Spectrochimica Acta Vol. 38A, No. 4, pp. 429–435, 1982
Printed in Great Britain.

0584-8539/82/040429-07$03.00/0

Dielectric spectroscopy and molecular theory of aligned nematics

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(*Received* 15 *January* 1981)

Abstract—The reorientation in the liquid crystal mesophase of a molecular dipole vector (μ) is coupled analytically to the centre of mass translational velocity (v). The resulting equations for the complex permittivity (ϵ^*) contain three phenomenological friction parameters, γ_μ, γ_v and $\gamma_{\mu v}\gamma_{v\mu}$. Here γ_μ is the orientational friction, γ_v that opposing the centre of mass translation and $\gamma_{\mu v}\gamma_{v\mu}$ a product of coupling frictions (off diagonal elements of the tensor γ). The Cole–Cole plot of ϵ^* can be flattened, split and skewed using different combinations of the elements of γ. It is possible to obtain more than one relaxation time from a given rotational friction γ_μ provided that the orientational/translation coupling is properly accounted for. The theory is developed to include inertial and memory effects. Dielectric phenomena across the nematic to isotropic phase transition are reproduced in a natural manner by taking into account the fact that when the macroscopic sample becomes isotropic the autocorrelation functions $\langle \mu(0) \cdot v(t) \rangle$ and $\langle v(0) \cdot \mu(t) \rangle$ vanish using symmetry rules concerning parity, reflection and time reversal.

1. INTRODUCTION

In the classical theory of dielectric relaxation in isotropic liquids (DEBYE[1]) the reorientation of the molecular dipole is opposed by a scalar friction coefficient γ. This has its origin essentially in the fact that Debye considered the rotational diffusion of a spherically symmetric molecule within which is embedded a permanent dipole moment. PERRIN[2] has of course extended the basic idea to the asymmetric top, where γ is a tensor, assumed to be diagonalizable, and where there appear (theoretically) three relaxation times. In an isotropic liquid such as nitrobenzene these cannot be resolved experimentally. However, it is well known[3] that the dielectric spectrum of an aligned nematogen is composed of more than one loss feature, depending on whether the measuring and aligning fields are parallel or perpendicular. These are easily resolved in molecules which can exist in a nematic state but which are otherwise similar in shape and size and in electrical properties to nitrobenzene, except that they usually have long alkyl chains attached to the aromatic framework.

Up to now the explanation of such features has rested on a hydrodynamic basis involving the use of the director potential[4–6]. The molecular origin of this is not discussed. Therefore there is no real basis for its use other than the purely phenomenological. The "director" is a macroscopic idea, and there is no basis for its existence in the microscopic Liouville equation of the molecular ensemble.[7]. It is possible, however, to manipulate the Liouville equation by the use of projection operators into a form which is more convenient for use in dielectric spectroscopy in the range from static to THz (far i.r.). The *molecular* Liouville equation can for example be written as in equation (1) below, first developed by MORI[8].

This has proven to be of great value in explaining, for example, features of depolarized Rayleigh scattering of light[9] (first discovered in the late sixties) using in some cases molecular theories as opposed to hydrodynamic. This is essentially because it is possible to consider the time evolution of *column vectors* (A) made up of dynamically independent variables. For the purposes of this paper we will write

$$\mathbf{A} = \begin{bmatrix} \mu \\ \mathbf{v} \end{bmatrix}$$

where μ is the molecular dipole moment and v the centre of mass *translational* velocity. The reason will become clear as the paper is developed. Equation (1) below may then be used to calculate the behaviour of the autocorrelation function (a.c.f.s) $\langle \mu(0) \cdot \mathbf{v}(t) \rangle$ and/or $\langle \mathbf{v}(t) \cdot \mu(0) \rangle$ where $\langle\ \rangle$ denotes an ensemble average over the macroscopic sample of dielectric. It is well known[10] that these a.c.f.s will vanish if μ and v: (a) have different time reversal symmetry; (b) have different parity; and (c) are different in reflection symmetry. These rules apply however *only in an isotropic medium. In the aligned nematic phase these symmetry constraints do not apply and the a.c.f.s mentioned above can exist.*

The rest of the paper is based on this fact and is an attempt to outline very simply some of the consequences for the molecular approach to dielectric spectroscopy in liquid crystals, or more specifically, in the aligned (and birefringent) nematic mesophase of polar molecules. We are not concerned whether or not the a.c.f.s exist, but only with the fact that they *may* exist. Consequently we are at pains to point out that the statistical autocorrelation of molecular μ and molecular v *can* be used to explain why the dielectric spectrum

of an aligned nematogen peaks more than once *provided that the macroscopic sample remains birefringent.* We do *not* wish to make any sweeping claim that this is the origin of all liquid crystalline properties. We do not however have recourse to the nematic director, which has a hypothetical existence independent of that of the molecular entity[6].

The theory is consciously over simplified and self-contradictory in that we do not wish to obscure matters by considering anything other than the Debye spherical diffuser coupled to its own centre of mass translational velocity. This is *of course* inconsistent with the fact that the molecules of the nematogen are asymmetric tops; and anything but spherical. Our basic theory is however applicable more generally, i.e. to Perrin rather than Debye. The complexity of this extension is well known. In the practical sense the general theory of Perrin is rarely if ever *useful* in isotropic liquids as mentioned already. Similarly, it is very rare for more than two peaks to be resolved in the dielectric spectrum of the aligned nematic. These can be explained qualitatively by the simple theory developed here. This is all we wish to do. It follows dialectically that there is no purpose in trying to match this with the *details* of the experimental data. An oversimplified theory can be forced to fit a set of data, of course, but to little purpose. The correct way of embellishing the present approach would be via molecular dynamics computer simulation of $\langle \mathbf{v}(t) \cdot \boldsymbol{\mu}(0) \rangle$ or $\langle \boldsymbol{\mu}(0) \cdot \mathbf{v}(t) \rangle$ in the aligned nematic.

The paper is developed as follows. In Section 2 we manipulate the molecular Liouville equation to the point where it may be approximated successively by utilising the Mori continued fraction. The equation of motion in this case is for the column vector

$$\mathbf{A} = \begin{bmatrix} \mathbf{u} \\ \mathbf{v} \end{bmatrix}$$

where $\mathbf{v}$ is the centre of mass linear velocity.

In Section 3 the autocorrelation functions of interest are extracted from the theory and Fourier transformed to produce the final spectral bandshapes. We discuss how the number of free parameters may be kept to a minimum by the use of molecular dynamics simulations of the nature of the molecular diffusion. If this is isotropic the influence of rototranslational effects[11, 12] on the spectrum is expected to be vanishingly small.

In Section 4 the results of some simulations on a C_{2v} symmetry triatomic are presented as an illustration of the strategy discussed in Section 3.

2. EQUATIONS OF MOTION

The basic equation is the integro-differential form of the Liouville formalism[13] developed originally by KUBO[14] and ZWANZIG[15]

$$\dot{\mathbf{A}}(t) = i\boldsymbol{\Omega}_{\mathbf{A}} \cdot \mathbf{A}(t) - \int_0^t \mathrm{d}\tau \boldsymbol{\phi}_{\mathbf{A}}(t-\tau)\mathbf{A}(\tau) + \mathbf{F}_{\mathbf{A}}(t). \tag{1}$$

Here $\boldsymbol{\Omega}_{\mathbf{A}}$ is a resonance frequency operator, the matrix kernel $\boldsymbol{\phi}_{\mathbf{A}}(t)$ is the memory tensor and $\mathbf{F}_{\mathbf{A}}(t)$ is a 'generalized force' or 'torque' propagated by projection from A(0). EVANS, GRIGOLINI and FERRARIO[16] have shown recently that equation (1) may be replaced by a Markovian matrix equation

$$\dot{\mathbf{V}} = i\boldsymbol{\omega} \cdot \mathbf{V} - \boldsymbol{\alpha} \cdot \mathbf{V} - \boldsymbol{\sigma} \cdot \mathbf{V} + \boldsymbol{\Phi}(t) \tag{2}$$

where $\mathbf{V}$ is an n-dimensional column vector of m components, which are, in turn, m-dimensional vectors.

So we have

$$\mathbf{V} = \begin{bmatrix} \mathbf{A}_1 \\ \vdots \\ \mathbf{A}_n \end{bmatrix}; \quad \boldsymbol{\omega} = \begin{bmatrix} \boldsymbol{\Omega}_1' & 0 & 0 \ldots & 0 \\ 0 & \boldsymbol{\Omega}_2' & 0 \ldots & 0 \\ 0 & 0 & \boldsymbol{\Omega}_3' & \\ 0 & 0 & 0 & \boldsymbol{\Omega}_n' \end{bmatrix}$$

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \omega_{12} & 0 \ldots & 0 \ldots \\ \omega_{21} & 0 & \omega_{23} & 0 \ldots \\ 0 & \omega_{32} & 0 \ \omega_{34} & 0 \ldots \\ 0 & 0 & \omega_{43}\ 0 & \omega_{45} \ldots \\ & & & \end{bmatrix}; \quad \boldsymbol{\sigma} = \begin{bmatrix} \gamma & 0 \ldots \\ 0 & \end{bmatrix}$$

$$\boldsymbol{\Phi} = \begin{bmatrix} \mathbf{F}(t) \\ \vdots \\ \cdot \end{bmatrix}$$

Equation (1) may be rationally approximated by expanding the memory matrix in a continued fraction

$$\cfrac{1}{\cdot \cfrac{1}{\cdot \cfrac{1}{\Delta_{n-2}^2 + 1p - i\boldsymbol{\Omega}_{n-1}} \Delta_{n-1}^2} \cdot} = \boldsymbol{\Phi}(p)$$

$$\cfrac{1}{1p - i\boldsymbol{\Omega}_1 + \boldsymbol{\gamma}} \Delta_1^2 + 1_p - i\boldsymbol{\Omega}_2. \tag{3}$$

This allows us to define the grand matrices $\boldsymbol{\gamma}$, $\boldsymbol{\omega}$, $\boldsymbol{\alpha}$, $\boldsymbol{\sigma}$ and $\boldsymbol{\Phi}$ in terms of the coefficients appearing in the continued fraction. We have

$$\boldsymbol{\Omega}_n' = \boldsymbol{\Omega}; \quad \boldsymbol{\Omega}_{n-1}' = \boldsymbol{\Omega}_{n-1}$$

$$-\Delta_1^2 = \omega_{21} \cdot \omega_{12}; -\Delta_2^2 = \omega_{32} \cdot \omega_{23}.$$

The first approximant of equation (3) corresponds to equation (2) in the form:

$$\dot{\mathbf{A}}_1 = -\omega_{12}\cdot\mathbf{A}_2 - \gamma\cdot\mathbf{A}_1 + \mathbf{F}(t)$$
$$\mathbf{A}_2 = \mathbf{0}. \tag{4}$$

The rototranslational diffusion in space of a single molecule is governed by equation (4) in the simplest case where $\mathbf{F}(t)$ is both Gaussian and Markovian. To evaluate the mutual influence of the orientational vector μ and the centre of mass velocity vector $\mathbf{v}$ it is sufficient to write

$$\mathbf{A}_1 = \begin{bmatrix}\mu\\ \mathbf{v}\end{bmatrix};\quad \mathbf{F} = \begin{bmatrix}\Gamma\\ \mathbf{F}\end{bmatrix}$$

where Γ is Mori-propagated from μ and $\mathbf{F}$ is Mori-propagated from $\mathbf{v}$. In general the friction grand-matrix is

$$\gamma = \begin{bmatrix}\gamma_\mu & \gamma_{\mu v}\\ \gamma_{v\mu} & \gamma_v\end{bmatrix}$$

where γ_μ and γ_v are tensors for asymmetric diffusion, but scalars for isotropic diffusion. The off-diagonal elements are measures of the rototranslational interaction. Equation (4) can now be written as

$$\dot{\mu} = -\gamma_\mu\cdot\mu - \gamma_{\mu v}\cdot\mathbf{v} + \Gamma(t) \tag{5}$$

$$\dot{\mathbf{v}} = -\gamma_{v\mu}\cdot\mu - \gamma_v\cdot\mathbf{v} + \mathbf{F}(t). \tag{6}$$

By Laplace transformation

$$-\mu(0) + p\tilde{\mu} = -\gamma_v\cdot\tilde{\mathbf{v}} - \gamma_{v\mu}\cdot\tilde{\mu} + \tilde{\mathbf{F}}$$

$$-\mu(0) + p\tilde{\mu} = -\gamma_\mu\cdot\tilde{\mu}' - \gamma_{\mu v}\cdot\tilde{\mathbf{v}} + \Gamma$$

so that

$$-\mathbf{v}(0) + p\tilde{\mathbf{v}} = \left[-\gamma_v + \frac{\gamma_{v\mu}\cdot\gamma_{\mu v}}{1p+\gamma_\mu}\right]\tilde{\mathbf{v}} + \tilde{\mathbf{F}}'$$
$$\equiv -\beta_v(p)\tilde{\mathbf{v}} + \tilde{\mathbf{F}}'$$

where

$$\tilde{\mathbf{F}}' = \tilde{\mathbf{F}} + \frac{\tilde{\Gamma} + \mu(0)}{1p+\gamma_\mu}.$$

If we now examine the memory kernel $\beta_v(p)$ in the case $|\gamma_{v\mu}|, |\gamma_{\mu v}| \ll \gamma_\mu, \gamma_v$ we may make the markovian assumption

$$\beta_v(p) = \gamma_v - \frac{\gamma_{v\mu}\cdot\gamma_{\mu v}}{1p+\gamma_\mu}$$
$$= \gamma_v\cdot[1 - \gamma_{\mu v}\cdot\gamma_{v\mu}/\gamma_\mu\cdot\gamma_v]. \tag{7}$$

Similarly

$$\beta_\mu(p) = \gamma_\mu\cdot[1 - \gamma_{\mu v}\cdot\gamma_{v\mu}/\gamma_\mu\cdot\gamma_v]. \tag{8}$$

Equations (7) and (8) imply that in the presence of off-diagonal elements of γ translational and orientational frictions are diminished if $\gamma_{\mu v}$ and $\gamma_{v\mu}$ have the same signs. Otherwise, the rotation/translation interaction increases both the rotational and translational frictions separately considered.

The physical meaning of equations (5) and (6) may be clarified in the decoupled limit by noting that the orientational equation of motion then reduces to

$$\dot{\mu} = -\gamma_\mu\cdot\mu + \Gamma(\tau). \tag{9}$$

This is in turn the Langevin equation analagous to the Favro equation[13] for rotational diffusion

$$\frac{\mathrm{d}}{\mathrm{d}t}f(\Omega, t) = -\hat{M}\cdot\mathbf{D}\cdot\hat{M}f(\Omega, t) \tag{10}$$

where $\mathbf{D}$ is a diffusion tensor and $\hat{M}$ is identical with the quantum-mechanical angular momentum operator. Here $f(\Omega, t)$ is a probability density function governing the set of Euler angles $\Omega \equiv (\theta, \phi, \chi)$. Equation (10) can be converted into equation (9) following the method used by NEE and ZWANZIG[17]. This involves linearizing Euler's equations and restricting the nature of the body under consideration to an inertial spherical top undergoing, by implication, isotropic rotational diffusion. The diagonal elements of γ are in this case all equal. Note that in equations (9) and (10) memory effects can be introduced by making $\mathbf{D}$ or γ time dependent. In equations (5) and (6), therefore, the γs are scalars.

Solving equations (5) and (6) for the orientational auto-correlation function we have

$$\frac{\langle\mu(\tau)\cdot\mu(0)\rangle}{\langle\mu(0)\cdot\mu(0)\rangle} = \mathscr{L}_a^{-1}\left[\frac{p+\gamma_v}{(p+\gamma_v)(p+\gamma_\mu) - \gamma_{\mu v}\gamma_{v\mu}}\right] \tag{11}$$

$$\to \mathscr{L}_a^{-1}(p+\gamma_\mu)^{-1} \tag{12}$$

when $\gamma_{\mu v} = \gamma_{v\mu} = 0$. *The orientational autocorrelation function is exponential* [*equation* (12)] *only when rototranslational interaction is negligible.* Inverting equation (12) gives

$$\frac{\langle\mu(\tau)\cdot\mu(0)\rangle}{\langle\mu(0)\cdot\mu(0)\rangle} = \mathrm{e}^{-bt}\left[\cos(c-b^2)^{1/2}t + \frac{\gamma_v - b}{(c-b^2)^{1/2}}\sin(c-b^2)^{1/2}t\right],\quad c > b^2$$

$$= \mathrm{e}^{-bt}\left[\cosh(b^2-c)^{1/2}t + \frac{\gamma_v - b}{(b^2-c)^{1/2}}\sinh(b^2-c)^{1/2}t\right],\quad c < b^2 \tag{13}$$

$$\langle\mu(\tau)\cdot\mathbf{v}(0)\rangle/\langle\mu(0)\cdot\mu(0)\rangle$$

$$= -\gamma_{v\mu}\, e^{-bt} \sin (c - b^2)^{1/2} t, \quad c > b^2$$

$$= -\gamma_{\mu v}\, e^{-bt} \sinh (b^2 - c)^{1/2} t, \quad b^2 < c. \quad (14)$$

Here $b = 2(\gamma_v + \gamma_\mu)$: $c = \gamma_v\gamma_\mu - \gamma_{v\mu}\gamma_{\mu v}$. The dielectric complex permittivity is related to the Fourier transform of $\langle \mu(t) \cdot \mu(0) \rangle$, but not straightforwardly, because what is observable in zero-THz spectroscopy is a macroscopic volume of interacting dipoles. The task of relating the multi-particle and single particle dipole correlation functions is tremendously protracted, but progress has been made recently using micro–macro theorems (MADDEN and KIVELSON[18]). EVANS *et al.*[19] have recently pointed out that the dielectric friction of NEE and ZWANZIG[17] has no effect on the direct Fourier transform of $\langle \mu(t) \cdot \mu(0) \rangle$, but only on the integrated intensity of the power absoption coefficient [$\alpha(\omega)$]. However, the effect on the loss curve [$\epsilon''(\omega)$] is to displace it, as usual, to peak at lower frequencies. If we are concerned with the shape of the $\alpha(\omega)$ curve it is reasonable to neglect all internal field corrections. In this case

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_p)\omega_0 \int_0^\infty \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \cos \omega t \, dt \quad (15)$$

$$\epsilon'(\omega) = \epsilon_0(\epsilon_0 - \epsilon_p)\omega_0 \int_0^\infty \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \sin \omega t \, dt. \quad (16)$$

Here $\mathbf{u} = \boldsymbol{\mu}/|\boldsymbol{\mu}|$; and ϵ_p is the high frequency limit of $\epsilon'(\omega)$. This is not ϵ_∞ of the semicircular Cole–Cole plot if we wish to take into account the far i.r. part of the dielectric permittivity or power absorption coefficient. Using equations (15) and (16) we have:

$$\epsilon''(\omega) = \frac{(\epsilon_0 - \epsilon_p)\omega[\omega^2\gamma_\mu + \gamma_v(\gamma_v\gamma_\mu - \gamma_{\mu v}\gamma_{v\mu})]}{[\gamma_v\gamma_\mu - \gamma_{\mu v}\gamma_{v\mu} - \omega^2]^2 + \omega^2[\gamma_\mu + \gamma_v]^2} \quad (17)$$
$$\rightarrow (\epsilon_0 - \epsilon_\infty)\omega\gamma_\mu/[\omega^2 + \gamma_\mu^2] \quad \text{if } \gamma_{\mu v}\gamma_{v\mu} = 0$$

$$\epsilon'(\omega) = \frac{\epsilon_0 - (\epsilon_0 - \epsilon_p)\omega^2[\gamma_v^2 + \gamma_{\mu v}\gamma_{v\mu} + \omega^2]}{[\gamma_v\gamma_\mu - \gamma_{\mu v}\gamma_{v\mu} - \omega^2]^2 + \omega^2[\gamma_\mu + \gamma_v]^2}$$

$$\rightarrow \frac{\epsilon_0 - (\epsilon_0 - \epsilon_p)\omega^2}{\omega^2 + \gamma_\mu^2}, \quad \text{if } \gamma_{\mu v}\gamma_{v\mu} = 0. \quad (18)$$

The power absorption coefficient is given by the solution of Maxwell's equations

$$\alpha(\omega) = \frac{2\sqrt{2}\epsilon''(\omega)\bar{\nu}}{[(\epsilon''(\omega)^2 + \epsilon'(\omega)^2)^{1/2} + \epsilon'(\omega)]^{1/2}}$$

with $\omega = 2\pi\bar{\nu}c$.

If the influence of centre of mass translation on orientation is strong the complex permittivity is likewise affected as shown in Fig. 1.

It is well known that Markov statistics cannot be used to account for the intense Poley absorption

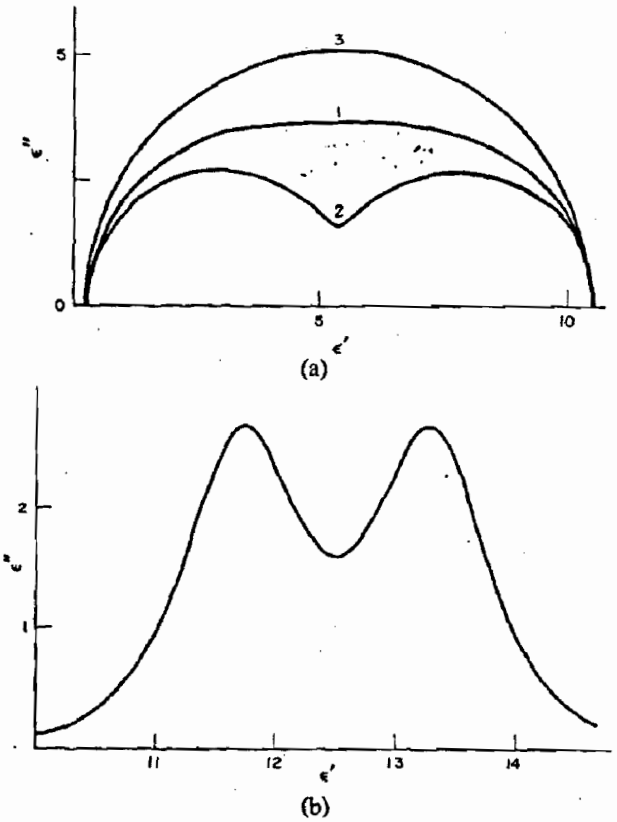

Fig. 1. (a) Effect of strong rotation–translation interaction on the semicircular Cole–Cole plot. (1) $\gamma_v = \gamma_\mu = 10 \times 10^{12}\ s^{-1}$; $\gamma_{v\mu}\gamma_{\mu v} = 50 \times 10^{24}\ s^{-2}$; (2) $\gamma_v = \gamma_\mu = 10 \times 10^{12}\ s^{-1}$; $\gamma_{v\mu}\gamma_{\mu v} = 90 \times 10^{24}\ s^{-2}$; (3) semicircles. (b) Loss curve for strong orientation/translation coupling.

encountered in the far i.r. region for all dipolar molecules in the liquid state[20]. Equations (17) and (18) are therefore inadequate to extract the effects of the orientation–translation interaction from the complete zero-THz profile (inclusive of the far i.r.) except by concentrating on the low frequency loss alone. However, strong effects of rotation–translation coupling have been observed recently by tracer diffusion experiments[21] where the area beneath the linear velocity auto-correlation function is measured. (The diffusion coefficient is related to this quantity.) In our treatment of this effect the velocity autocorrelation function is given by an expression similar to equation (13). The response of this a.c.f. to orientational coupling is shown in Fig. 2 as a function of $\gamma_{v\mu}\gamma_{\mu v}$.

To improve the basic description of the complete experimental zero-THz profile it is necessary to expand the system of equations (4). It is convenient to truncate the system at the level corresponding to an exponentially decaying *second* memory tensor. In the limit of vanishingly small rotation–translation interaction the equations of motion separate into their translational and orientational components. The former corresponds identically with the translational itinerant oscillator model of DAMLE *et al.*[22], and/or COFFEY *et al.*[23]. The latter corresponds exactly with the orientational theory developed by QUENTREC and BEZOT[24], BAROJAS, LEVESQUE and

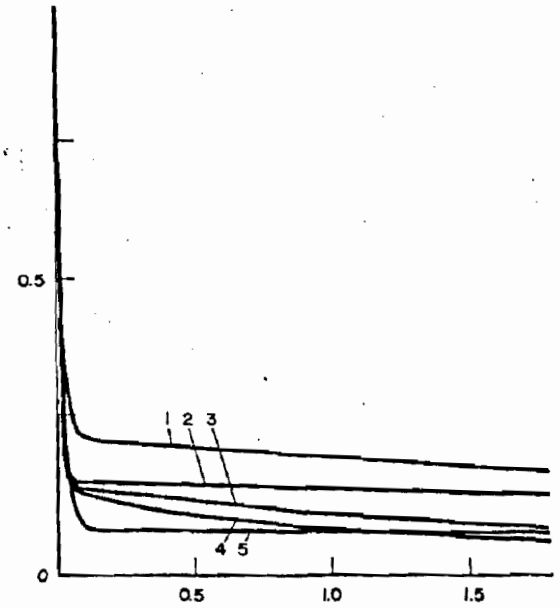

Fig. 2. Response of the velocity autocorrelation function to an increasing coupling parameter $\gamma_{v\mu}\gamma_{\mu v}$. (1) $\gamma_v = 10\times10^{12}$ s^{-1}; $\gamma_\mu = 2\times10^{12}$ s^{-1}; $\gamma_{v\mu}\gamma_{\mu v} = 10\times10^{24}$ s^{-2}; (2) $\gamma_v = 10\times10^{12}$ s^{-1}; $\gamma_\mu = 10\times10^{12}$ s^{-1}; $\gamma_{v\mu}\gamma_{\mu v} = 90\times10^{24}$ s^{-2}; (3) $\gamma_v = 10\times10^{12}$ s^{-1}; $\gamma_\mu = 10\times10^{12}$ s^{-1}; $\gamma_{v\mu}\gamma_{\mu v} = 50\times10^{24}$ s^{-2}; (4) $\gamma_v = 10\times10^{12}$ s^{-1}; $\gamma_\mu = 10\times10^{12}$ s^{-1}; $\gamma_{v\mu}\gamma_{\mu v} = 10\times10^{24}$ s^{-2}; (5) $\gamma_v = 2\times10^{12}$ s^{-1}; $\gamma_\mu = 10\times10^{12}$ s^{-1}; $\gamma_{v\mu}\gamma_{\mu v} = 10\times10^{24}$ s^{-2}. Abscissa: ps.

QUENTREC[25], and EVANS *et al.*[26] for molecular dynamics results and for zero-THz profiles of liquids, plastic crystals and nematogens. The uncoupled orientational theory of this system forms the basis of the macro–micro theorem developed by Kivelson and Madden and also the extension to include memory effects of the NEE–ZWANZIG theory[17] by LOBO, ROBINSON and RODRIQUEZ[27]. In the multi-Markovian representation the complete orientation–translation system may be expressed as

$$\begin{aligned}\dot{\mathbf{A}}_1 &= -\omega_{12}\cdot\mathbf{A}_2 - \gamma\cdot\mathbf{A}_1 + \mathbf{F}(t)\\ \dot{\mathbf{A}}_2 &= -\omega_{21}\cdot\mathbf{A}_1 - \omega_{23}\cdot\mathbf{A}_3\\ \dot{\mathbf{A}}_3 &= -\omega_{32}\cdot\mathbf{A}_2 - \omega_{34}\cdot\mathbf{A}_4\\ \mathbf{A}_4 &= \mathbf{0}.\end{aligned} \tag{19}$$

The solution in terms of the orientational (dipole) auto-correlation function is

$$\begin{aligned}\langle\mu(t)\cdot\mu(0)\rangle = \hat{\mathscr{L}}_a^{-1}[&p(p^2+\Delta_2^{v2})[(p+\gamma_\mu)(p+\gamma_v) - \gamma_{v\mu}\gamma_{\mu v}]\\ &+ p^2[\Delta_1^{\mu 2}(p+\gamma_v)+\Delta_1^{v2}(p+\gamma_\mu)]\\ &+ \Delta_1^{\mu 2}(\Delta_1^{v2}p + (p+\gamma_v)\Delta_2^{v2})]/\bar{G}(p)\end{aligned} \tag{20}$$

where

$$\begin{aligned}\bar{G}(p) = (p^2+\Delta_2^{v2})(p^2+\Delta_2^{\mu 2})&\\ \times[(p+\gamma_v)(p+\gamma_\mu) - \gamma_{\mu v}\gamma_{v\mu}]&\\ + p[(p+\gamma_v)\Delta_2^{v2}\Delta_1^{\mu 2} + (p+\gamma_\mu)\Delta_1^{v2}\Delta_2^{\mu 2})&\\ + p^3[\Delta_1^{\mu 2}(p+\gamma_v) + \Delta_1^{v2}(p+\gamma_\mu)].&\end{aligned}$$

The autocorrelation function is intractable analytically from equation (20) but the loss and permittivity may be extracted by Fourier–Laplace transform. When $\gamma_{v\mu}\gamma_{\mu v} = 0$ equation (20) reduces to

$$\frac{\langle\mu(t)\cdot\mu(0)\rangle}{\langle\mu(0)\cdot\mu(0)\rangle} = \mathscr{L}_a^{-1}\frac{p^2+\gamma_\mu p+\Delta_1^{\mu 2}}{p^3+\gamma_\mu p^2+(\Delta_1^{\mu 2}+\Delta_2^{\mu 2})p+\Delta_2^{\mu 2}\gamma_\mu}$$

which has been discussed at length in the literature[26]. The equilibrium Δ averages which appear in equation (20) are defined generally as

$$\Delta_2^{v2} = \langle\dot{v}^2(0)\rangle/\langle v^2(0)\rangle;\quad \Delta_2^{\mu 2} = \langle\dot{\mu}^2(0)\rangle/\langle\mu^2(0)\rangle;$$

$$\Delta_1^{v2} = \frac{\langle\ddot{v}^2(0)\rangle}{\langle\dot{v}^2(0)\rangle} - \frac{\langle\dot{v}^2(0)\rangle}{\langle v^2(0)\rangle};\ \Delta_1^{\mu 2} = \frac{\langle\ddot{\mu}^2(0)\rangle}{\langle\dot{\mu}^2(0)\rangle} - \frac{\langle\dot{\mu}^2(0)\rangle}{\langle\mu^2(0)\rangle}$$

so that $\Delta_1^{\mu 2}$ involves the equilibrium mean square torque and Δ_1^{v2} the equilibrium mean square force, both of which may be simulated in a molecular dynamics run. The loss and permittivity from equation (20) are therefore obtainable by Fourier–Laplace inversion.

3. BANDSHAPES AND COLE–COLE PLOTS

Although the Cole–Cole plot is usually the least discriminating method of presenting the results of dielectric measurements it is well known to have some general features which are interpreted empirically: for example the COLE–DAVIDSON skewed arc and flattened arc of the Fuoss–Kirkwood treatment[28]. *Figures* 2 *and* 3 *illustrate that the skewness and flatness can be reproduced from equations* (17) *and* (18) *by introducing different types of rotation–translation coupling.* For example, when the translational friction is greater than the orientational friction and the two motions are moderately coupled we obtain the beginnings of a Cole–Davidson skewed arc. When the rotational and translational frictions are interchanged, the Cole–Cole plot is skewed in the other sense. Finally when both orientational and translational frictions are equal and strongly coupled (Fig. 1) the Cole–Cole arc is flattened. Flattening of the Cole–Cole arc occurs when there is a strong mutual effect of orientation and translation. In the limit of strong interaction ($\gamma_\mu\gamma_v \approx \gamma_{\mu v}\gamma_{v\mu}$) the loss curve is split into two distinct relaxations (Fig. 1), although only one purely rotational relaxation time is used. This may be thought of as being equivalent to the Rytov splitting[9] observable[29] in the spectrum of depolarized, scattered light, where the phenomenological Mori equations are identical with equations (17) and (18), except that the quantities γ_μ, γ_v and $\gamma_{v\mu}\gamma_{\mu v}$ have a different physical meaning.

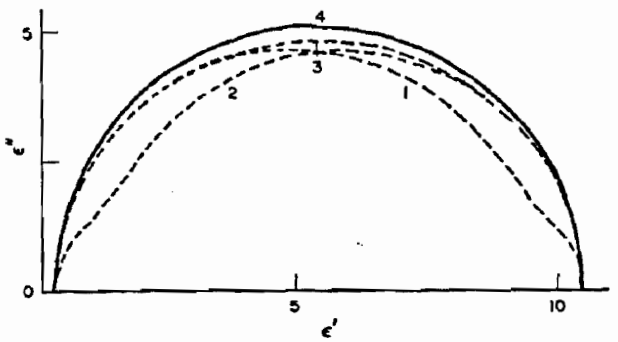

Fig. 3. Skewing the Cole–Cole plot with coupling parameters. (1) $\gamma_v = 2\times10^{12}\,s^{-1}$; $\gamma_\mu = 10\times10^{12}\,s^{-1}$; $\gamma_{\mu v}\gamma_{v\mu} = 10\times10^{24}\,s^{-2}$; (2) $\gamma_v = 10\times10^{12}\,s^{-1}$; $\gamma_\mu = 10\times10^{12}\,s^{-1}$; $\gamma_{\mu v}\gamma_{v\mu} = 10\times10^{24}\,s^{-2}$; (3) $\gamma_v = 10\times10^{12}\,s^{-1}$ $\gamma_\mu = 2\times10^{12}\,s^{-1}$; $\gamma_{\mu v}\gamma_{v\mu} = 10\times10^{24}\,s^{-2}$.

Note that in deriving equations (17) and (18) we have made the simplification of neglecting the effects of geometrical and diffusive anisotropy (of both rotational and translational kind). If anisotropy of diffusion is taken into account the equations (17) and (18) will be complicated by the presence of three translational frictions, three rotational frictions and three rototranslational friction elements. NEE and ZWANZIG[17] have shown that it is possible to reproduce the Cole–Davidson skewed arc by considering rotational diffusion constrained to the surface of a cone by an imposed external potential. By incorporating the effect of rototranslational coupling and using the model of anisotropic diffusion most of the empirical forms can be reproduced analytically.

The use of computer simulation to counter the problem of too many parameters may be illustrated by simulating the component autocorrelation functions of linear velocity $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$ and angular momentum $\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle$. This reveals the areas beneath $\langle v_i(t)v_i(0)\rangle$; $i = x, y, z$ and provides an idea of the differences between the translational frictions $\gamma_x^{(v)}$, $\gamma_y^{(v)}$ and $\gamma_z^{(v)}$ and rotational frictions $\gamma_x^{(J)}$, $\gamma_y^{(J)}$ and $\gamma_z^{(J)}$. This is described for a C_{2v} triatomic in Section 4.

4. SIMULATION OF COMPONENT CORRELATION TIMES

The purpose of this section is to illustrate the appearance of orientational and translational auto correlation functions as computed in a molecular dynamics simulation of an isotropic liquid. In principle, if the total sample under consideration is not isotropic, as in the aligned nematic, it would be possible to simulate functions such as $\langle \mu(t)\cdot v(0)\rangle$ and investigate them in detail. The technique of molecular dynamics simulation is important in this context because it provides a means of building up a function of theoretical interest which is accessible experimentally only through the intermediacy of generalized Langevin theory.

A molecular dynamics simulation of a triatomic molecule ($\alpha\beta\alpha$) was carried out with a two-step predictor/corrector method (U.M.R.C.C. CDC 7600). The molecule was given a bond length of 1×10^{-10} m, an included angle of 60°, an α atom mass of 2.5×10^{-25} kg and a β atom mass of 2.5×10^{-25} kg. Thermodynamic conditions were set at 220 K, with a volume of 10^{-4} m^3. The equations of motion were solved with a two-step predictor–corrector algorithm written by RENAUD and SINGER[30] and communicated to the author. It was subsequently modified to calculate autocorrelation functions over a total span of 3000 time steps of 0.01 ps each, using a recording interval to magnetic tape of 0.03 ps. The molecules interact via a 3×3 Lennard–Jones atom–atom potential with parameters $\epsilon/k = 173.5$ K, $\sigma = 3\times10^{-10}$ m.

Autocorrelation functions of the velocity and angular momentum components are illustrated in Figs. 4 and 5. In neither case is the anisotropy of the motion very pronounced, but even in the isotropic diffuser CH_4, for example, cog-wheel effects are known from neutron-scattering spectra to produce strong mutual interrelations between orientational and translational diffusion[31].

5. DISCUSSION

The points developed in this paper may be summarized as follows:

(1) In the aligned nematic environment it is possible to consider directly the mutual interaction of orientational and translational diffusion using the equation (1) with the column vector

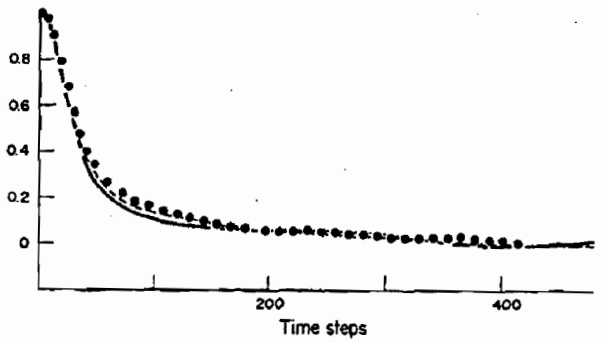

Fig. 4. Angular momentum autocorrelation functions, simulated by molecular dynamics on a C_{2v} triatomic. – – – $\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle/\langle \mathbf{J}(0)\cdot\mathbf{J}(0)\rangle$; —— $\langle J_y(t)J_y(0)\rangle/\langle J_y(0)J_y(0)\rangle$; ● $\langle J_z(t)J_z(0)\rangle/\langle J_z(0)J_z(0)\rangle$.

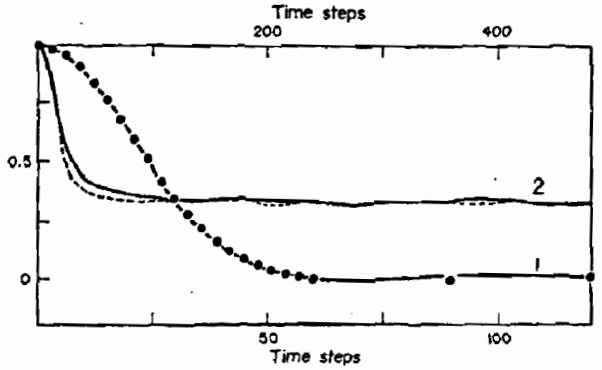

Fig. 5. Linear centre of mass velocity autocorrelation functions simulated by molecular dynamics; ——(1) $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle/\langle \mathbf{v}(0)\cdot\mathbf{v}(0)\rangle$, ● $\langle v_z(t)v_z(0)\rangle/\langle v_z(0)v_z(0)\rangle$; ——(2) $\langle v^2(t)v^2(0)\rangle/\langle v^2(0)v^2(0)\rangle$; ● $\langle v_x^2(t)v_x^2(0)\rangle/\langle v_x^2(0)v_x^2(0)\rangle$; – – – $\langle v_x^2(t)v_x^2(0)\rangle/\langle v_x^2(0)v_x^2(0)\rangle$.

$$A = \begin{bmatrix} \mu \\ \mathbf{v} \end{bmatrix}$$

where μ is the dipole orientation vector and $\mathbf{v}$ the centre of mass linear velocity.

(2) The Debye equations are then modified in such a way that Cole–Davidson skewness, symmetrical flattening and splitting of the Cole–Cole plot can be incorporated within the same analytical framework.

Acknowledgement—The S.R.C. is thanked for financial support.

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