable in the FIR region of the spectrum. A complete analysis would require the solution of the Kramers equation for the problem using the method of Brinkman (cf. Evans *et al.* 1982). It is however possible to study the effects of anharmonicity on the correlation functions when such effects are small by using the method of the equivalent linear system due to Krylov & Bogoliubov (McLachlan 1956; Caughey 1963). This is detailed in the following section.

8. Application of the method of Krylov and Bogoliubov

The analysis just completed assumes that the potential well in which the dipoles oscillate is infinitely deep. (This prevents 'flips' in the orientation of the dipoles or 'escape' from one well into a neighbouring one. It also does not take account of the large oscillation effects that may occur in nonlinear vibrating systems). We shall now try to assess the principle effects of nonlinearity: that is how changing the shape of the potential from that of an infinitely deep parabola to a cosine well of finite depth will cause the spectrum to depart from that of a harmonic oscillator. We use the equivalent linear system concept, which is a development of the work of Krylov & Bogoliubov on deterministic nonlinear systems (McLachlan 1956). It appears to have been first applied to stochastic systems by Caughey (1963). The suggestion that it should be applied to the present problem is due to Marchesoni (Marchesoni *et al.* 1985).

We illustrate by considering (Caughey 1963):

$$\ddot{y}+\beta\dot{y}+\omega_0^2 y+bg(y,\dot{y},t)=f(t), \tag{128}$$

where b is a small constant, f is a white-noise stimulus. It is supposed that β and b are small in some sense such that the system is lightly damped and weakly nonlinear. We rewrite (128) as

$$\ddot{y}+\beta_{\mathrm{eq}}\dot{y}+\omega_{\mathrm{eq}}^2 y+e(y,\dot{y},t)=f(t), \tag{129}$$

where β_{eq} is the equivalent linear damping coefficient and ω_{eq}^2 is the equivalent linear stiffness coefficient (both per unit mass) and e is called the error term. If e is zero then (129) is linear and is readily solved. The smaller e is, then the smaller the error in neglecting it. We therefore chose ω_{eq} and β_{eq} so that e is a minimum.

Thus the motion should approximate a sinusoid with a slow random modulation of amplitude and phase, that is

$$y(t) \approx A(t) \sin[\omega_{eq} t + \phi(t)]. \tag{130}$$

The amplitude $A(t)$ and phase $\phi(t)$ are both slowly varying functions of time; that is, they do not change appreciably over one cycle of the motion. If one now minimizes (129) with respect to β_{eq} and ω_{eq}, assuming the process is stationary, one finds that (Caughey 1963)

$$\beta_{eq} = \beta + b\overline{\dot{y}g(y, \dot{y}, t)}/\overline{\dot{y}^2}, \tag{131}$$

$$\omega_{eq}^2 = \omega_0^2 + b\overline{yg(y, \dot{y}, t)}/\overline{y^2}, \tag{132}$$

where the bars denote a time average. In our dielectric problem the function g is *non-hereditary*; that is, it does not depend on the *past history* of the motion. Thus the time averages may be replaced by the ensemble averages

$$\beta_{eq} = \beta + b\langle \dot{y}g(y)\rangle / \langle \dot{y}^2\rangle, \tag{133}$$

$$\omega_{eq}^2 = \omega_0^2 + b\langle yg(y)\rangle / \langle y^2\rangle. \tag{134}$$

The $\dot{y}$ term has been omitted in g because g does not depend on $\dot{y}$ in the two-dipole problem, as we shall see presently. If the error $e(y, \dot{y}, t)$ is neglected in (128) the response is Gaussian if $f(t)$ is Gaussian. The underlying probability density is

$$W(y, \dot{y}) = \frac{1}{2\pi}(\langle y^2\rangle\langle \dot{y}^2\rangle)^{-\frac{1}{2}} \exp\left[-\frac{1}{2}\left(\frac{y^2}{\langle y^2\rangle} + \frac{\dot{y}^2}{\langle \dot{y}^2\rangle}\right)\right]. \tag{135}$$

Thus if e is neglected (133) and (134) reduce to

$$\beta_{eq} = \beta, \tag{136}$$

$$\omega_{eq}^2 = \omega_0^2 + b\langle yg(y)\rangle / \langle y^2\rangle. \tag{137}$$

To apply the method to our present system we write the η equation, namely

$$\ddot{\eta} + \beta\dot{\eta} + V_0(1/I_1 + 1/I_2)\sin 2\eta = \tfrac{1}{2}(\lambda_1/I_1 - \lambda_2/I_2) \tag{138}$$

as

$$\ddot{\eta} + \beta\dot{\eta} + \tfrac{1}{2}\omega_0^2 \sin 2\eta = \tfrac{1}{2}(\lambda_1/I_1 - \lambda_2/I_2) \tag{139}$$

and compare it with (128). By subtraction (139) becomes

$$\ddot{\eta} + \beta\dot{\eta} + \omega_0^2\eta + \tfrac{1}{2}\omega_0^2(\sin 2\eta - 2\eta) = f(t). \tag{140}$$

Thus

$$b = \tfrac{1}{2}\omega_0^2, \tag{141}$$

$$f(t) = \tfrac{1}{2}(\lambda_1/I_1 - \lambda_2/I_2), \tag{142}$$

$$g(\eta) = (\sin 2\eta - 2\eta), \tag{143}$$

so that

$$\omega_{eq}^2 = \omega_0^2\left[1 + \frac{1}{2}\frac{\langle \eta \sin 2\eta - 2\eta^2\rangle_0}{\langle \eta^2\rangle_0}\right] \tag{144}$$

The evaluation of the averages in (144) with the use of (135) always leads to a complicated power series that does not give much insight into the physics of the problem. An approximation that gives a simple expression for ω_{eq} is

$$\sin 2\eta = 2\eta - \frac{(2\eta)^3}{3!}. \tag{145}$$

This corresponds to replacing the pendulum equation by the Duffing equation (McLachlan 1956). Thus (144) reduces to

$$\omega_{eq}^2 = \omega_0^2[1-\tfrac{2}{3}\langle\eta^4\rangle_0/\langle\eta^2\rangle_0]. \tag{146}$$

In the Gaussian approximation we have

$$\langle\eta^4\rangle_0 = 3\langle\eta^2\rangle_0^2 \tag{147}$$

and then (146) becomes

$$\omega_{eq}^2 = \omega_0^2[1-2\langle\eta^2\rangle_0]. \tag{148}$$

From (66)

$$\langle\eta^2\rangle_0 = \gamma_1 = kT/8V_0 \tag{149}$$

and so

$$\omega_{eq}^2 = \omega_0^2[1-kT/4V_0]. \tag{150}$$

This indicates a temperature dependence of the frequency of oscillation as first indicated by Marchesoni *et al.* (1985) or equivalently a dependence of the shape of the decay function on the thermal velocity as noted by Coffey *et al.* (1982*a*) and Reid (1983). This is a direct consequence of the nonlinear nature of the system and is a manifestation of the lengthening of the periodic time with increase in amplitude that occurs in nonlinear vibrating systems.

Note that ω_{eq} will depend on all powers of T; the linear dependence is simply because we have replaced the sine nonlinearity with a cubic one. The energy or temperature dependence arising from the cubic term will, however, almost always be the dominant term of the nonlinear behaviour. This temperature dependence of the natural frequency of oscillation automatically implies that the frequency of maximum FIR absorption should decrease as the temperature is increased.

According to (125), then,

$$\omega_{m1\,eq} \approx 2\omega_0(1-\gamma_1-\beta^2/4\omega_0^2), \tag{151}$$

which decreases linearly with temperature in accordance with recent experiments on CH_2Cl_2 (Evans *et al.* 1982; Marchesoni *et al.* 1985). Note that this equation also allows us to plot $\omega_{m1\,eq}$ as a function of barrier height V_0. Our expression for $\omega_{m1\,eq}$ suggests that the Q-factor of the system decreases with temperature because

$$Q = \omega_{eq}/\beta = Q_0(1-\gamma_1) \tag{152}$$

to first order in γ_1. This indicates that the sharpness of the resonance peak decreases as temperature increases. It is also of interest to investigate how the angular velocity correlation functions are affected by the nonlinear behaviour of the system. We have

$$\omega_{1\,eq} = (\omega_{eq}^2-\tfrac{1}{4}\beta^2)^{\frac{1}{2}} \tag{153}$$

or

$$\omega_{1\,eq} = \sqrt{(\omega_1^2-kT/2J)}. \tag{154}$$

Thus

$$\langle \dot{\eta}(0)\,\dot{\eta}(t)\rangle_0 = (kT/4J)\,e^{-\frac{1}{2}\beta t}\,[\cos\sqrt{(\omega_1^2 - kT/2J)}\,t - (\beta/2\omega_1)\sin\sqrt{(\omega_1^2 - kT/2J)}\,t], \tag{155}$$

$$\sqrt{\langle \dot{\eta}^2\rangle} = \sqrt{(kT/2J)}, \tag{156}$$

thus showing the connection between the oscillation and the orbital periods of the $\dot{\eta}$ variable.

This dependence of the shape of the angular velocity correlation functions on the thermal velocity is borne out by exact numerical solution of the pendulum problem as carried out by Coffey *et al.* (1982*a*) and by Reid (1983). Thus the Krylov and Bogoliubov method is able to qualitatively reproduce many features of the full nonlinear solution. It also has the advantage that it allows one to obtain analytic formulae for the spectrum that is not possible from methods based on the Brinkman equations. Finally, we remark that our analysis has effectively ignored relaxation due to barrier crossing by the dipoles. This is taken account of exactly by the full nonlinear solution based on the Brinkman equations. It may be incorporated approximately into our analysis by using the method of Praestgaard & van Kampen (1981) as adapted by Marchesoni & Vij (1985). This will again allow us to obtain analytic formulae for the spectrum. In a future publication we shall make comparisons between the present solution and that based on an exact solution of the Brinkman equations.

We thank Professor F. J. M. Farley, Dr F. Marchesoni, Professor B. K. P. Scaife, Professor W. Schröer and Dr J. K. Vij for helpful conversations. We also thank Ms F. Cleary and Ms R. Egan for checking of the formulae in the manuscript. The Nuffield Foundation and the Science Stimulation Programme of the EEC are thanked for travel grants. Trinity College Dublin and the Irish Department of Education are thanked for the award of a Research Studentship to P. M. C. The analysis in terms of normal modes was suggested by Professor F. J. M. Farley.

References

Budó, A. 1949 *J. chem. Phys.* **17**, 686–691.

Calderwood, J. H., Coffey, W. T., Morita, A. & Walker, S. 1976 *Proc. R. Soc. Lond.* A **352**, 275–288.

Calderwood, J. H. & Coffey, W. T. 1977 *Proc. R. Soc. Lond.* A **356**, 269–286.

Caughey, T. K. 1963 *J. acoust. Soc. Am.* **35**, 1706–1711.

Coffey, W. T. & Evans, M. W. 1978 *Molec. Phys.* **35**, 975–983.

Coffey, W. T., Rybarsch, C. & Schröer, W. 1982*a* *Phys. Lett.* A **88**, 331–334.

Coffey, W. T., Rybarsch, C. & Schröer, W. 1982*b* *Chem. Phys. Lett.* **92**, 245–249.

Coffey, W. T., Evans, M. W. Grigolini, P. 1984 *Molecular diffusion and spectra*. New York: John Wiley.

Coffey, W. T. 1985 Development and application of the theory of Brownian motion. In *Dynamical processes in condensed matter* (M. W. Evans). *Adv. chem. Phys.* **63**, 69–252.

Coffey, W. T. 1986 *Chem. Phys. Lett.* **123**, 416–422.

Cramér, H. 1970 Random variables and probability distributions. *Cambridge tracts on mathematics and mathematical physics*, no. 36. Cambridge University Press.

Croxton, C. A. 1974 Liquid state physics – a statistical mechanical introduction. *Cambridge Monographs on Physics*. Cambridge University Press.

Evans, M. W., Evans, G. J., Coffey, W. T. & Grigolini, P. 1982 *Molecular dynamics and the theory of broad-band spectroscopy*. New York: John Wiley.

Frenkel, J. 1946 *The kinetic theory of liquids*. Oxford University Press.
Fröhlich, H. 1949 *Theory of dielectrics*. Oxford University Press.
Hill, N. E. 1963 *Proc. phys. Soc.* **82**, 723–727.
Marchesoni, F. & Vij, J. K. 1985 *Z. Phys.* B. **58**, 187–198.
Marchesoni, F., Vij, J. K. & Coffey, W. T. 1985 *Z. Phys.* B **61**, 357–366.
McConnell, J. R. 1980 *Rotational Brownian motion and dielectric theory*. London: Academic Press.
McLachlan, N. W. 1956 *Ordinary nonlinear differential equations*. Oxford University Press.
Praestgaard, E. & van Kampen, N. G. 1981 *Molec. Phys.* **43**, 33–45.
Reid, C. J. 1983 *Molec. Phys.* **49**, 331–345.
Risken, H. & Vollmer, H. D. 1982 *Molec. Phys.* **46**, 1073–1076.
Rocard, M. Y. 1933 *J. Phys., Paris* **4**, 247–250.
Scaife, B. K. P. 1971 *Complex permittivity*. London: The English Universities Press.
Sears, V. F. 1965 *Proc. phys. Soc.* **86**, 953–964.
Wyllie, G. 1971 *J. Phys.* C. **4**, 564–568.

Appendix A. Calculation of orientational correlation functions from angular velocity correlation functions

To see how this is accomplished we first recall some elementary properties of correlation functions. If we define a correlation function $C(t)$ by (A, B are random variables)

$$C(t) = \langle A(t)\, B(0)\rangle, \tag{A 1}$$

then one may prove that (Evans *et al.* 1982)

$$\langle \dot{A}(t)\, B(0)\rangle = -\langle A(t)\, \dot{B}(0)\rangle \tag{A 2}$$

and

$$\langle \dot{A}(0)\, A(0)\rangle = 0. \tag{A 3}$$

Also, in the particular case of the autocorrelation function where $A = B$

$$\langle \dot{A}(t)\, A(0)\rangle = -\langle A(t)\, \dot{A}(0)\rangle. \tag{A 4}$$

In what follows we shall make use of these relations to find a connection between orientational and angular velocity correlation functions. We first introduce the Laplace transforms

$$\Phi_1(s) = \mathscr{L}\{\phi_1(t)\}, \quad \Phi_2(s) = \mathscr{L}\{\phi_2(t)\}. \tag{A 5}$$

Also

$$\mathscr{L}\{\dot{\phi}_1(t)\} = s\Phi_1(s) - \phi_1(0). \tag{A 6}$$

Now the Laplace transform of the angular-velocity ACF is

$$\begin{aligned}\mathscr{L}\{\langle \dot{\phi}_1(0)\, \dot{\phi}_1(t)\rangle_0\} &= \langle \dot{\phi}_1(0)\, \mathscr{L}\{\dot{\phi}_1(t)\}\rangle_0 \\ &= \langle \dot{\phi}_1(0)\, [s\Phi_1(s) - \phi_1(0)]\rangle_0 = s\langle \dot{\phi}_1(0)\, \Phi_1(s)\rangle_0\end{aligned} \tag{A 7}$$

by (A 3). Thus

$$\langle \dot{\phi}_1(0)\, \Phi_1(s)\rangle_0 = \frac{1}{s}\langle \dot{\phi}_1(0)\, \mathscr{L}\{\dot{\phi}_1(t)\}\rangle_0.$$

Now

$$\begin{aligned}\mathscr{L}\{\langle \phi_1(t)\, \dot{\phi}_1(0)\rangle_0\} &= \langle \dot{\phi}_1(0)\, \Phi_1(s)\rangle_0 = -\mathscr{L}\{\langle \dot{\phi}_1(t)\, \phi_1(0)\rangle_0\} \\ &= -s\langle \Phi_1(s)\, \phi_1(0)\rangle_0 + \langle \phi_1^2(0)\rangle_0,\end{aligned} \tag{A 8}$$

but by (A 7)

$$\mathscr{L}\{\langle \dot{\phi}_1(0)\, \dot{\phi}_1(t)\rangle_0\} = s\langle \dot{\phi}_1(0)\, \Phi_1(s)\rangle_0; \tag{A 9}$$

that is,

$$\frac{1}{s^2}\mathscr{L}\{\langle\dot{\phi}_1(0)\,\dot{\phi}_1(t)\rangle_0\} = -\langle\Phi_1(s)\,\phi_1(0)\rangle_0 + \langle\phi_1^2(0)\rangle_0/s \tag{A 10}$$

or

$$(1/s^2)\,\mathscr{L}\{\langle\dot{\phi}_1(0)\,\dot{\phi}_1(t)\rangle_0\} = \tfrac{1}{2}\mathscr{L}\{\langle(\Delta\phi_1)^2\rangle_0\}. \tag{A 11}$$

Similarly

$$(1/s^2)\,\mathscr{L}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_2(t)\rangle_0\} = \tfrac{1}{2}\mathscr{L}\{\langle(\Delta\phi_2)^2\rangle_0\}. \tag{A 12}$$

Thus we may compute $\langle(\Delta\phi_1)^2\rangle_0$ and $\langle(\Delta\phi_2)^2\rangle_0$ from a knowledge of the angular-velocity ACFS. We now proceed to the calculation of the orientational cross correlation function. It is helpful to first write down

$$\tfrac{1}{2}\mathscr{L}\{\langle\Delta^2\phi_1\,\phi_2\rangle_0\} = \tfrac{1}{2}\langle(\phi_1^2+\phi_2^2)/s - 2\phi_2(0)\,\Phi_1(s)\rangle_0, \tag{A 13}$$

because

$$\langle\phi_1^2(0)\rangle_0 = \langle\phi_1^2(t)\rangle_0, \tag{A 14}$$

$$\langle\phi_2^2(0)\rangle_0 = \langle\phi_2^2(t)\rangle_0. \tag{A 15}$$

We also note the property of cross-correlation functions

$$\langle\dot{\phi}_1(0)\,\dot{\phi}_2(t)\rangle_0 = \langle\dot{\phi}_2(0)\,\dot{\phi}_1(t)\rangle_0. \tag{A 16}$$

Taking the Laplace transform of the left-hand side of equation (A 16) we have

$$\mathscr{L}\{\langle\dot{\phi}_1(0)\,\dot{\phi}_2(t)\rangle_0\} = \langle\dot{\phi}_1(0)\,[s\Phi_2(s)-\phi_2(0)]\rangle_0 = s\langle\dot{\phi}_1(0)\,\Phi_2(s)\rangle_0. \tag{A 17}$$

Thus

$$\langle\dot{\phi}_1(0)\,\Phi_2(s)\rangle_0 = (1/s)\,\mathscr{L}\{\langle\dot{\phi}_1(0)\,\dot{\phi}_2(t)\rangle_0\} \tag{A 18}$$

and similarly

$$\langle\dot{\phi}_2(0)\,\Phi_1(s)\rangle_0 = (1/s)\,\mathscr{L}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_1(t)\rangle_0\}. \tag{A 19}$$

Now by (A 2)

$$\langle\phi_2(0)\,\dot{\phi}_1(t)\rangle_0 = -\langle\phi_1(t)\,\dot{\phi}_2(0)\rangle_0. \tag{A 20}$$

Taking the Laplace transform of the left-hand side of (A 20) yields

$$\mathscr{L}\{\langle\phi_2(0)\,\dot{\phi}_1(t)\rangle_0\} = \langle\phi_2(0)\,\mathscr{L}\{\dot{\phi}_1(t)\}\rangle_0 = s\langle\phi_2(0)\,\Phi_1(s)\rangle_0 - \langle\phi_1(0)\,\phi_2(0)\rangle_0. \tag{A 21}$$

Thus with (A 20)

$$-\langle\Phi_1(s)\,\dot{\phi}_2(0)\rangle_0 = s\langle\phi_2(0)\,\Phi_1(s)\rangle_0 - \langle\phi_1(0)\,\phi_2(0)\rangle_0 \tag{A 22}$$

and with (A 19)

$$-\frac{1}{s^2}\mathscr{L}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_1(t)\rangle_0\} = \langle\phi_2(0)\,\Phi_1(s)\rangle_0 - \langle\phi_2(0)\,\phi_1(0)\rangle_0/s. \tag{A 23}$$

Whence

$$\langle\phi_2(0)\,\Phi_1(s)\rangle_0 = -(1/s^2)\,\mathscr{L}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_1(t)\rangle_0\} + (1/s)\,\langle\phi_2(0)\,\phi_1(0)\rangle_0. \tag{A 24}$$

We now substitute (A 24) into (A 13) to get

$$\tfrac{1}{2}\mathscr{L}\{\langle\Delta^2\phi_1\,\phi_2\rangle_0\} = \tfrac{1}{2}[\langle(\phi_1^2+\phi_2^2)/s\rangle_0 + (2/s^2)\,\mathscr{L}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_1(t)\rangle_0\} - 2\langle\phi_2(0)\,\phi_1(0)\rangle_0/s]. \tag{A 25}$$

Thus

$$\tfrac{1}{2}\mathscr{L}\{\langle\Delta^2\phi_1\,\phi_2\rangle_0\} = \tfrac{1}{2}\langle(\phi_1-\phi_2)^2\rangle_0/s + (1/s^2)\,\mathscr{L}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_1(t)\rangle_0\}, \tag{A 26}$$

where the first term on the right-hand side of (A 25) is to be evaluated at $t = 0$.

Because the stationary distribution in the absence of an external field is

$$f = A\exp\{-(1/2kT)(I_1\dot{\phi}_1^2 + I_2\dot{\phi}_2^2) + (2V_0/kT)[1-\tfrac{1}{2}(\phi_1-\phi_2)^2]\} \tag{A 27}$$

(A is a given constant) then

$$\langle(\phi_1-\phi_2)^2\rangle_0 = \frac{\displaystyle\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-(V_0/kT)(\phi_1-\phi_2)^2}(\phi_1-\phi_2)^2\,d\phi_1\,d\phi_2}{\displaystyle\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-(V_0/kT)(\phi_1-\phi_2)^2}\,d\phi_1\,d\phi_2}. \tag{A 28}$$

(The velocity-dependent part of the solution simply integrates out.) Now

$$\eta = \tfrac{1}{2}(\phi_1-\phi_2)$$

then (A 28) reduces to

$$\langle(\phi_1-\phi_2)^2\rangle_0 = \frac{\displaystyle\int_{-\infty}^{\infty} e^{-(4V_0/kT)\eta^2}4\eta^2\,d\eta}{\displaystyle\int_{-\infty}^{\infty} e^{-(4V_0/kT)\eta^2}\,d\eta}. \tag{A 29}$$

We now recall that (a is constant)

$$\int_{-\infty}^{\infty} e^{-ap^2}\,dp = (\pi/a)^{\frac{1}{2}}, \tag{A 30}$$

$$\frac{\partial}{\partial a}\int_{-\infty}^{\infty} e^{-ap^2}\,dp = -\int_{-\infty}^{\infty} p^2 e^{-ap^2}\,dp = -\frac{1}{2a}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}, \tag{A 31}$$

so that

$$\frac{\displaystyle\int_{-\infty}^{\infty} p^2 e^{-ap^2}\,dp}{\displaystyle\int_{-\infty}^{\infty} e^{-ap^2}\,dp} = \frac{(1/2a)(\pi/a)^{\frac{1}{2}}}{(\pi/a)^{\frac{1}{2}}} = \frac{1}{2a} \tag{A 32}$$

whence with

$$a = 4V_0/kT, \tag{A 33}$$

$$1/2a = kT/8V_0, \tag{A 34}$$

we have

$$\tfrac{1}{2}\mathscr{L}\{\langle\Delta^2\phi_1\phi_2\rangle_0\} = kT/4V_0 s + (1/s^2)\mathscr{L}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_1(t)\rangle_0\}. \tag{A 36}$$

We now summarize the results of this section

$$\langle\cos\phi_1(0)\cos\phi_1(t)\rangle_0 = \tfrac{1}{2}\exp[-\tfrac{1}{2}\langle(\Delta\phi_1)^2\rangle_0], \tag{A 36}$$

$$\langle\cos\phi_2(0)\cos\phi_2(t)\rangle_0 = \tfrac{1}{2}\exp[-\tfrac{1}{2}\langle(\Delta\phi_2)^2\rangle_0], \tag{A 37}$$

$$\langle\cos\phi_2(0)\cos\phi_1(t)\rangle_0 = \tfrac{1}{2}\exp[-\tfrac{1}{2}\langle(\Delta\phi_1\phi_2)^2\rangle_0], \tag{A 38}$$

$$\tfrac{1}{2}\mathscr{L}\{\langle\Delta\phi_1)^2\rangle_0\} = (1/s^2)\mathscr{L}\{\langle\dot{\phi}_1(0)\,\dot{\phi}_1(t)\rangle_0\}, \tag{A 39}$$

$$\tfrac{1}{2}\mathscr{L}\{\langle(\Delta\phi_2)^2\rangle_0\} = (1/s^2)\mathscr{L}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_2(t)\rangle_0\}, \tag{A 40}$$

$$\tfrac{1}{2}\mathscr{L}\{\langle(\Delta\phi_1\phi_2)^2\rangle_0\} = kT/4V_0 s + (1/s^2)\mathscr{L}\{\langle\dot{\phi}_2(0)\,\dot{\phi}_1(t)\rangle_0\}. \tag{A 41}$$

The mean dipole moment is

$$\langle(\boldsymbol{m}(0)\cdot\boldsymbol{e})(\boldsymbol{m}(t)\cdot\boldsymbol{e})\rangle_0 = \tfrac{1}{2}(\{\mu_1^2 \exp[-\tfrac{1}{2}\langle(\Delta\phi_1)^2\rangle_0] + \mu_2^2 \exp[-\tfrac{1}{2}\langle(\Delta\phi_2)^2\rangle_0] + 2\mu_1\mu_2 \exp[-\tfrac{1}{2}\langle(\Delta\phi_1\phi_2)^2\rangle_0]\}). \tag{A 42}$$

A useful check on these results is to compare the value of (A 42) when $t = 0$ with that obtained from (62) at $t = 0$.

With the aid of the initial value theorem of Laplace transformation, namely

$$\lim_{t\to 0} f(t) = \lim_{s\to\infty} sF(s), \tag{A 43}$$

where $F(s) = \mathscr{L}\{f(t)\}$ and from (A 39)–(A 41) one readily finds that (A 42) has the initial value

$$\tfrac{1}{2}(\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\,\mathrm{e}^{-kT/4V_0}). \tag{A 44}$$

Equation (62), on the other hand, has initial value

$$\tfrac{1}{2}(\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\,\mathrm{e}^{-2\langle\eta^2\rangle_0}), \tag{A 45}$$

which is the same as (A 44) on recalling that

$$\langle\eta^2\rangle_0 = kT/8V_0. \tag{A 46}$$

Appendix B. A complete analytic formula for the complex polarizability: theoretical evidence for the existence of a peak structure at high frequencies

In the main body of the paper we have contented ourselves with giving the first three terms in the series expansion of the complex polarizability. It has also been noted that the second and third terms of the series resonate at the fundamental and its second harmonic respectively. It is instructive to give the complete expression for the complex polarizability in the form of a triple sum as this shows a curious harmonic peak structure at high frequencies. This peak structure should not, however, be readily observable in liquids as the friction coefficient β is generally so large as to damp out all peaks save that at the fundamental frequency. We may derive the triple sum for $\alpha(\omega)$ as follows. Referring to our expression for C_χ we find on expanding the outer exponential that

$$C_\chi = \frac{1}{2}\left(\exp\frac{\gamma}{2}\right)\sum_{p=0}^{\infty}\frac{(-\frac{1}{2}\gamma)^p}{p!}\exp[-(\tfrac{1}{2}\gamma+p)\beta t]. \tag{B 1}$$

With the aid of (B 1), $M(t)$ may now (on writing $x(t)$ in the form $R\,\mathrm{e}^{-\frac{1}{2}\beta t}\sin(\omega_1 t+\psi)$ then the use of the binomial theorem combined with the series expansion of the exponential function as described for the torsional oscillator in Coffey *et al.* (1984, chapter 4) or Calderwood *et al.* (1976)) be expressed as the triple sum (for simplicity $\mu_1 = \mu_2 = \mu$)

$$\frac{\mu^2}{2}\exp\frac{\gamma}{2}\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{m=0}^{q}\left\{\frac{(-1)^m}{q!}\left(\frac{\omega_0}{2\mathrm{i}\omega_1}\right)^q\binom{q}{m}\frac{(-\frac{1}{2}\gamma)^p}{p!}\right.$$
$$\times[(a_1^2\gamma_1)^q\,\mathrm{e}^{-a_1^2\gamma_1}+(a_2^2\gamma_1)^q\,\mathrm{e}^{-a_2^2\gamma_1}+2\,\mathrm{e}^{-\frac{1}{2}(a_1^2+a_2^2)\gamma_1}(-a_1a_2\gamma_1)^q] \tag{B 2}$$
$$\times[\mathrm{e}^{-\mathrm{i}(2m-q)\psi}\cdot\mathrm{e}^{-\frac{1}{2}q\beta t}\,\mathrm{e}^{-\mathrm{i}(2m-q)\omega_1 t}\,\mathrm{e}^{-(\frac{1}{2}\gamma+p)\beta t}],$$

where the phase angle ψ is given by

$$\psi = \tan^{-1} 2\omega_1/\beta. \tag{B 3}$$

On substituting (B 2) into the complex polarizability formula and making use of the shifting theorem of Fourier transformation we immediately find the complete expression for $\alpha(\omega)$ as

$$\begin{aligned}\frac{\mu^2}{2kT}\,e^{\frac{1}{2}\gamma} \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{m=0}^{q} \Bigg\{ &\frac{(-1)^m}{q!}\left(\frac{\omega_0}{2i\omega_1}\right)^q \binom{q}{m}\left(\frac{-\frac{1}{2}\gamma}{p!}\right)^p [(a_1^2\gamma_1)^q\, e^{-a_1^2\gamma_1} \\ &+ (a_2^2\gamma_1)^q\, e^{-a_2^2\gamma_1} + 2\,e^{-\frac{1}{2}(a_1^2+a_2^2)\gamma_1}(-a_1 a_2 \gamma_1)^q]\, e^{-i(2m-q)\psi} \\ &\times \frac{[\frac{1}{2}(q+\gamma+2p)\beta + i(2m-q)\omega_1]}{\frac{1}{2}(q+\gamma+2p)\beta + i(\omega+2m-q\omega_1)}\Bigg\}. \end{aligned} \tag{B 4}$$

By inspection of this formula we find that resonant peaks will arise whenever

$$\omega = (q-2m)\,\omega_1. \tag{B 5}$$

If the friction becomes very small it is evident that (B 4) becomes a series of delta functions of the general form $\delta(\omega \pm n\omega_0)$, $n = 0, 1, 2, 3$. This follows from the definition of $\delta(y)$ as

$$\delta(y) = \lim_{\lambda\to 0} \frac{1}{\pi}\frac{\lambda}{\lambda^2+y^2}. \tag{B 6}$$

This conclusion may also be aimed at directly from our closed form expression for $M(t)$ (70) by allowing β to tend to zero in that expression and expressing the resulting double transcendental functions, which are all of the form $\exp(\pm\cos\omega t)$, as a Fourier series, the coefficients of which are the Bessel functions of imaginary argument. This series is then substituted into the $\alpha(\omega)$ formula to yield the undamped spectrum as

$$\begin{aligned}\alpha(\omega) = \frac{\mu^2}{2kT}\Bigg([1+e^{-\frac{1}{2}\gamma_1}] - i\omega \sum_{n=-\infty}^{n=\infty} \{[&e^{-a_1^2\gamma_1} J_n(i a_1^2\gamma_1) + e^{-a_2^2\gamma_1} J_n(i a_2^2\gamma_1)] \\ &\times e^{-\frac{1}{2}in\pi}\,\delta(\omega+n\omega_0) + 2\,e^{-\frac{1}{2}(a_1^2+a_2^2)\gamma_1} J_n(i a_1 a_2 \gamma_1)\, e^{\frac{1}{2}in\pi}\,\delta(\omega-n\omega_0)\}\Bigg). \end{aligned} \tag{B 7}$$

where J_n denotes the Bessel function of the first kind of integer order.

We must also note that our theoretical analysis of the model has been in terms of parameters V_0, I_1, I_2, etc. For numerical analysis and for comparison with experimental spectra, etc., we have found that it is always easier to introduce the parameter set. (Our remarks hold equally for the nonlinear version of the model.)

$$\hat{\alpha} = (kT/I_1)^{\frac{1}{2}}, \quad \hat{\gamma} = V_0/I_1\hat{\alpha}, \quad \beta, \quad I_r = I_2/I_1, \tag{B 8}$$

$\hat{\alpha}$ is the thermal energy parameter, $\hat{\gamma}$ the barrier height parameter, β the friction and I_r the moment of inertia parameter. $M(t)$ then becomes in terms of these

$$\begin{aligned} M(t) = \tfrac{1}{2}\mu^2 \exp[-\tfrac{1}{2}a_2(\hat{\alpha}^2/\beta^2)(\beta t - 1 + e^{-\beta t})] \\ \times \{\exp[-a_1^2(\hat{\alpha}/8\hat{\gamma})(1-x)] + \exp[-\tfrac{1}{2}(a_1^2+a_2^2)(\hat{\alpha}/8\hat{\gamma})] \\ \times \exp[-a_1 a_2(\hat{\alpha}x/8\hat{\gamma})] + \exp[-a_2^2(\hat{\alpha}/8\hat{\gamma})(1-x)]\}. \end{aligned} \tag{B 9}$$

The motion is then completely specified by $\hat{\alpha}$, $\hat{\gamma}$, β, I_r. For example, the natural frequency of oscillation is $\sqrt{(4\hat{\alpha}\hat{\gamma}a_1^{-1})}$ whereas the Debye relaxation time is $2\beta^2/(a_2\hat{\alpha}^2)$. This parameter set also has the advantage that it arises quite naturally when the variables are separated in the Fokker–Planck–Kramers equation underlying the model.

Finally we note that (B 9) is written for the case where the correlation function of the random torques λ_1, λ_2 is defined as

$$\langle \lambda_i(t)\,\lambda_j(t)\rangle = 2\delta_{i,j}\,kT\,\beta I_i\,\delta(t), \quad i,j = 1,2, \tag{B 10}$$

$\delta_{i,j}$ being the Kronecker delta and $\delta(t)$ the Dirac delta function. Some authors prefer to define the correlation function above as

$$\langle \lambda_i(t)\,\lambda_j(t)\rangle = 4\delta_{i,j}\,kT\beta I_i\,\delta(t). \tag{B 11}$$

The effect of doing this simply makes

$$a_2\hat{\alpha}^2/2\beta \to a_2\hat{\alpha}^2/\beta^2$$

and

$$\hat{\alpha}/8\hat{\gamma} \to \hat{\alpha}\nu/4\hat{\gamma} \tag{B 12}$$

in (B 9).