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# Complex susceptibility of the cage model of polar liquids

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## Abstract

The Langevin equations of motion of the cage model of polar liquids originally proposed by Hill (1963 *Proc. Phys. Soc.* **82** 723) are solved for the first time for the particular case of rotation about a fixed axis, using a newly developed matrix continued fraction method. It is shown that the cage model predicts both the low-frequency Debye relaxation and a pronounced high-frequency (Poley) absorption peak in the far-infrared (FIR) region. The similarity of the equations of motion of the cage model to the equations which arise in the problem of generalizing the Onsager model of polar fluids to include a time-varying applied field suggests that the FIR (Poley) absorption may have its origins in the combined influence of molecular inertia and the torque due to the reaction field in the frequency-dependent version of the Onsager model. The complex susceptibility yielded by the cage model is shown to be in good agreement with experimental data on CH<sub>3</sub>Cl that were taken as a typical example. Moreover, a simple approximate formula based on a small-oscillation approximation can describe accurately the dielectric spectra in most cases of interest.

## 1. Introduction

The far-infrared (FIR) absorption spectrum of low-viscosity liquids contains a broad peak of resonant character with a resonant frequency and intensity which decrease with increasing temperature [1, 2]. This phenomenon is known as the Poley absorption [3]. It takes its name from the work of Poley [3] who observed that the difference  $\epsilon_\infty - n_{ir}^2$  between the high-frequency dielectric permittivity  $\epsilon_\infty$  and the square of the infrared refractive index  $n_{ir}^2$  of several dipolar liquids was proportional to the square of the dipole moment of a molecule,

leading him to predict a significant power absorption in these liquids in the FIR region. A detailed review of the problem and of various theoretical approaches to its solution is given in [1] and [2], where the interested reader can find many related references.

As far as other physical systems are concerned FIR absorption has also been observed in supercooled viscous liquids and glasses (for a detailed review see [4]). A similar resonance phenomenon seems to occur [4] in the crystalline structures of ice clathrates where dipolar (and non-dipolar) molecules are trapped in the small-size symmetrical and rigid cages formed by tetrahedral hydrogen-bounded water molecules. The encaged molecules undergo both torsional oscillations and orientational diffusion [4]. Thus, like liquids and glasses, the spectra of ice clathrates exhibit a resonance-type peak in the FIR region, a broad relaxation spectrum due to the motion of the encaged molecules at intermediate frequencies (in this instance measured at low temperatures in the megahertz region but also occurring at high temperatures in the microwave region as in simple polar liquids) and a very low-frequency broad-band relaxation process due to orientational motion of the water molecules confined at the lattice sites. The former relaxation process has a small activation energy [4] and its relaxation rate follows the Arrhenius law. Yet another phenomenon which appears to be related to those described above is the peak in the low-frequency (in the region of acoustic phonons of the corresponding crystals) Raman spectra for a variety of glasses which appears to be an intrinsic feature of the glassy state [4]. Since the scattering intensity associated with this feature was analysed by using the Bose–Einstein statistics, the peak in the low-energy Raman spectra has been called the boson peak. Referring to the opening part of our discussion, dielectric loss spectra of several viscous liquids and glasses also exhibit a peak in the terahertz frequency range (particularly in the 40–80  $\text{cm}^{-1}$  range of the FIR spectra) [4]. That peak has again been identified as the boson peak, because the scattering function for the light is approximately proportional to the magnitude of the dielectric loss,  $\epsilon''$ .

The apparent similarities between the low-frequency Raman scattering peak and Poley FIR absorption peak has led one of us [4], on an analysis of the experimental data, to the conclusion that these are simply two different names for the same underlying molecular process which may be regarded as analogous to the torsion oscillations of molecules confined to the cage-like structures of an ice clathrate [1, 2]. Moreover, the overriding advantage of such a representation of the relaxation process is that it leads to the modelling of the process as the inertial effects [1, 2, 5, 6] of the rotational Brownian motion of a rigid dipolar molecule undergoing torsional oscillations about a temporary equilibrium position in the potential well created by its cage of neighbours. It follows from the foregoing discussion that the schematic description of the process corresponds to the itinerant oscillator or cage model of polar fluids originally suggested by Hill [7, 8]. Hill considered a specific mechanism whereby at any instant an individual polar molecule may be regarded as confined to a temporary equilibrium position in a cage formed by its neighbours where the potential energy surface may in general have several minima. The molecule is considered to librate (i.e. execute oscillations about temporary equilibrium positions) in this cage. Using an approximate analysis of this model based on the Smoluchowski equation [9] for the rotational diffusion of an assembly of non-interacting dipolar molecules proposed by Debye [10], Hill demonstrated that the frequency of the Poley absorption peak is inversely proportional to the square root of the moment of inertia of a molecule. Hill's model was later rigorously generalized to take full account of inertial effects. Furthermore, the angular velocity and orientational correlation functions were evaluated in the small oscillation approximation, using the Langevin equation of the theory of the Brownian motion, in a series of papers [11–13] beginning with the work of Wyllie [11]. These results are summarized in [1, 2, 9, 11]. The disadvantage of all these analyses, however, is that they invariably rely on a small-oscillation approximation because no reliable method of treating

the finite oscillation of the pendulum when the Brownian torques are included had existed [9]. Thus some of the most important non-linear aspects of the relaxation processes were omitted, an example being the dependence of the frequency of oscillation of the dipole on the amplitude of the oscillation. A preliminary attempt to include non-linear or anharmonic effects has been made in [14, 15]. Only very recently [16] has it become possible to treat the Brownian motion in a potential other than a parabolic one in a general fashion using matrix continued fractions. The solution has been illustrated [16] by considering the Brownian motion of a rotator in a cosine potential with a *fixed* equilibrium position rather than the *temporary* one of Hill's model.

It is the purpose of this paper to illustrate how Hill's model [7] may be solved exactly in the limit of a very large cage and small dipole using the existing results [15–17] for the free Brownian rotator [6] and the matrix continued fraction method for the fixed centre of oscillation cosine potential model [16]. The exact calculations allow one to judge how accurately expressions for the complex susceptibility based on the small-oscillation approximation may describe the system. In order to achieve our objective, we shall first summarize how, in the limit of large cage moment of inertia, the equations of motion of the cage and dipole will in general decouple. Moreover, we shall give the exact solution for the complex susceptibility for rotation about a fixed axis utilizing the newly developed matrix continued fraction method of [16]. In addition, we shall indicate how the problem may also be solved for rotation in space. Furthermore, we shall remark on the similarity of the cage or itinerant oscillator model to the problem of generalizing [18, 19] the Onsager model of the static permittivity of polar fluids to calculate the frequency-dependent complex susceptibility. Thus we shall pose our discussion of the Hill model in the context of the generalization of the Onsager model which suggests that the origin of the Poley absorption may lie in the long-range dipole–dipole interaction of the engaged molecule with its neighbours. We remark that in its original static form the Onsager model constitutes the first attempt to take into account the contribution of the long-range dipole–dipole interactions to the static permittivity of a polar fluid. The key difference between the dynamic Onsager model and its static counterpart is that when a time-varying external field is applied the reaction field produced by the action of the orienting dipole on its surroundings will lag [18, 19] behind the dipole. The net effect of this is to produce a torque on the dipole. If the inertia of the dipole is taken into account the torque will naturally give rise (as well as to the microwave Debye absorption peak) to a resonance absorption peak with peak frequency in the FIR region thus explaining the Poley absorption. The whole process is analogous to the behaviour of a driven damped pendulum in a uniform gravitational field with a time-varying centre of oscillation [2, 20].

In order to proceed, we first describe the problem of generalizing the Onsager model to include the frequency dependence of the relative permittivity and how this problem may be linked to the cage or itinerant oscillator model.

## 2. Generalization of the Onsager model—relation to the cage model

The Onsager model [1, 18, 19] consists essentially of a very large spherical dielectric sample of static relative permittivity  $\epsilon$  placed in a spatially uniform electric field which is applied along the polar axis. The effect of the long-range dipole–dipole coupling is taken account of by imagining that a particular (reference or tagged) dipole of the sample is situated within an empty spherical cavity at the centre of the sample (now a shell or cage). The polarizing effect of the dipole then creates a reaction field which exerts a torque on the dipole if the dipole direction is not the same as the reaction field direction, as is so in the time-varying case [18, 19]. In calculating the polarization of the sample when placed in the uniform external field, it is assumed that the shell may be treated macroscopically (i.e. by continuum electrostatics) while the orientation of

the (tagged) dipole in the cavity is treated using classical statistical mechanics. The treatment in the static case then yields the famous Onsager equation [1] (whence the static permittivity may be calculated) which was subsequently generalized to a macroscopic cavity by Kirkwood and Fröhlich [21]. We remark that in the static case the reaction field is a uniform field which is parallel to the dipole direction so that *it cannot orient the dipole*.

In order to attempt a generalization of the Onsager model to a time-varying applied field of angular frequency  $\omega$  for the purpose of explaining the FIR absorption peak, we shall suppose, following a suggestion of Fröhlich [22], that the surroundings of a tagged dipole, namely the shell or cage, may be treated as an inertia-corrected Debye dielectric [1, 2] so that the sample now has permittivity  $\varepsilon(\omega)$ . Thus, the electrical interactions between cage dipoles are ignored; the only interaction taken account of is that between the cage and the tagged dipole. We shall also suppose that a weak external uniform applied field parallel to the polar axis is switched off at an instant  $t = 0$  so that we may utilize the methods of linear response theory. The Langevin equation of motion of the surroundings is then

$$I_s \dot{\omega}_s(t) + \zeta_\mu[\omega_s(t) - \omega_\mu(t)] + \zeta_s \omega_s(t) + \mathbf{R}(t) \times \frac{\partial}{\partial \mathbf{R}} V[\boldsymbol{\mu}(t) \cdot \mathbf{R}(t)] = -\boldsymbol{\lambda}_\mu(t) + \boldsymbol{\lambda}_s(t), \quad (1)$$

while the Langevin equation of motion of the dipole  $\boldsymbol{\mu}$  in the cavity is

$$I_\mu \dot{\omega}_\mu(t) + \zeta_\mu[\omega_\mu(t) - \omega_s(t)] + \boldsymbol{\mu}(t) \times \frac{\partial}{\partial \boldsymbol{\mu}} V[\boldsymbol{\mu}(t) \cdot \mathbf{R}(t)] = \boldsymbol{\lambda}_\mu(t), \quad (2)$$

where we note that by Newton's third law

$$\boldsymbol{\mu} \times \frac{\partial V}{\partial \boldsymbol{\mu}} + \mathbf{R} \times \frac{\partial V}{\partial \mathbf{R}} = 0. \quad (3)$$

Note that we do not have to introduce the dipole moment of the surroundings explicitly as their influence is represented by  $\mathbf{R}(t)$ . In the Langevin equations (1) and (2), which reflect the balance of the torques acting on the cage and dipole, respectively,  $I_s$  is the moment of inertia of the surroundings (i.e. the cage) of the cavity which are supposed to rotate with angular velocity  $\omega_s$ ,  $\zeta_s \omega_s$  and  $\boldsymbol{\lambda}_s$  are the stochastic torques on the surroundings which are generated by the heat bath,  $I_\mu$  is the moment of inertia of the cavity dipole and  $\frac{\partial V}{\partial \boldsymbol{\mu}} \times \boldsymbol{\mu}$  is the torque on  $\boldsymbol{\mu}$ . The torque arises because in a time-varying applied field  $\boldsymbol{\mu}$  will not be parallel to the reaction field  $\mathbf{R}(t)$  unlike in a static field. The terms  $\zeta_\mu(\omega_\mu - \omega_s)$  and  $\boldsymbol{\lambda}_\mu$  represent the dissipative Brownian torques acting on  $\boldsymbol{\mu}$  due to the heat bath;  $\omega_\mu$  is the angular velocity of the dipole. Equations (1) and (2) are recognizably a form of the equations of motion of the itinerant oscillator model [9, 23] with a time-dependent potential. In the above equations the white-noise torques  $\boldsymbol{\lambda}_s$  and  $\boldsymbol{\lambda}_\mu$  are centred Gaussian random variables so that they obey Isserlis's theorem [9] and have correlation functions

$$\overline{\lambda_s^{(i)}(t) \lambda_s^{(j)}(t')} = 2kT \zeta_s \delta_{ij} \delta(t - t'), \quad (4)$$

$$\overline{\lambda_\mu^{(i)}(t) \lambda_\mu^{(j)}(t')} = 2kT \zeta_\mu \delta_{ij} \delta(t - t'), \quad (5)$$

where  $\delta_{ij}$  is Kronecker's delta,  $\delta(t - t')$  is the Dirac delta function, and  $i, j = 1, 2, 3$  refer to distinct Cartesian axes fixed in the system of mutually coupled rotators represented by equations (1) and (2). It is also assumed that  $\boldsymbol{\lambda}_s$  and  $\boldsymbol{\lambda}_\mu$  are uncorrelated, the overbars denoting the statistical average over the realizations in a small time  $|t - t'|$  of the Gaussian white-noise processes  $\boldsymbol{\lambda}_s$  and  $\boldsymbol{\lambda}_\mu$ . Thus the Langevin equations (1) and (2) are stochastic differential equations. We also note that the system is in general governed by the time-dependent Hamiltonian  $H$  given by

$$H = \frac{1}{2} I_s \omega_s^2 + \frac{1}{2} I_\mu \omega_\mu^2 + V(\boldsymbol{\mu} \cdot \mathbf{R}). \quad (6)$$

The instantaneous orientation of the dipole  $\mu$  is governed by the kinematic relation [1]

$$\dot{\mu}(t) = \omega_{\mu}(t) \times \mu(t). \quad (7)$$

Our objective is to calculate from the system of equations (1)–(7) the dipole autocorrelation function of an assembly of encaged dipoles

$$C_{\mu}(t) = \frac{\langle \mu(0) \cdot \mu(t) \rangle_0}{\langle \mu(0) \cdot \mu(0) \rangle_0}, \quad (8)$$

hence the complex susceptibility  $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$  of such an assembly from the linear response theory formula [18, 19]

$$\frac{\chi(\omega)}{\chi'(0)} = 1 - i\omega \int_0^{\infty} C_{\mu}(t) e^{-i\omega t} dt \quad (9)$$

( $\chi'(0) = \chi(0)$  is the static susceptibility). In equation (8), the zero inside the angular brackets, which denote equilibrium averages, refers to the instant at which the external uniform field  $F_0$  is switched off and the subscript zero outside the brackets indicates that the average is to be evaluated in the absence of that field. The complex susceptibility and permittivity are related by [1]

$$\chi(\omega) = \frac{\varepsilon(\omega) - n_{ir}^2}{4\pi G(\omega)} \quad (10)$$

where  $G(\omega)$  is the internal field correction factor [2].

The stochastic differential equations (1) and (2) cannot be integrated to yield equation (8) in explicit form as they stand. The reasons are: they are mutually coupled via the term  $I_{\mu}\dot{\omega}_{\mu}$  in equation (1) and  $\omega_s$  in equation (2); moreover, we have no knowledge of the functional form of the time-dependent reaction field  $R(t)$  save that it should still be spatially uniform; and that by quasi-electrostatics its Fourier transform  $\tilde{R}(\omega)$  should be of the order of magnitude [1]

$$\frac{\mu[\varepsilon(\omega) - n_{ir}^2]}{2\pi\varepsilon_0 a^3 [2\varepsilon(\omega) + n_{ir}^2]} \equiv \tilde{g}(\omega), \quad (11)$$

where  $a$  is the radius of the cavity. In the Onsager model the radius of the cavity  $a$  is determined from

$$v = \frac{4}{3}\pi a^3 N, \quad (12)$$

so that  $\frac{4}{3}\pi a^3$  is the mean volume/molecule, and  $N$  is the number of molecules in the spherical sample. It is apparent, since we do not know the functional form of  $R(t)$ , that no further progress can be made unless we make an assumption concerning the time-varying amplitude of  $R(t)$ . Thus we shall assume that the amplitude  $\tilde{g}(\omega)$  of the reaction field factor, equation (11), is only a very slowly varying function of the frequency (corresponding to a *quasi-stationary* function of the time) so that we may replace it by a constant. Thus the time dependence of  $R(t)$  arises solely from the time-varying angle between  $\mu$  and  $R$ . We shall now demonstrate how the variables may be separated in equations (1) and (2) by making the plausible assumption that the moment of inertia of the tagged dipole is much less than that of the surroundings or cage of dipoles. If this is so the dipole autocorrelation function  $C_{\mu}(t)$  will automatically factor into the product of the autocorrelation function of the surrounding inertia-corrected Debye dielectric and the autocorrelation function of the orientation of the dipole relative to its surroundings. We remark that the treatment closely resembles that of the egg model of orientation of a single-domain ferromagnetic particle in a ferrofluid proposed by Shliomis and Stepanov [24].

### 3. Calculation of the dipole correlation function

By addition and subtraction of equations (1) and (2) we have

$$I_\mu \dot{\omega}_\mu(t) + I_s \dot{\omega}_s(t) + \zeta_s \omega_s(t) = \lambda_s(t), \quad (13)$$

$$\begin{aligned} \dot{\omega}_\mu(t) - \dot{\omega}_s(t) + (\omega_\mu(t) - \omega_s(t)) \left( \frac{\zeta_\mu}{I_\mu} + \frac{\zeta_s}{I_s} \right) + \boldsymbol{\mu}(t) \times \frac{\partial V}{\partial \boldsymbol{\mu}} \left( \frac{1}{I_\mu} + \frac{1}{I_s} \right) - \frac{\zeta_s}{I_s} \omega_s(t) \\ = \lambda_\mu(t) \left( \frac{1}{I_\mu} + \frac{1}{I_s} \right) - \frac{\lambda_s(t)}{I_s}. \end{aligned} \quad (14)$$

In the limit  $I_\mu \ll I_s$ , equations (13) and (14) become [15]

$$I_s \dot{\omega}_s(t) + \zeta_s \omega_s(t) = \lambda_s(t) \quad (15)$$

and

$$I_\mu \dot{\boldsymbol{\Omega}}_R(t) + \zeta_\mu \boldsymbol{\Omega}_R(t) + \boldsymbol{\mu}(t) \times \frac{\partial}{\partial \boldsymbol{\mu}} V[\boldsymbol{\mu}(t) \cdot \boldsymbol{R}(t)] = \lambda_\mu(t), \quad (16)$$

where the relative angular velocity of the dipole and cage is

$$\boldsymbol{\Omega}_R = \boldsymbol{\omega}_\mu - \boldsymbol{\omega}_s \quad (17)$$

so that the equations of motion decouple in the relative angular velocity  $\boldsymbol{\Omega}_R$  and  $\boldsymbol{\omega}_s$ .

Thus the cage and dipole orientation processes may be considered as *statistically independent* in the limit of a very large cage and small dipole. Hence the autocorrelation function of the tagged dipole from equation (8) factors into the product of the autocorrelation function of the inertia-corrected Debye process corresponding to the behaviour of the cage or surroundings of the tagged dipole and the longitudinal  $\langle \cos \vartheta(0) \cos \vartheta(t) \rangle_0$  and transverse  $\langle \sin \vartheta(0) \cos \phi(0) \sin \vartheta(t) \cos \phi(t) \rangle_0$ ,  $\langle \sin \vartheta(0) \sin \phi(0) \sin \vartheta(t) \sin \phi(t) \rangle_0$  autocorrelation functions of the motion in the cosine potential

$$V = -\mu R \cos \vartheta(t). \quad (18)$$

The calculation of orientational autocorrelation functions from the free rotator equation (15) which describes the rotational Brownian motion of a sphere is relatively easy because Sack [6] has shown how the one-sided Fourier transform of the orientational autocorrelation functions (here the longitudinal and transverse autocorrelation functions) may be expressed as continued fractions. The corresponding calculation from equation (16) for the three-dimensional rotation in a potential is very difficult because of the non-linear relation between  $\boldsymbol{\omega}_\mu$  and  $\boldsymbol{\mu}$  [25] arising from the kinematic equation (7).

A considerable simplification of the problem can be achieved in two particular cases, however: (a) in the non-inertial limit and (b) for rotation about a fixed axis. In case (a), a general method proposed by Kalmykov [9, 26] for the calculation of the non-inertial response of three-dimensional rotators and described in the preliminary approach to the present problem given in [15] may be used to write differential recurrence relations for the longitudinal and transverse autocorrelation functions. The method is valid even when the form of  $\boldsymbol{R}(t)$  is not explicitly given. Moreover, if the quasi-stationary assumption for the amplitude of  $\boldsymbol{R}(t)$  holds the autocorrelation function from equation (8) may be calculated numerically. Preliminary analysis of this case, based on the work of Waldron *et al* [9, 27] on non-inertial dielectric relaxation in a strong uniform field, indicates that for very strong fields such as the reaction field both longitudinal and transverse relaxation times decrease as the inverse of the field strength. Moreover, the corresponding spectra exhibit marked Debye-like behaviour, effectively with a single relaxation time which may be an explanation of the nearly pure Debye-like behaviour of

strongly associated liquids at low frequencies. In case (b), the kinematic relation equation (7) reduces to the linear equation

$$\dot{\boldsymbol{\mu}}(t) = \omega_{\mu}(t) \mathbf{k} \times \boldsymbol{\mu}(t), \quad (19)$$

which describes rotation in a plane ( $\mathbf{k}$  is a unit vector perpendicular to the plane). Thus, equations (15) and (16) reduce [23] in the limit  $I_{\mu} \ll I_s$  to the itinerant oscillator equations

$$I_s \ddot{\psi}(t) + \zeta_s \dot{\psi}(t) = \lambda_s(t), \quad (20)$$

$$I_{\mu} \ddot{\theta}(t) + \zeta_{\mu} \dot{\theta}(t) + \mu R(t) \sin \theta(t) = \lambda_{\mu}(t), \quad (21)$$

where

$$\Omega_R = \dot{\theta} = \dot{\phi}_{\mu} - \dot{\phi}_s, \quad \omega_s = \dot{\psi} = \dot{\phi}_s. \quad (22)$$

Here the tagged dipole autocorrelation function is [23]

$$C_{\mu}(t) = 2\wp_s(t)\wp_{\theta}(t) = 2\langle \cos \psi(0) \cos \psi(t) \rangle_0 \langle \cos \Delta\theta(t) \rangle_0 \quad (23)$$

and the cage autocorrelation function is

$$\wp_s(t) = \langle \cos \psi(0) \cos \psi(t) \rangle_0 = \frac{1}{2} \exp\{-t/\tau_D + \gamma - \gamma \exp[-t/(\gamma\tau_D)]\}. \quad (24)$$

Here

$$\Delta\theta = \theta(t) - \theta(0), \quad \gamma = kT I_s / \zeta_s^2 \quad \text{and} \quad \tau_D = \zeta_s / (kT). \quad (25)$$

The angle  $\psi(t)$  is taken as the instantaneous angle of rotation of the cage. The cage autocorrelation function equation (24) is the inertia-corrected Debye result for an assembly of non-interacting fixed axis rotators giving rise to the characteristic low-frequency (microwave) Debye peak and a return to transparency at high frequencies without any resonant behaviour (see, for example, figure 33 in [18]). Here  $\gamma$  is the inertial parameter introduced by Gross and Sack [5, 6] and  $\tau_D$  is the Debye relaxation time of the surroundings. The autocorrelation function  $\wp_{\theta}(t) = \langle \cos \Delta\theta(t) \rangle_0$  comprising the sum of the sine and cosine (longitudinal and transverse) autocorrelation functions of the angle  $\theta(t)$  between the dipole and the reaction field has been examined in detail by Coffey *et al* [9, 28, 29] in the small-oscillation (itinerant oscillator) approximation. Invariably  $\wp_{\theta}(t)$  gives rise to a pronounced FIR absorption peak in the frequency domain. The characteristic frequency  $\omega_0$  of this peak on making the quasi-stationary assumption  $R = \text{constant}$  for  $R(t)$  is given by

$$\omega_0^2 = \frac{\xi}{2\eta^2} \quad (26)$$

and the complete expression for  $C_{\mu}(t')$  is

$$C_{\mu}(t') = \exp\left\{-\left[\frac{\eta t'}{\tau_D} - \gamma + \gamma \exp\left(-\frac{\eta t'}{\gamma\tau_D}\right)\right]\right\} \\ \times \exp\left\{-\frac{1}{\xi} \left[1 - \exp\left(-\frac{\beta' t'}{2}\right)\right] \left(\cos \omega_1' t' + \frac{\beta'}{2\omega_1'} \sin \omega_1' t'\right)\right\}. \quad (27)$$

The damped natural angular frequency  $\omega_1$  is given by

$$\omega_1^2 = \omega_0^2 - \frac{\beta'^2}{4} = \frac{\xi}{2} - \frac{\beta'^2}{4} \quad (28)$$

and

$$t' = \frac{t}{\eta}, \quad \eta = \sqrt{\frac{I_{\mu}}{2kT}}, \quad \beta' = \frac{\zeta_{\mu}\eta}{I_{\mu}}, \quad \xi = \frac{\mu R}{kT}. \quad (29)$$



It is apparent that equation (27) represents a discrete set of damped resonances and Debye relaxation mechanisms, as may be seen by writing the complex susceptibility in series form [9, 13]. We remark in passing that an equation, very similar in mathematical form but not identical to the small-oscillation solution, equation (27), may be obtained [1] by applying Mori theory [30] to the angular velocity correlation function of the tagged dipole. Here the notion of a cage is dispensed with and instead the angular velocity is supposed to obey a generalized Langevin equation incorporating memory effects. The solution of that equation is then represented in the frequency domain as a continued fraction which is truncated after the third convergent (three-variable Mori theory [1]). The solution of that equation in the frequency domain is then represented by a continued fraction. A comparison of the two approaches has been made in [29]. Moreover, the three-variable Mori theory has been extensively compared with experiment by Evans *et al* [1]. We now return to the principal theme of our paper, namely the behaviour of the complex susceptibility as yielded by equation (23) when the small-oscillation approximation is discarded.

#### 4. Exact solution for the complex susceptibility using matrix continued fractions

The complex susceptibility yielded by equation (23) combined with equation (9) when the small-oscillation approximation is abandoned, may be calculated using the shift theorem for Fourier transforms combined with the matrix continued fraction solution for the fixed centre of oscillation cosine potential model treated in detail in [16]. Thus, we shall merely outline that solution as far as it is needed here and refer the reader to [16] for the various matrix manipulations etc. We have, on considering the orientational autocorrelation function of the surroundings  $\wp_s(t)$  and expanding the double exponential,

$$\wp_s(t) = \frac{e^\gamma}{2} \sum_{n=0}^{\infty} \frac{(-\gamma)^n}{n!} e^{-(1+n/\gamma)t/\tau_D}. \quad (30)$$

Now in view of the shift theorem for Fourier transforms as applied to the one-sided Fourier transform defined as [31]

$$\mathfrak{F}\{f(t)\} = \tilde{f}(i\omega) = \int_0^{\infty} e^{-i\omega t} f(t) dt$$

so that

$$\mathfrak{F}\{e^{-at} f(t)\} = \tilde{f}(i\omega + a)$$

we have the following expression for the Fourier transform of the composite expression for the dipole autocorrelation function given by equation (23):

$$\mathfrak{F}\{2\wp_s(t)\wp_\theta(t)\} = e^\gamma \sum_{n=0}^{\infty} \frac{(-\gamma)^n}{n!} \tilde{\wp}_\theta(i\omega + \tau_D^{-1} + n/(\gamma\tau_D)). \quad (31)$$

The Fourier transform  $\tilde{\wp}_\theta(i\omega)$  is to be determined from equation (21) by the matrix continued fraction method [16]. Equation (31) is useful for the calculation of the complex susceptibility  $\chi_\mu$  which is given by equation (9) because the spectrum  $\tilde{C}_\mu(i\omega)$  now involves only the quantity  $\tilde{\wp}_\theta(i\omega)$  which is determined from equation (21). That equation in turn is clearly the same as equation (4) of Coffey *et al* [16], which has already been solved using the matrix continued fraction technique. We summarize as follows. The Green function or transition probability corresponding to equation (21) is determined from the differential recurrence relation which may be derived either from the Fokker–Planck equation (by means of a Fourier expansion of

the transition probability) or by averaging the Langevin equation over its realizations in a small time  $\Delta t$  given a sharp set of values of  $\theta$  and  $r$  at time  $t$  [9, 17]. The recurrence relation is [16]

$$\eta \frac{d}{dt} (H_n e^{-iq\theta}) = -\beta' n H_n e^{-iq\theta} - \frac{iq}{2} (H_{n+1} e^{-iq\theta} + 2n H_{n-1} e^{-iq\theta}) - \frac{in\xi}{2} (H_{n-1} e^{-i(q+1)\theta} - H_{n-1} e^{-i(q-1)\theta}) \quad (32)$$

where  $H_n = H_n(\eta\theta)$  are the Hermite polynomials,  $n = 0, 1, 2, \dots$ ,  $q = 0, \pm 1, \pm 2, \dots$

Our interest, as dictated by equation (23), is in the equilibrium average of  $\langle \cos \Delta\theta(t) \rangle_0$  so that it is advantageous to obtain a hierarchy which will allow us to calculate  $\langle \cos \Delta\theta(t) \rangle_0$  directly. Hence let us introduce the functions

$$c_{nq}(t) = \langle H_n(\eta\dot{\theta}(t)) e^{-iq\theta(t)-\theta(0)} \rangle(t). \quad (33)$$

Multiplying equation (32) by  $e^{-i\theta_0}$  ( $\theta_0 = \theta(0)$  denotes a sharp initial value) and averaging over a Maxwell-Boltzmann distribution of  $\theta_0$  and  $\dot{\theta}_0$ , which procedure is denoted by the angular brackets, we automatically have a differential recurrence relation for  $c_{n,q}(t)$ , i.e. the equilibrium averages given by equation (33), namely

$$\eta \dot{c}_{n,q}(t) = -\beta' n c_{n,q}(t) - \frac{iq}{2} [c_{n+1,q}(t) + 2n c_{n-1,q}(t)] - \frac{in\xi}{2} [c_{n-1,q+1}(t) - c_{n-1,q-1}(t)]. \quad (34)$$

In particular, in the present problem we are interested in

$$\wp_\theta(t) = \langle \cos \Delta\theta(t) \rangle_0 = \frac{1}{2} (c_{0,1}(t) + c_{0,-1}(t)). \quad (35)$$

Thus by equations (9) and (31) the complex susceptibility is

$$\frac{\chi(\omega)}{\chi'(0)} = 1 - \frac{i\omega e^\gamma}{c_{0,1}(0) + c_{0,-1}(0)} \sum_{n=0}^{\infty} \frac{(-\gamma)^n}{n!} [\tilde{c}_{0,1}(i\omega + \tau_D^{-1} + n(\gamma\tau_D)^{-1}) + \tilde{c}_{0,-1}(i\omega + \tau_D^{-1} + n(\gamma\tau_D)^{-1})]. \quad (36)$$

Now, the scalar recurrence equation (34) can be transformed into the matrix *three-term* recurrence equation

$$\eta \frac{d}{dt} \mathbf{C}_n(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}(t) + \mathbf{Q}_n \mathbf{C}_n(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}(t) + \mathbf{R} \delta_{n,2} \quad (n \geq 1), \quad (37)$$

where the column vectors  $\mathbf{C}_n(t)$  are defined as

$$\mathbf{C}_0(t) = \mathbf{0}, \quad \mathbf{C}_1(t) = \begin{pmatrix} \vdots \\ c_{0,-2} \\ c_{0,-1} \\ c_{0,1} \\ c_{0,2} \\ \vdots \end{pmatrix}, \quad \mathbf{C}_n(t) = \begin{pmatrix} \vdots \\ c_{n-1,-2} \\ c_{n-1,-1} \\ c_{n-1,0} \\ c_{n-1,1} \\ c_{n-1,2} \\ \vdots \end{pmatrix} \quad n \geq 2 \quad (38)$$

and the column vector  $\mathbf{R}$  and the matrices  $\mathbf{Q}_n^-$ ,  $\mathbf{Q}_n$  and  $\mathbf{Q}_n^+$  are given in the appendix.

By applying the one-sided Fourier transform to equation (37), we obtain the matrix recurrence relations

$$i\eta\omega \tilde{\mathbf{C}}_1(i\omega) - \eta \mathbf{C}_1(0) = \mathbf{Q}_1^+ \tilde{\mathbf{C}}_2(i\omega), \quad (39)$$

$$i\eta\omega \tilde{\mathbf{C}}_n(i\omega) = \mathbf{Q}_n \tilde{\mathbf{C}}_n(i\omega) + \mathbf{Q}_n^+ \tilde{\mathbf{C}}_{n+1}(i\omega) + \mathbf{Q}_n^- \tilde{\mathbf{C}}_{n-1}(i\omega) + \frac{\mathbf{R}}{i\omega} \delta_{n,2} \quad (n \geq 2), \quad (40)$$

where the initial value vector is (in terms of the modified Bessel functions  $I_q(\xi)$  of the first kind of order  $q$ )

$$C_1(0) = \frac{1}{I_0(\xi)} \begin{pmatrix} \vdots \\ I_3(\xi) \\ I_2(\xi) \\ I_0(\xi) \\ I_1(\xi) \\ \vdots \end{pmatrix} \quad (41)$$

and we have used the fact that  $C_n(0) = 0$  for  $n \geq 2$  because  $\langle H_n \rangle = 0$  ( $n \geq 1$ ) for the (equilibrium) Maxwell–Boltzmann distribution function. By invoking the general method for solving the matrix recurrence equation (37) [9], we have the exact solution for the spectrum  $\tilde{C}_1(i\omega)$  in terms of matrix continued fractions, i.e.

$$\tilde{C}_1(i\omega) = \Delta_1(\eta C_1(0) + Q_1^+ \Delta_2 R/i\omega), \quad (42)$$

where the matrix continued fractions  $\Delta_n$  ( $n = 1, 2$ ) are given by

$$\Delta_n = \frac{I}{i\eta\omega I - Q_n - Q_n^+ \frac{I}{i\eta\omega I - Q_{n+1} - Q_{n+1}^+ \frac{I}{i\eta\omega I - Q_{n+2} - Q_{n+2}^+ \dots}} Q_{n+1}^-}, \quad (43)$$

$I$  is the unit matrix of infinite dimension, and the fraction lines designate the matrix inversions. The foregoing equations allow us to determine the complex polarizability exactly.

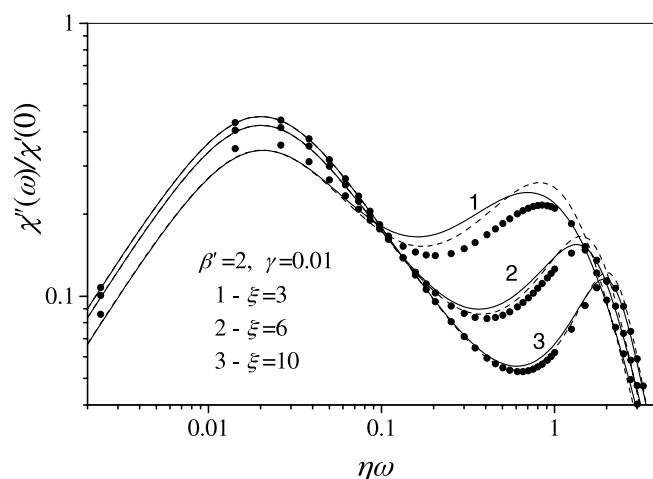
We remark that the presently available small-oscillation (itinerant oscillator) approximation for  $\chi(\omega)$  [28, 29] has the advantage of being very easy to use for the purpose of comparison with experimental observations since the solution in the time domain is available in closed form (equation (27)). Moreover, if the inertial parameter  $\gamma$  is sufficiently small ( $\leq 0.1$ ) and  $I_\mu \omega_0^2 \ll kT$  the complex polarizability for small oscillations, i.e. equation (27), may be closely approximated in the frequency domain [28, 29] by the simple expression (see equations (4.4.3) and (4.4.4) of [9])

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{(i\omega\tau_D + 1)(i\omega\gamma\tau_D + 1)} + \frac{kT}{I_\mu \omega_0^2} \frac{i\omega\tau_D}{i\omega\tau_D + 1} \left[ \left( 1 - \frac{\omega^2}{\omega_0^2} \right) + \frac{\zeta_\mu}{I_\mu} \frac{i\omega}{\omega_0^2} \right]^{-1}. \quad (44)$$

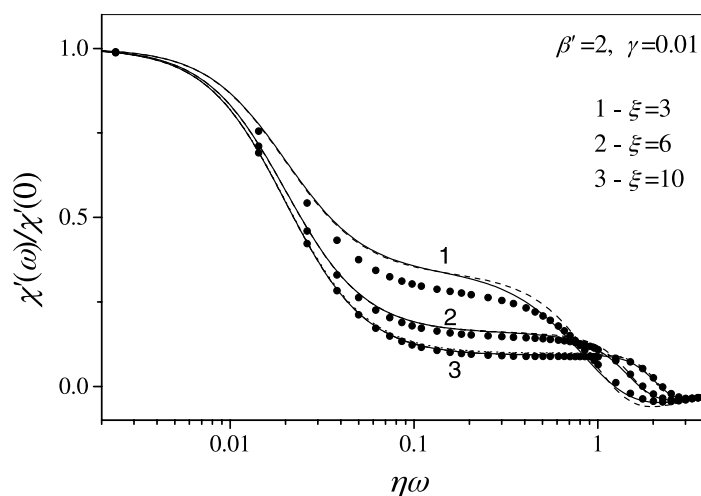
Equation (44) was originally given in [12] for the single friction itinerant oscillator model (see also [1]). The first term in equation (44) is essentially the Rocard equation of the inertia-corrected Debye theory of dielectric relaxation and so is due to the cage motion; the second damped harmonic oscillator term represents in our picture the high-frequency effects due to the cage-tagged dipole interaction.

## 5. Numerical results and comparison with experimental data

In figure 1, we show plots of the imaginary part  $\chi''(\omega)$  of the complex susceptibility from the exact solution equation (36) for  $\beta' = 2$  and  $\gamma = 0.01$  and illustrate the effect of varying the reaction field parameter  $\xi$ . The real part of the susceptibility  $\chi'(\omega)$  is shown in figure 2. Superimposed on these are  $\chi'(\omega)$  and  $\chi''(\omega)$  as yielded by the harmonic oscillator approximation equation (27) that is the conventional itinerant oscillator model. The approximate equation (44) is compared with the exact solution equation (36). These results are also shown in figures 1 and 2. The advantage of doing this is that it demonstrates the extent to which one is justified in using the small-oscillation approximation equation (27) or (44) in order to describe the relaxation process. The above behaviour is entirely in accord with



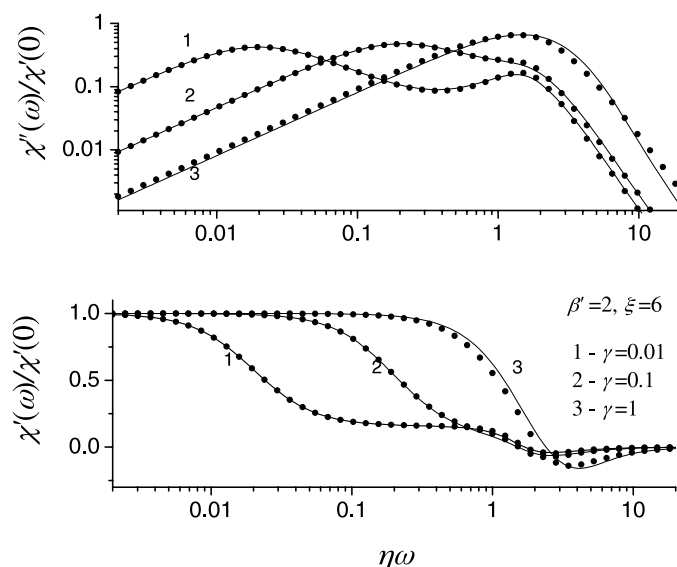
**Figure 1.** Imaginary part of the complex susceptibility  $\chi''(\omega)$  versus normalized frequency  $\eta\omega$  for various values of the reaction field parameter. Solid curves correspond to the exact cosine potential solution equation (36), circles correspond to the small oscillation solution equation (27), dashed curves correspond to the approximate small-oscillation solution, equation (44).



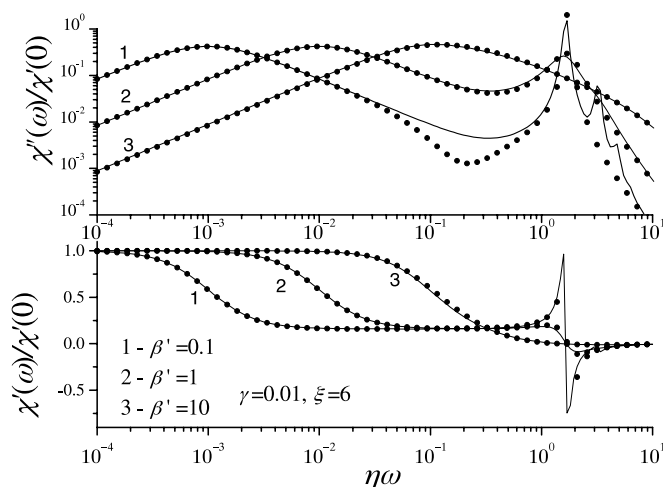
**Figure 2.** The same as in figure 1 for the real part of the complex susceptibility  $\chi'(\omega)$ .

intuitive considerations, as one would expect the harmonic or simple pendulum approximation to become less and less accurate as the reaction field parameter is decreased. Nevertheless, it appears that equation (44), which is simple to implement numerically, provides a reasonable approximation for a large reaction field parameter.

In figure 3, we demonstrate the effect of varying the cage inertial parameter  $\gamma$  for fixed dipole friction parameter  $\beta'$  and large reaction field parameter  $\xi$ . It appears that if  $\gamma < 1$  then the small oscillation approximation given by equation (44) again provides a very close approximation to the exact solution based on numerical evaluations of equation (36) for large  $\xi$ . The approximate equation (44) begins to fail at  $\gamma = 1$  and higher. This is to be expected as one is now dealing with the region in which the Rocard approximation for the complex

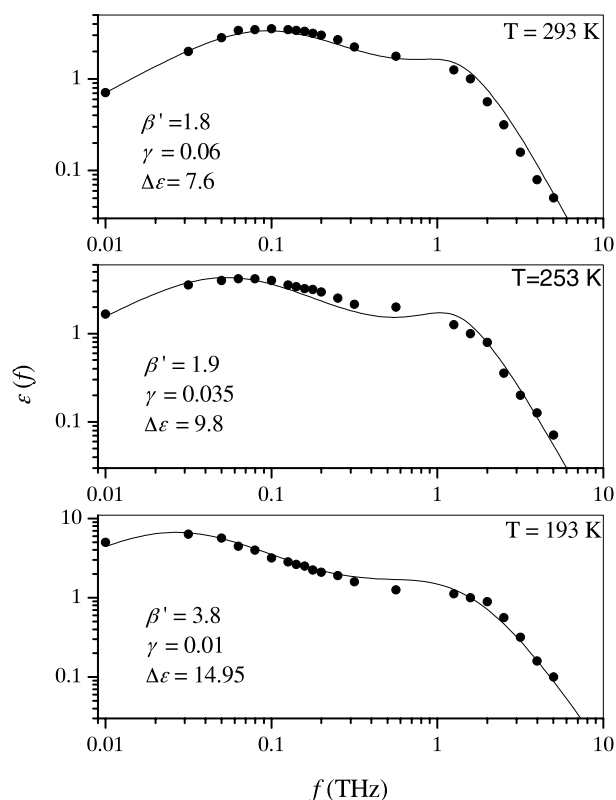


**Figure 3.** Effect of varying the cage inertial parameter  $\gamma$ :  $\chi'(\omega)$  and  $\chi''(\omega)$  versus  $\eta\omega$ . Solid curves correspond to the exact cosine potential solution equation (36) and circles correspond to the approximate equation (44).



**Figure 4.** Effect of varying the dipole friction parameter  $\beta'$ :  $\chi'(\omega)$  and  $\chi''(\omega)$  versus  $\eta\omega$ . Solid curves correspond to the exact cosine potential solution, equation (36), and circles correspond to the approximate equation (44).

susceptibility of a free rotator is no longer valid. In figure 4, we fix the cage inertial parameter  $\gamma$  and the reaction field parameter  $\xi$  and we demonstrate the effect of varying the dipole friction parameter for a reasonably high value of the reaction field parameter so that one can expect the harmonic approximation of equation (44) to be valid. Again, the agreement with the exact cosine potential solution equation (36) is good for relatively high values of  $\beta'$  (see curves 2 and 3). For relatively small values of  $\beta'$ , however, there is some discrepancy in the intermediate frequency region. At high frequencies the harmonic approximation, equation (44), cannot



**Figure 5.** Dielectric loss  $\varepsilon''(f)$  versus frequency  $f$  ( $f = \omega/2\pi$ ). Solid curves correspond to the exact cosine potential solution, equation (36), and circles are experimental data for the symmetrical top molecule  $\text{CH}_3\text{Cl}$  [34, 35].

predict the comb-like peak structure of the exact solution. (The peaks occur at the harmonics of the fundamental frequency.) This to be expected because equation (44) results from an expansion of the correlation function (a double transcendental function with sines and cosines in its argument) which is truncated at the fundamental frequency term so that the comb-like structure may not be reproduced (see equation (4.2.4.3) of [9] for the exact expression for the complex polarizability from equation (27)). Nevertheless, equation (44) provides a reasonable description of the fundamental frequency peak in the FIR region as is obvious by inspection of figure 4. We remark that a similar comb-like structure occurs in the theory of ferromagnetic resonance [32] of single-domain ferromagnetic particles, which involves the solution of differential recurrence relations resembling equation (33), and in the theory of quantum noise in ring laser gyroscopes [33].

In figure 5, a comparison of typical experimental data for the symmetric top molecule  $\text{CH}_3\text{Cl}$  at various temperatures [34] with the theoretical dielectric loss spectrum  $\varepsilon''(\omega) = (\varepsilon_0 - n_{ir}^2)\chi''(\omega)/\chi'(0)$  predicted by equations (10) and (36) is shown (here, we ignore the internal field correction on the frequency dependence of  $\varepsilon''(\omega)$ , i.e. we let  $G(\omega) = 1$  in equation (10)). The moment of inertia, which was used in the calculation, is the reduced moment of inertia  $I_r$  defined by

$$\frac{1}{I_r} = \frac{1}{I_b} + \frac{1}{I_c},$$

where  $I_b$  and  $I_c$  are the principal moments of inertia about molecular axes perpendicular to the axis of symmetry. For the symmetric top molecule  $\text{CH}_3\text{Cl}$ ,  $I_b = I_c = 57 \times 10^{-40}$  [35]. The use of the reduced moment  $I_r$  allows one to obtain the correct value for the dipolar integral absorption (Gordon's sum rule [1]) for two-dimensional models. The dipole-cage interaction energy is regarded as a constant and the parameter  $\xi$ , which is the dipole-cage interaction energy represented in units of thermal energy, was calculated by means of the equation  $\xi = 193\xi_0/T$ . The experimental values of  $\Delta\varepsilon = \varepsilon_0 - n_{ir}^2$  were taken from [34]. The model parameters  $\xi_0$ ,  $\gamma$  and  $\beta'$  were adjusted from the best fit of experimental data (in the present case, that is methyl chloride, the value of  $\xi_0$  consistent with the best fit is  $\approx 8$ ). It is apparent that the overall fit provided by utilizing the exact solution embodied in equation (36) is superior to that provided by utilizing the small-oscillation solution equation (27) or the approximate equation (44). Previous fits of the model to the experimental data have been carried out using equation (44) (see, for example, [36]).

Moreover, the solution for small oscillations (equation (27)) has been compared with the experimental data by Walsh and Déjardin [29]. The main difficulty in fitting the small-oscillation solution to the experimental data is that usually one may achieve a good fit in one region of the spectrum only at the expense of a poorer fit in another region of the spectrum (see, for example, [9], figures 4.5.1–4.5.3). In these figures, it is obvious that a best fit of the FIR spectrum is accompanied by a poorer fit in the intermediate frequency region lying between the microwave and FIR regions. The use of the exact (cosine potential) solution certainly removes this difficulty as a reasonable fit can be achieved in all regions of the spectrum simultaneously, as is apparent from the plots shown in figure 5. We emphasize, however, that for practical purposes the approximate small-oscillation formula (equation (44)) can provide a reasonable qualitative description of the experimental results if the field parameter  $\xi$  is sufficiently large. The approximate formula (equation (44)) also has the advantage of being very easy to use in practice.

## 6. Conclusions

We have shown in this paper how the equations of motion of the cage model of polar fluids originally proposed by Hill [7] may be solved exactly using matrix continued fractions. Furthermore, these equations automatically lead to a microwave absorption peak having its origin in the reorientational motion of the cage and a pronounced FIR absorption peak having its origin in the oscillations of the dipole in the cage-dipole interaction potential. The equations of motion of the dipole and cage may be justified in terms of a generalization of the Onsager model of the static susceptibility of polar fluids to include the dynamical behaviour. A conclusion which may be drawn from this is that the origin of the Poley absorption peak is the interaction between the dipole and its surrounding cage of neighbours which causes librations of the dipole. The model appears to reproduce satisfactorily the main features of the microwave and FIR absorption of  $\text{CH}_3\text{Cl}$ . In addition, it is shown that the simple closed form expression (equation (44)) for the complex susceptibility which was originally derived in the context of the small-oscillation version of the cage model (i.e. the itinerant oscillator model) can also provide a reasonable approximation to the cage model polarizability for large values of the reaction field parameter  $\xi$ .

The results given here may also be extended to rotation in space. As far as the cage motion is concerned, the complex susceptibility for small  $\gamma$  will still be governed by the Rocard equation since the equations of motion again factorize. However, the solution for the dipole correlation function is much more complicated because of the difficulty of handling differential recurrence relations pertaining to rotation in space in the presence of a potential.

Yet another direction in which the present model may be extended is fractional dynamics [37], where one supposes that the surroundings of the dipole or cage obey not the simple Langevin equation (14) but instead a generalized Langevin equation with a memory function given by the Riemann–Liouville fractional derivative [37] while equation (15) remains a conventional (or if one prefers, also a fractional) Langevin equation. In this way it will be possible to incorporate slow relaxation effects into the cage model.

We remark that activation processes which involve crossing of the cage dipole over an internal potential barrier may also be incorporated into the present model by adding a  $\cos 2\theta$  term to the potential in equation (22). This may give rise to a Debye-like relaxation process at very low frequencies with relaxation time governed by the Arrhenius law, the prefactor of which may be calculated precisely using the Kramers theory of escape of particles over potential barriers [38]. We remark that a  $\cos 2\theta$  term in the potential has also been considered by Polimeno and Freed [39] in their discussion of a many-body stochastic approach to rotational motions in liquids. Their discussion is given in the context of a simplified description of a liquid in which only three bodies are retained, namely a solute molecule (body 1), a slowly relaxing local structure or solvent cage (body 2) and a fast stochastic field as a source of fluctuating torque. In general, one may remark that this approach, which is based on projection operators and the numerical solution of many-body Fokker–Planck–Kramers equations, is likely to be of much interest in the context of the extension of the model described in this paper to rotation in space.

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### Appendix

The column vector  $\mathbf{R}$  and the matrices  $\mathbf{Q}_n^+$ ,  $\mathbf{Q}_n^-$  and  $\mathbf{Q}_n$  in equation (37) are given by

$$\mathbf{R} = \frac{i\xi I_1(\xi)}{2I_0(\xi)} \begin{pmatrix} \vdots \\ 0 \\ -1 \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} \quad (\text{A.1})$$

and

$$\mathbf{Q}_n^+ = -\frac{i}{2} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \\ \dots & -2 & 0 & 0 & 0 & 0 & \dots \\ \dots & 0 & -1 & 0 & 0 & 0 & \dots \\ \dots & 0 & 0 & 0 & 0 & 0 & \dots \\ \dots & 0 & 0 & 0 & 1 & 0 & \dots \\ \dots & 0 & 0 & 0 & 0 & 2 & \dots \\ \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (\text{A.2})$$



$$Q_n^- = -\frac{i(n-1)}{2} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \\ \cdots & -4 & \xi & 0 & 0 & 0 & \cdots \\ \cdots & -\xi & -2 & \xi & 0 & 0 & \cdots \\ \cdots & 0 & -\xi & 0 & \xi & 0 & \cdots \\ \cdots & 0 & 0 & -\xi & 2 & \xi & \cdots \\ \cdots & 0 & 0 & 0 & -\xi & 4 & \cdots \\ \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (\text{A.3})$$

$$Q_n = -(n-1)\beta'I, \quad (\text{A.4})$$

where  $I$  is the unit matrix of infinite dimension. The exceptions are the matrices  $Q_1^+$  and  $Q_2^-$ , which are given by

$$Q_1^+ = -\frac{i}{2} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \\ \cdots & -2 & 0 & 0 & 0 & 0 & \cdots \\ \cdots & 0 & -1 & 0 & 0 & 0 & \cdots \\ \cdots & 0 & 0 & 0 & 1 & 0 & \cdots \\ \cdots & 0 & 0 & 0 & 0 & 2 & \cdots \\ \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (\text{A.5})$$

$$Q_2^- = -\frac{i}{2} \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \\ \cdots & -4 & \xi & 0 & 0 & \cdots \\ \cdots & -\xi & -2 & 0 & 0 & \cdots \\ \cdots & 0 & -\xi & \xi & 0 & \cdots \\ \cdots & 0 & 0 & 2 & \xi & \cdots \\ \cdots & 0 & 0 & -\xi & 4 & \cdots \\ \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (\text{A.6})$$

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