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THE EFFECT OF DIPOLE–DIPOLE INTERACTION ON ZERO–THz FREQUENCY POLARISATION

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Received 1 December 1978; in final form 22 December 1978

The effect of intramolecular dipole–dipole interaction on polarisation at frequencies from $0-10^{12}$ Hz in dipolar media is investigated using a numerical solution of the Sturm–Liouville eigenvalue problem to which the governing Smoluchowski equation reduces. The results of Budó for the long-wavelength limit are extended to all frequencies up to the far infrared, where the predominant inertial effects are treated using a preliminary first-order correction. The numerical method of Pryce may be used to investigate much more realistic interaction potentials than the simple harmonic and cosine form considered by Budó. These simple forms are, however, sufficient to indicate that the integrated absorption intensity per molecule in the far infrared is very sensitive to dipole–dipole interaction and relative hydrodynamic drag on both interacting groups. Applications of the theory to the disordered solid and nematic phases are considered.

1. Introduction

The effect of electrodynamic interactions on the overall loss curve of dipolar fluids and plastic crystals is one which has bedevilled theoreticians in the field for over half a century [1]. There are at least two ways in which dipole–dipole interaction, for instance, manifests itself: (a) on the microscopic (molecular) scale, and (b) in the transmission of information to the macroscopic observables such as dielectric loss (ϵ''), permittivity (ϵ'), power absorption coefficient ($\alpha(\omega)$) and refractive index ($n(\bar{\nu})$). In this letter we describe a recently developed means [2] of investigating aspect (a) by calculating numerically [3,4] the effect of dipole–dipole interaction on the microscopic complex polarisability of molecules consisting of two dipolar groups with freedom to rotate intramolecularly. Although this problem was elegantly but laboriously solved in the long-wavelength limit by Budó [5] in 1949, we may take advantage of an algorithm recently developed [4] for solving the governing Sturm–Liouville equation of the system for the relevant eigenvalues and eigenfunctions. We can therefore investigate fully the effect of this type of dipole–dipole coupling on the complete zero–THz ($0-10^{12}$ Hz) bandshapes inclusive of the far infrared [6] where inertial effects are of paramount importance.

The system of intramolecular interactions considered by Budó is applicable to intermolecular dipole–dipole or other type of potential provided that some geometrical constraints are imposed. For example, the separate dipoles would be embedded in molecules whose relative centre-of-mass motion would be small. The Budó model could be applied unchanged to the disordered solid phases of certain hexasubstituted benzenes, or to the smectic phases (perhaps also the nematic) of liquid crystals, where the nematic pseudopotential is imposed upon the brownian motion. The development of powerful numerical techniques has also in principle obviated the need for using over-simplified potentials such as the harmonic and cosine types considered by Budó. For example, we may now consider a multipole expansion [7] of the electrostatic interaction potential in the disordered solid phases [8] of some hexasubstituted benzenes where the constraint of libration about the hexad axis and absence of centre-of-mass translation implies that the Budó geometry may be used for solving the Smoluchowski or Kramers equation governing the stochastic properties of the system. In a more approximate vein, libration with respect to the nematic phase director [9] may also be treated via a Sturm–Liouville equation provided the interaction potential considered is that between molecule and director vector, which, of course, is not predominantly or even necessarily electrostatic. One important consequence of our numerical treatment is that we are able to show clearly that in terms of power absorption, or its equivalent on the microscopic scale, $\omega\alpha''(\omega)$ (where $\alpha''(\omega)$ is the imaginary part of the polarisability), the Gordon sum rule [10] no longer applies. This is to say that the integrated intensity per molecule

$$A_0 = N^{-1}\int \omega\alpha''(\omega)\,\mathrm{d}\omega$$

evidently does not remain constant as the strength of dipole–dipole interaction is increased. On the contrary, A_0 is a very sensitive function of the coupling potential and relative frictional drag between the interacting dipolar groups. In this letter we present the complex polarisability as a function of frequency and dipole–dipole interaction strength for the potentials considered by Budó. In later developments we shall consider more realistic potentials, and more realistic treatments of the inertial problem.

2. Theoretical synopsis and numerical method

The system of dipole–dipole interaction considered by Budó has recently been developed to include first-order inertial corrections by Coffey [2]. We spare the reader any confusing mathematical detail except insofar as to list the primary equations which have to be solved for the complex polarisability. We shall discuss below the cases of interest experimentally to which the theory may be applicable in its present form and those specialised models of the fluid condition which it already embraces.

Budó has established that whatever the form of interaction potential the complex polarisability is determined by the following sum over eigenvalues:

$$\alpha^*_\mu(\omega) = \tfrac{1}{3}\,\beta E \sum_\lambda \frac{I_\lambda}{1 + \mathrm{i}\omega\tau_\lambda}. \tag{1}$$

Here E is the measuring field, $\beta = 1/kT$, τ_λ are relaxation times and I_λ weighting factors defined in terms of eigenfunctions to be defined. Eq. (1) applies in the absence of inertial considerations, a first-order correction being:

$$\alpha^*_\mu(\omega) = \tfrac{1}{2}\,\beta E \sum_\lambda \frac{I_\lambda}{1 + \mathrm{i}\omega\tau_\lambda - \omega^2\tau_\lambda I/\zeta_1}. \tag{2}$$

Here ζ_1 is the hydrodynamic friction on one polar group and I the associated moment of inertia. It is important to note that neither of these equations produces realistic resonance in the far infrared as essential experimentally [6], but the second has the advantage that transparency is regained at high frequency so that A_0 is finite and predictable in principle with a sum rule [11]. However, at low frequencies there is, from eq. (1), an infinite number of relaxation times since the governing eigenvalue problem is of Sturm–Liouville type:

$$\mathrm{d}^2 z_\lambda(\eta)/\mathrm{d}\eta^2 - 2\phi(\eta)\,\mathrm{d}z(\eta)/\mathrm{d}\eta + \lambda z_\lambda(\eta) = 0. \tag{3}$$

Here $\phi(\eta) = (1/kT)\,\mathrm{d}V(2\eta)/\mathrm{d}(2\eta)$, where $V(2\eta)$ is the dipole interaction potential as a function of the angle 2η, which is that separating the components μ_1 and μ_2 of the two dipolar groups μ_1 and μ_2 projected on to a common plane [5] perpendicular to an axis in the whole molecule (which is undergoing brownian motion). In solving eq. (3) numerically for the eigenfunctions $z_\lambda(\eta)$ we consider the forms:

$$V = -V_0\cos(2\eta), \tag{4}$$

$$V = (8/\pi^2)\,V_0\eta^2 \tag{5}$$

which give rise to the Hill equation:

$$\mathrm{d}^2Z/\mathrm{d}\eta^2 + (\lambda - \tfrac{1}{2}\beta^2V_0^2 + 2\beta V_0\cos 2\eta + \tfrac{1}{2}\beta^2V_0^2\cos 4\eta)\,Z = 0 \tag{6}$$

and Hermite equation:

$$\mathrm{d}^2z/\mathrm{d}x^2 - 2x\,\mathrm{d}z/\mathrm{d}x + \lambda z/y = 0, \tag{7}$$

respectively. In eqs. (6) and (7):

$x = y^{1/2}\eta$, where $y = (8/\pi^2)(V_0/kT)$, and

$$Z = z \exp\left[-\int (V_0/kT) \sin 2\eta \, d\eta\right].$$

I_λ and τ_λ of eqs. (1) and (2) are then defined in terms of the eigenfunctions $z_\lambda(\eta)$ and eigenvalues λ of either eqs. (6) or (7).

$$I_\lambda = \int_{-\pi/2}^{\pi/2} \exp[-\beta V(2\eta)] z_\lambda(\eta) [C_\lambda(\mu_1 + \mu_2)^2 \cos\eta + C'_\lambda(\mu_1 - \mu_2)^2 \sin\eta] \, d\eta \left[\int_{-\pi/2}^{\pi/2} \exp[-\beta V(2\eta)] \, d\eta\right]^{-1}; \tag{8}$$

$$\tau_\lambda = b/(a + \lambda). \tag{9}$$

In eq. (8) we have:

$$C_\lambda = \frac{\int_{-\pi/2}^{\pi/2} \exp[-\beta V_0(1 - \cos 2\eta)] z_\lambda(\eta) \cos\eta \, d\eta}{\int_{-\pi/2}^{\pi/2} \exp[-\beta V_0(1 - \cos 2\eta)] z_\lambda^2(\eta) \, d\eta}, \tag{10}$$

$$C'_\lambda = \frac{\int_{-\pi/2}^{\pi/2} \exp[-\beta V_0(1 - \cos 2\eta)] z_\lambda(\eta) \sin\eta \, d\eta}{\int_{-\pi/2}^{\pi/2} \exp[-\beta V_0(1 - \cos 2\eta)] z_\lambda^2(\eta) \, d\eta} \tag{11}$$

for the Hill case. In the Hermite case the weighting factor $\exp[-\beta V_0(1 - \cos 2\eta)]$ is replaced by $\exp(-4\beta V_0 \eta^2)$. The constants b and a are defined by:

$$a = 1 + 2\zeta_1/\zeta, \quad b = 2\zeta_1/kT, \tag{12}$$

where ζ_1 and ζ are the frictions on a rotating group and on the whole molecule respectively.

3. Numerical computation

Pryce [4] has recently evolved an algorith for solving the general Sturm–Liouville equation of second-order self-adjoint type that is robust and useful for application in several fields of chemical physics. The eigenvalue λ is determined by an iterative shooting method based on the scaled Prüfer form of the differential equation as described in Hargrave and Pryce [3]. The Prüfer equations are solved using a Runge–Kutta method with quadratures based on Merson's method. Local errors are controlled automatically. The eigenfunction for a given eigenvalue λ is evaluated at the integration mesh-points and stored on file. Examples of Hill type eigenfunctions are illustrated in fig. 1. The quadratures in eqs. (8) and (10) are evaluated with the fast and accurate N.A.G. routine Do1GAA with close control of uncertainties (numerically never more than $\pm 10^{-3}\%$). The eigenfunctions were automatically normalised so that:

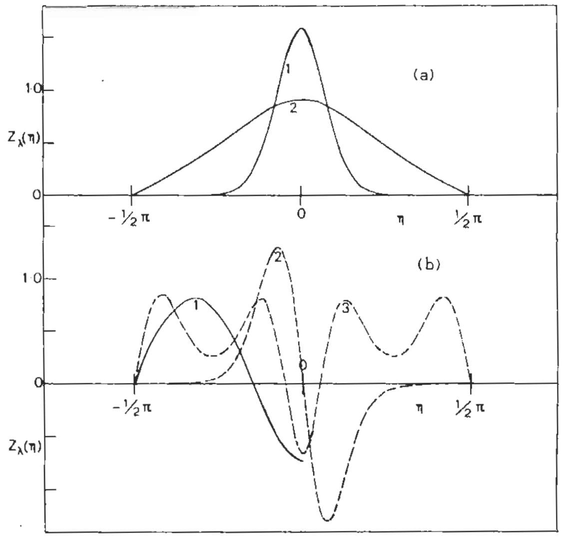


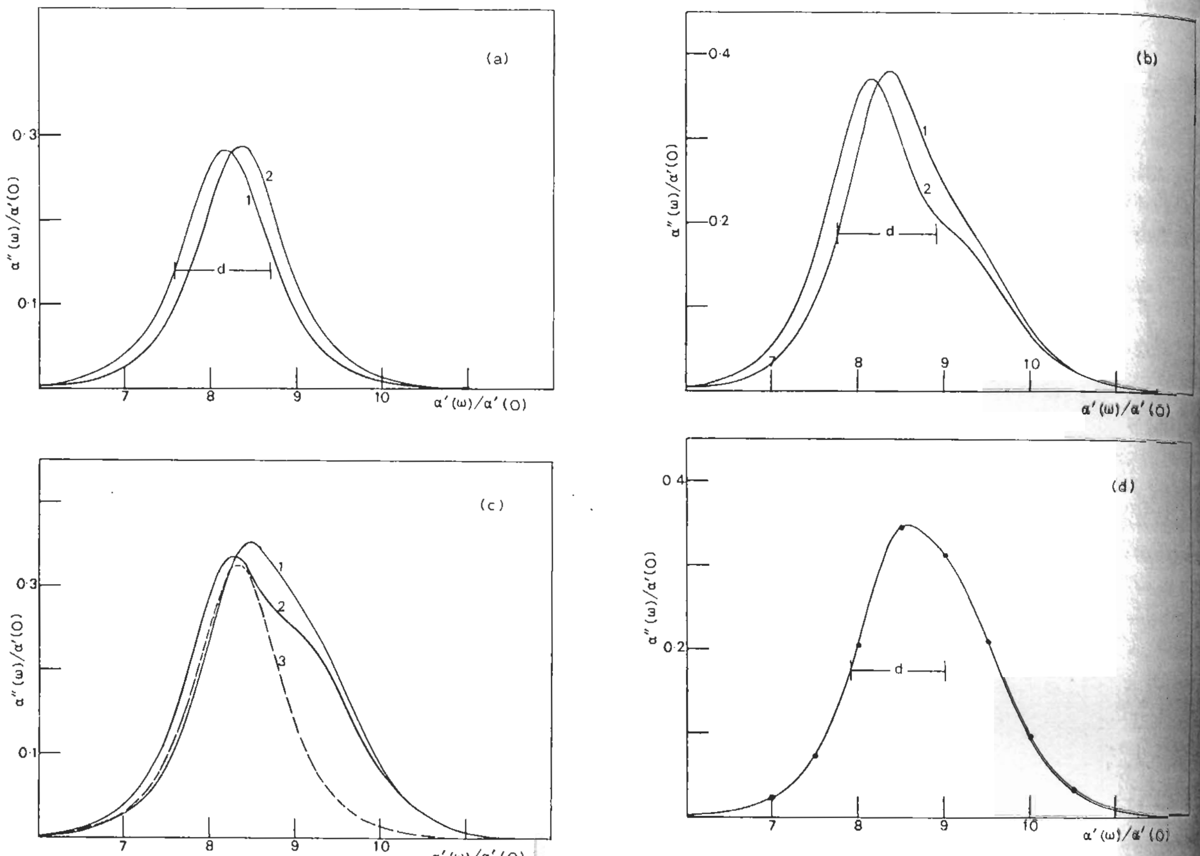
Fig. 1. Eigenfunctions of the Hill equation (6). (a) $Z_0(\eta)$; (1) $V_0/kT = 10.0$; (2) $V_0/kT = 1.0$. (b) (1) $V_0/kT = 1.0$, $Z_2(\eta)$; (2) $V_0/kT = 10.0$, $Z_1(\eta)$; (3) $V_0/kT = 10.0$, $Z_2(\eta)$.

$$\left[\int_{-\pi/2}^{\pi/2} Z^2(\eta) \, d\eta\right]^{1/2} = 1$$

and this was independently checked against the quadrature. The eigenvalue part of the programme will become available as N.A.G. mark VII Do2KDF. The complete listing used in this letter is available subject to N.A.G. copyright. The series (1) and (2) is initially rapidly convergent and 97% of the total polarisability is attained in four or five terms. The remaining 3% requires, however, many more terms, but with essentially no further gain in physical insight.

4. Results and discussion

The complex polarisability plots of $\alpha''(\omega)/\alpha'(0)$ versus $\log_{10}(\omega)$ of figs. 2a to 2d show up the fact that a harmonic interaction potential causes very little broadening of the Debye type [1] (with non-zero I_0 only).



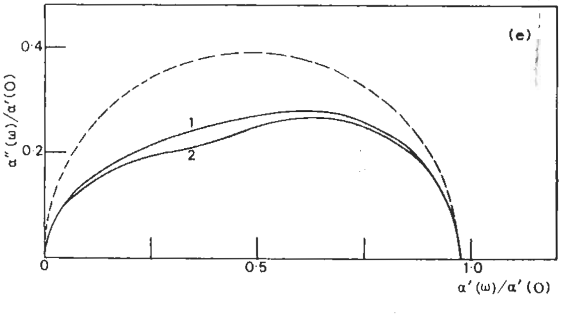


Fig. 2. Plot of complex polarisability $\alpha''(\omega)/\alpha'(0)$ versus log (ω/Hz). (a) Harmonic potential, $V_0/kT = 0.5$, $2\zeta_1/kT = 10^{-8}$ s, (1) $\zeta_1/\zeta = 0.125$, (2) $\zeta_1/\zeta = 0.5$; d = Debye halfwidth (1.12 decades). (b) Cosine potential, $V_0/kT = 2.0$, $2\zeta_1/kT = 10^{-8}$ s, (1) $\zeta_1/\zeta = 0.5$; (2) $\zeta_1/\zeta = 0.125$, d = Debye halfwidth. (c) Cosine potential, $V_0/kT = 1.0$, $2\zeta_1/kT = 10^{-8}$ s, (1) $\zeta_1/\zeta = 0.5$; (2) $\zeta_1/\zeta = 0.125$, (3) elastic potential, $\zeta_1/\zeta = 0.5$, $V_0/kT = 1.0$ (no broadening). (d) Cosine potential, $V_0/kT = 0.5$, $\zeta_1/\zeta = 0.5$, $2\zeta_1/kT = 10^{-8}$ s. First order inertia correction – no effect at low frequencies. (e) Cole–Cole plot for case (c), using the first five terms of eq. (1), 97% of the real part of the static polarisation has been summed. (1) Semicircle; (2) $\zeta_1/\zeta = 0.5$; (3) $\zeta_1/\zeta = 0.125$.

This is in contrast to the cosine type of interaction expected on physical grounds [6]. A distribution sensitive to the ratio ζ_1/ζ is clearly discernible with the latter type of potential. The plots of $\omega\alpha''(\omega)/\alpha'(0)$ versus $\log_{10}(\omega)$ (figs. 3a and 3b) illustrate a Debye plateau [6]. The macroscopic equivalent, the power absorption coefficient, is evidently sensitive to the degree of dipole–dipole coupling. However, the far infrared absorption of dipolar molecules observed experimentally exceeds the Debye plateau (independently of collision-induced effects) and to describe this accurately a governing Kramers or master equation is needed which is probably intractable except by numerical means. Inertial corrections, such as those of eq. (2), only produce a high-frequency return to transparency from this plateau level. The absorption above the

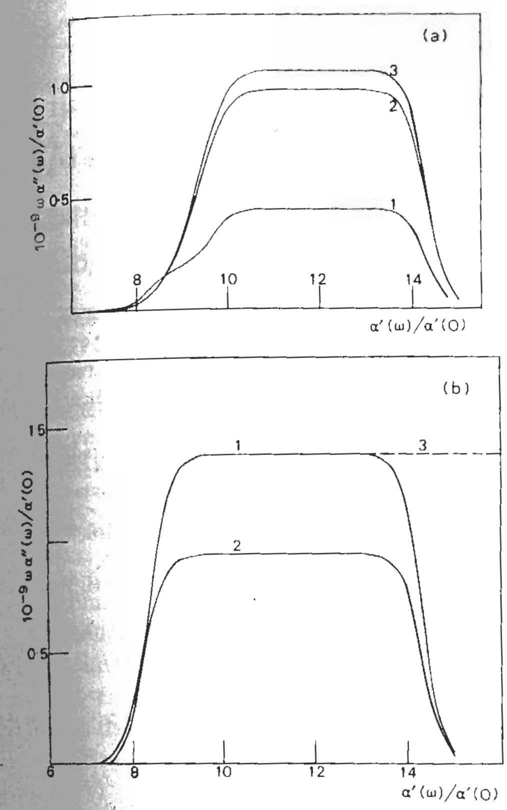


Fig. 3. Plots of $10^{-9}\,\omega\alpha''(\omega)/\alpha'(0)$ versus log (ω/Hz) for eq. (2), illustrating the Debye plateau. (a) Cosine potential, $2\zeta_1/kT = 10^{-8}$ s, $\zeta_1/\zeta = 0.5$, $\zeta_1/I = 5 \times 10^{-15}$ s, (1) $V_0/kT = 5.0$; (2) $V_0/kT = 1.0$; (3) $V_0/kT = 0.5$. (b) Harmonic potential, $V_0/kT = 0.5$, $2\zeta_1/kT = 10^{-8}$ s, $\zeta_1/I = 5 \times 10^{-15}$ s; (1) $\zeta_1/\zeta = 0.5$; (2) $\zeta_1/\zeta = 0.125$; (3) Debye equation.

Debye plateau is unobtainable with any type of dipole coupling potential.

It is clear from figs. 3 that the strength of internal dipole–dipole interaction affects the integrated intensity of the far infrared band. This is important in that the far infrared power absorption coefficient is sensitive to electrodynamic factors *independent* of those which cause induced absorption.

5. Application to intermolecular interaction

Although the study of intramolecular dipole–dipole interaction is important (for example, in polymer chains), an extension of the governing master equation to intermolecular interactions is clearly essential. Only then will begin to be resolved the problem of electrodynamics versus purely repulsive potential dynamics in determining the whole zero–THz profile for liquids consisting of interacting, strongly dipolar molecules. As a first step we discuss briefly here two experimental situations where the model in its Budó form may be applicable.

5.1. The rotator phase of hexasubstituted, dipolar benzene derivatives

In an incisive and pioneering treatment, Brot and Darmon [8] have succeeded in reproducing the loss features at low frequency of trichlorotrimethyl benzene in the disordered solid state over a range of temperature using semi-stochastic Monte-Carlo techniques. Charge–charge interaction potentials were summed over a block of 240 molecules. The relatively primitive Budó model may be used to investigate the extent to which the pair-interaction approximation is applicable. The geometric constraints are satisfied since the molecules are translationally invariant and stacked parallel, and the data is sufficient to determine V to any order in a multipole expansion [7] such as

$$V = -\{\mu_1\mu_2/R^3 + (3/R^4)(\Theta_2\mu_1 + \mu_2\Theta_1)\cos(2\eta) + (3\Theta_1\Theta_2/4R^5)[1 + 2\cos^2(2\eta)] + \ldots\}$$

in standard notation [7].

5.2. The nematic phase of 4η-heptyl 4'-cyanobiphenyl

In this case the long axis of the molecule is statistically parallel to the nematic phase director axis, and V could be considered as the nematic pseudo-potential. It is interesting that the recent data of Buka and Price [12,13] show a distribution of relaxation times in a fashion similar to that illustrated in figs. 2a to 2d.

6. Relation to models of the liquid state

The Budó equations reduce to those governing the planar itinerant librator [14] with the constraint applied that $\boldsymbol{E}$ is always coplanar with that defining the angle 2η, and provided V is harmonic. The dielectric loss is then governed by stochastic differential equations of motion which may be solved exactly with full inertial considerations. Consequently the Poley absorption is fairly well described [14] although the model is obviously limited in scope.

Acknowledgement

MWE thanks N.A.G. Central Office for their valuable help.

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