Electrodynamic Influences on the Dielectric Absorption of Disordered Molecular Solids

BY MYRON EVANS

Chemistry Department,
University College of Wales, Aberystwyth SY23 1NE

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A model of pairwise charge–charge interaction superimposed on rotational Brownian motion is developed for the complex microscopic polarisability of a translationally invariant lattice of molecules. The model is compared with the experimental results and Monte Carlo simulation of Darmon and Brot on the disordered solid phase of 1,2,3-trichlorotrimethylbenzene (TCTMB). It is found that the long range and cooperative nature of electrodynamic interaction precludes the use of over-simplified analytical techniques and that computer simulation is a much more successful and convenient method of investigating the molecular motions in the solid. It is unlikely that analytical techniques of moderate tractability can compete in the study of liquid state molecular dynamics, without themselves becoming computer-oriented, as in this paper.

The liquid state may be defined as that where the mutual interaction of molecular translation and reorientation is at a maximum. In addition, a strongly dipolar liquid consists of molecules whose kinematic properties are modulated by a strong additional electrodynamic interaction arising basically from the distribution of the electrons about the nuclei in each molecule. In mesophases, we have the additional problem of the director potential. The electrodynamic and kinematic factors may be balanced against each other by judicious use of spectroscopies designed to illuminate differently the overall motions and interactions. The purely kinematic (translational and rotational) aspects of molecular motion may be dealt with in an increasingly penetrative fashion by the technique of computer simulation,[1] but the treatment of molecular electrodynamics in this way is more difficult due to the effect of long-range interactions on the choice of periodic boundary conditions. The corresponding analytical problem in liquids is naturally acute and related directly to that of throwing light upon the dynamic internal field.[2] It therefore seems logical to pursue simplifications which will not at the same time divorce the mathematics from physical reality. One such simplification is that of removing translation by fixing the molecular centres of mass on a periodic lattice [3] and pursuing interrelated analytical,[4] experimental and simulation information. The indications obtained by a comparison of analytical theory with experiment should not contradict those obtained from the simulation. By a judicious selection of the experimental conditions under which a lattice of strongly dipolar molecules is to be studied it is possible to try out directly and accurately a group of model preconditions. In this paper we assume for convenience that the centre of mass of each molecule on a lattice is fixed and that the molecules are interacting electrodynamically and pairwise *via* Coulombic charges situated at atomic sites. The electrodynamic potential is superposed on an underlying rotational Brownian motion, thermally stimulated and governed by Markov statistics embodied in a Smoluchowski diffusion equation. How well does our set of assumptions accord with experimental data?

To answer this question we take a natural lattice of molecules in the solid state where electrodynamic factors are important, where rotational disorder is observable dielectrically over a range of temperatures and which has been simulated by computation. Our drastic analytical assumption of pairwise interaction may then be evaluated critically, the experimental conditions having been chosen to accord with the model constraints on translation. The disordered solid phase of some hexasubstituted benzenes have been considered in great detail by Brot and Darmon,[5] using a semi-stochastic Monte Carlo simulation of the preferred molecular orientations. In these solids the van der Waals forces impose several almost equivalent potential wells (nearly sterically symmetrical molecules). The electrodynamic forces are then relatively much more important in deepening one of the the wells with respect to the others and thus in determining a preferred structure. This is the case, for example, in 1,2,3-trichlorotrimethylbenzene (TCTMB), where the electrodynamic energy alone governs the orientational thermodynamic transition as the temperature is lowered. The thermal (librational) Brownian motion of the system at high temperatures is therefore strongly modulated by an external potential and electrodynamic torques appear as extra terms in the stochastic Langevin or Smoluchowski equation governing the complex microscopic polarisability.[6] The resulting Cole–Cole plot is theoretically that for a lattice of translationally invariant molecules interacting pairwise. The model is compared with the experimental results for TCTMB at different temperatures and with the Monte Carlo simulations.

THEORETICAL METHOD

A pair of TCTMB molecules is assumed translationally invariant with respect to each molecule. We chose for convenience a mutual axis joining the centres of each benzene ring in the crystal lattice (high temperature unit cell $P2_1/C, Z = 2$, low temperature: pseudomonoclinic cell $Z = 8$; crystallographic unit cell $PT, Z = 2\times 2$).

To write the Smoluchowski equation for the variation in configuration space of the probability distribution function $f(\theta, \phi_1, \phi_2, t)$ associated with the orientation of the molecule under the influence of a time varying field we shall suppose that each molecule experiences a frictional drag ζ arising from the thermal energy of the surroundings. Denote by $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ the resultant dipole vector in each molecule. These remain in planes perpendicular to the intercentre axis (axis 1). If we denote by V the intermolecular electrodynamic potential (due to charge–charge Coulomb interactions), then the system is governed by the following differential equation, (first devised by Budó [7] in another context), for the variation in configuration space of f at time t after the sudden removal at $t = 0$ of a unidirectional field of magnitude E:

$$\frac{\partial f}{\partial t} = \frac{kT}{\zeta_1}\left[\frac{\partial^2 f}{\partial \theta^2} + \operatorname{cotan}\theta\,\frac{\partial f}{\partial \theta} + (1+\operatorname{cotan}^2\theta)\left(\frac{\partial^2 f}{\partial \phi_1^2} + \frac{\partial^2 f}{\partial \phi_2^2}\right) + 2\operatorname{cotan}^2\theta\,\frac{\partial^2 f}{\partial \phi_1\,\partial \phi_2}\right] + \frac{\partial}{\partial \phi_1}\left(f\,\frac{\sin\theta}{\zeta_1}\frac{\partial V}{\partial \phi_1}\right) + \frac{\partial}{\partial \phi_2}\left(f\,\frac{\sin\theta}{\zeta_1}\frac{\partial V}{\partial \phi_2}\right); \qquad t > 0. \tag{1}$$

In eqn (1) θ and ψ are the polar angles which specify the direction of axis 1 relative to that of $\boldsymbol{E}$, while ϕ_1 and ϕ_2 are the azimuthal angles of $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ measured from the plane containing $\boldsymbol{E}$ and axis 1. V takes therefore the argument $(\phi_1 - \phi_2)$. Introducing, following Budó [7] and Coffey,[6] the variables $\chi = (\phi_1 + \phi_2)/2$; $\eta = (\phi_1 - \phi_2)/2$

simplifies the solution of eqn (1), which in general may be expressed as:

$$f(\theta, \chi, \eta, t) = A\,\mathrm{e}^{-\beta V(2\eta)} \sum_{n=0}^{\infty} \sum_{m=0}^{n} [A_{nm} X_n^m(\theta, \chi) F_{nm}(\eta, t) + B_{nm} Y_n^m(\theta, \chi) G_{nm}(\eta, t)] \quad (2)$$

where

$$X_n^m(\theta, \chi) = P_n^m(\cos\theta)\cos m\chi$$
$$Y_n^m(\theta, \chi) = P_n^m(\cos\theta)\sin m\chi$$

are spherical harmonics and where the functions $F_{nm}(\eta)$, $G_{nm}(\eta)$, A_{nm} and B_{nm} are to be determined from the initial condition associated with eqn (1):

$$f(\phi_1, \phi_2, \theta, 0) = A \exp\{-\beta[\mu_1 \sin\theta\cos\phi_1 + \mu_2 \sin\theta\cos\phi_2]E + V(\phi_1 - \phi_2)\}$$

where $\beta = 1/kT$ and A is a constant to be determined. One finds [6] the following differential equation for $F_{nm}(\eta, t)$ and an exactly similar equation for $G_{nm}(\eta, t)$:

$$\frac{\partial F_{nm}}{\partial t}(\eta, t) = -\frac{kT}{2\zeta_1}[n(n+1) - m^2/2]F_{nm}(\eta, t) - \frac{V'(2\eta)}{\zeta_1}\frac{\partial F_{nm}}{\partial \eta}(\eta, t) + \frac{kT}{2\zeta_1}\frac{\partial^2 F_{nm}}{\partial \eta^2} \quad (3)$$

where $V' \equiv \partial V(2\eta)/\partial(2\eta)$.

Define

$$\tilde{F}_{nm}(\eta, \omega) = \int_0^\infty F_{nm}(\eta, t)\,\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}t, \quad (4)$$

then eqn (3) reduces to:

$$\frac{\mathrm{d}^2 F_{nm}}{\mathrm{d}\eta^2} - 2\phi(\eta)\frac{\mathrm{d}F_{nm}}{\mathrm{d}\eta} - [2n(n+1) - m^2 + \mathrm{i}\omega b]F_{nm} = -bF_{nm}(\eta, 0) \quad (5)$$

where

$$\phi(\eta) = V'(2\eta)/kT, \quad b = 2\zeta_1/kT.$$

Now expand the left hand side of eqn (5) in a series of eigenfunctions $Z_\lambda(\eta)$ of the Sturm–Liouville equation:

$$\frac{\mathrm{d}^2 Z_\lambda(\eta)}{\mathrm{d}\eta^2} - 2\phi(\eta)\frac{\mathrm{d}Z_\lambda(\eta)}{\mathrm{d}\eta} + \lambda Z_\lambda(\eta) = 0 \quad (6)$$

so that

$$\left.\begin{aligned} F_{nm}(\eta, 0) &= \sum_\lambda C_\lambda Z_\lambda(\eta) \\ G_{nm}(\eta, 0) &= \sum_\lambda C'_\lambda Z_\lambda(\eta) \\ \tilde{F}_{nm}(\eta, \omega) &= \sum_\lambda D_\lambda Z_\lambda(\eta) \\ \tilde{G}_{nm}(\eta, \omega) &= \sum_\lambda D'_\lambda Z_\lambda(\eta) \end{aligned}\right\} . \quad (7)$$

Using orthogonality properties of the system (5)-(7) we have:

$$\tilde{F}_{nm}(\eta, \omega) = \sum_\lambda \frac{C_\lambda b Z_\lambda(\eta)}{[\lambda + n(n+1)(a-1) - m^2(a-2)][1 + \mathrm{i}\omega\tau_\lambda]} \quad (8)$$

with a similar equation for $G_{nm}(\eta, \omega)$. The relaxation times τ_λ are given by:

$$\tau_{\lambda_{nm}} = b/[\lambda_{nm} + 2n(n+1) - m^2]. \quad (9)$$

In the case of dielectric spectroscopy, $n = m = 1$. The polarisation is not a simple exponential decay as in the case $V = 0$ but is instead a superposition of a very large number of exponentials. The complex polarisability

$$\alpha_\mu^*(\omega) = \alpha_\mu'(\omega) - \mathrm{i}\alpha_\mu''(\omega)$$

arising when the rotating group is subjected to an electric field which varies harmonically with time at an angular frequency ω may now be calculated by means of the linear response theory relation [8] which connects the after-effect and alternating field solutions together:

$$\alpha_\mu^*(\omega) = -\int_0^\infty \frac{\mathrm{d}}{\mathrm{d}t} \langle \boldsymbol{m} \,.\, \boldsymbol{e} \rangle_0 \exp(-\mathrm{i}\omega t)\, \mathrm{d}t$$

$$\equiv \alpha_\mu'(0) - \mathrm{i}\omega \int_0^\infty \langle \boldsymbol{m} \,.\, \boldsymbol{e} \rangle_0 \, \mathrm{e}^{-\mathrm{i}\omega t}\, \mathrm{d}t \tag{10}$$

where $\langle\ \rangle_0$ denotes ensemble averaging in the absence of $\boldsymbol{E}$. In eqn (10) $\langle \boldsymbol{m} \,.\, \boldsymbol{e} \rangle$ is the mean dipole moment:

$$\langle \boldsymbol{m} \,.\, \boldsymbol{e} \rangle = \frac{-\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_0^{2\pi} f(\chi,\eta,\theta,t)[(\mu_1+\mu_2)X_1^1(\theta,\chi)\cos\eta - (\mu_1-\mu_2)Y_1^1(\theta,\chi)\sin\eta]\,\mathrm{d}\Omega}{\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_0^{2\pi} f(\chi,\eta,\theta,t)\,\mathrm{d}\Omega} \tag{11}$$

(where $\mathrm{d}\Omega = \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\psi\, \mathrm{d}\phi_1\, \mathrm{d}\phi_2$).

$$= \frac{\beta E}{3} \sum_\lambda \left[\mathrm{e}^{-t/\tau_\lambda} \int_{-\pi}^{\pi} \mathrm{e}^{-\beta V(2\eta)} Z_\lambda(\eta)[C_\lambda(\mu_1+\mu_2)^2 \cos\eta + C_\lambda'(\mu_1-\mu_2)^2 \sin\eta]\, \mathrm{d}\eta \right] \tag{12}$$

where

$$C_\lambda = \int_{-\pi}^{\pi} g(\eta)Z(\eta)\cos\eta\, \mathrm{d}\eta \bigg/ \int_{-\pi}^{\pi} g(\eta)Z^2(\eta)\, \mathrm{d}\eta$$

$$C_\lambda' = \int_{-\pi}^{\pi} g(\eta)Z(\eta)\sin\eta\, \mathrm{d}\eta \bigg/ \int_{-\pi}^{\pi} g(\eta)Z^2(\eta)\, \mathrm{d}\eta$$

and the weighting function $g(\eta)$ is defined by:

$$g(\eta) = \exp\left[-2\int_0^\eta \phi(\eta)\, \mathrm{d}\eta\right]. \tag{13}$$

From eqn (12) and (10)

$$\alpha_\mu^*(\omega) = \frac{\beta E}{3} \sum_\lambda I_\lambda/(1+\mathrm{i}\omega\tau_\lambda) \tag{14}$$

I_λ is the sum in eqn (12).

A first order inertial correction to eqn (14) along the lines devised by Sack [9] would read:

$$\alpha_\mu^*(\omega) = \frac{\beta E}{2} \sum_\lambda I_\lambda \bigg/ \left(1+\mathrm{i}\omega\tau_\lambda - \frac{\omega^2\tau_\lambda I}{\zeta_1}\right) \tag{15}$$

where I is the molecular inertia component about an axis perpendicular to that of μ_1 or μ_2.

The problem of estimating the complex polarisability is analytically reduced, therefore, to that of computing the eigenvalues and eigenfunctions of the Sturm–Liouville eqn (6), given a suitable form for $V(2\eta)$.

PAIR INTERACTION *via* DISCRETE CHARGES

The translationally invariant lattice has been considered by Zwanzig [3] using point dipoles. The dipole field effects represented by external torque terms in his diffusion equation result in the appearance of a second, faster relaxation in addition to Debye relaxation by rotational diffusion with modified relaxation times. Cole [4] later extended Zwanzig's work to the dipole relaxation of a sphere and of a spherical region in surrounding dielectric, using Zwanzig's assumed distribution function equation for Brownian motion and a modified one based on Kirkwood's transport theory. The appearance of a second relaxation in Zwanzig's lattice is of course consistent to first order with the infinite number appearing from eqn (6), whatever the form of $V(2\eta)$. Our relaxation times correspond inversely to the eigenvalues of the Sturm–Liouville equation. Zwanzig's initial equation is a modified Smoluchowski equation for the Brownian rotations of dipoles in a rigid cubic lattice of a spherical sample *in vacuo*. However, as pointed out by Cole, if the time evolution of the necessary one- and two-particle configurational distribution functions are described by generalised Smoluchowski equations in which appear the dipole forces averaged over all other dipole orientations then the long range dipole forces introduce no new shorter relaxation times at all. The experimental results of Brot and Darmon [5] for TCTMB show however a symmetric broadening at low temperatures in the Cole–Cole arc (fig. 2) and for pentachlorotoluene the presence of many shorter relaxation times is indicated by a Cole–Davidson type of distribution. Their semi-stochastic Monte Carlo calculations, using charge–charge interactions between atomic sites, bear these out very closely. The point dipole model is found, however, to be altogether too crude, the simulated degenerate configurations of TCTMB within the point dipole approximation are not those which are observed experimentally at low temperature. The point dipole approximation is inadequate to predict the stable configuration at low temperatures since the dipolar character in TCTMB is distributed among several atoms which are localized far from the molecular centre.

We have to choose a form for $V(2\eta)$ between a multipole expansion and a direct evaluation of the Coulomb energy between discrete charges localised correctly on the molecules. For each pair of TCTMB molecules there will be 144 site–site interactions.

MULTIPOLE EXPANSION

In a molecule of C_{2v} symmetry such as TCTMB the use of a multipole representation of the electrodynamic potential is limited by the fact that the number of independent terms increases impractically as the series evolves. For example, there are three quadrupole components, two of which are independent, seven octopole terms and 21 hexadecapole terms: [10]

$$\Theta_{xx} = \Theta_{yy} = \Theta_{zz} = -\Theta_{xx}+\Theta_{yy} \tag{16}$$

$$\Omega_{xxz} = \Omega_{zxx} = \Omega_{xzx}; \quad \Omega_{yyz} = \Omega_{zyy} = \Omega_{yzy}; \quad \Omega_{zzz} = -(\Omega_{xxz}+\Omega_{yyz}) \tag{17}$$

etc. These terms quickly make the numerical solution of eqn (6) too costly.

SITE–SITE INTERACTION

This is formally governed by the equation: [5]

$$V = \frac{1}{n_2^2}\left(\frac{\mu}{\mu_v}\right)^2 \sum_{ij} \frac{q_i q_j}{r_{ij}} \tag{18}$$

where i and j refer to atoms in the reference molecule and one stacked parallel to it in the TCTMB lattice (see Darmon and Brot, fig. 7). The potential V is superimposed upon and governs what we shall assume to be rotational Brownian motion about the sixfold pseudo-hexad axis defining the axis 1. In eqn (18) μ_v is the dipole moment of TCTMB measured in benzene solution by Darmon and Brot and μ a rigid moment defined as follows. When placed at the centre of the molecule of solute which has a refractive index n_2, this dipolar rigid moment μ will produce in the solvent of refractive index n_1 the same field as the external moment μ_e which has been placed directly in the solvent. The correction term $(\mu/\mu_v)^2(1/n_2^2)$ is then designed to consider the crystal as a polarisable continuum in which permanent charges are immersed. This has the advantage of enabling the direct use of electrostatic formulae for a material medium provided the electric charges are correctly chosen. Polarisation phenomena are then automatically accounted for. As pointed out by Darmon and Brot, the absolute electrostatic energy is meaningless in the continuum approach, but here, as in the Monte Carlo simulation, we are interested only in the difference caused to an underlying stochastic process by the imposition of an electrodynamic torque [the angle derivative of $V(2\eta)$].

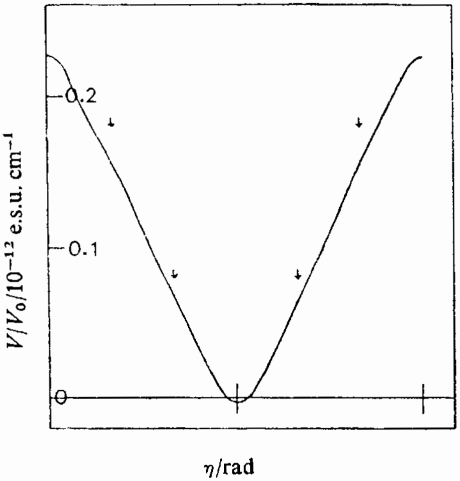

FIG. 1.—Diagram of $V(2\eta)$ for $0 \leqslant \eta \leqslant \pi$.

The charges q_i and q_j have been estimated [5] for each atom of TCTMB by decomposing the total moment into bond moments and taking account of mesomeric and induction effects. These correspond to the definition of an isolated molecule (of moment μ_v) but for the continuum approach they are all multiplied by μ/μ_v as above. Considering a common rotation axis through the centres of each benzene ring, then to a good approximation:

$$r_{ij} = [R_0^2 + r_i^2 + r_j^2 - 2r_i r_j \cos(2\eta)]^{\frac{1}{2}} \tag{19}$$

where R_0 is the intercentre distance and r_i that from the ring centre to each atom on molecule i. Eqn (6) reduces then to the normal form:

$$\frac{d^2 z}{d\eta^2} + z\left(\lambda - \phi^2(\eta) + \frac{d\phi(\eta)}{d\eta}\right) = 0 \qquad (20)$$

with $z = Z \exp\left[-\int \phi(\eta)\, d\eta\right]$. Here we have:

$$\begin{aligned} \phi(\eta) &= dV(2\eta)/d(2\eta) \\ &= -\frac{1}{n_2^2}(\mu/\mu_v)^2 \sum_{ij} \frac{r_i r_j q_i q_j \sin(2\eta)}{[R_0^2 + r_i^2 + r_j^2 - 2r_i r_j \cos(2\eta)]^{\frac{3}{2}}}. \end{aligned}$$

The bowl-shaped potential $V(2)$ is illustrated in fig. 1 as the sum over the 144 site–site interactions of the molecule pair. The average electrostatic energy difference is positive, unlike ordered lattices, due to constraints imposed by molecular van der Waals profiles and relative positions. We take R_0 as the b lattice constant which decreases as the temperature is lowered and as the lattice undergoes a disorder–order thermodynamic phase change. We now proceed to evaluate the Cole–Cole plot of $\alpha''(\omega)/\alpha(0)$ plotted against $\alpha'(\omega)/\alpha(0)$ as a function of R_0 by solving the Sturm–Liouville eqn (20) numerically using a robust and powerful algorithm newly developed by Pryce.[11]

NUMERICAL METHODS

The algorithm finds the eigenvalues λ and eigenfunctions $Z_\lambda(\eta)$ by a shooting method based on the scaled Prüfer form of eqn (20) as described by Hargrave and Pryce [12] with certain modifications. The Prüfer equations are integrated using a

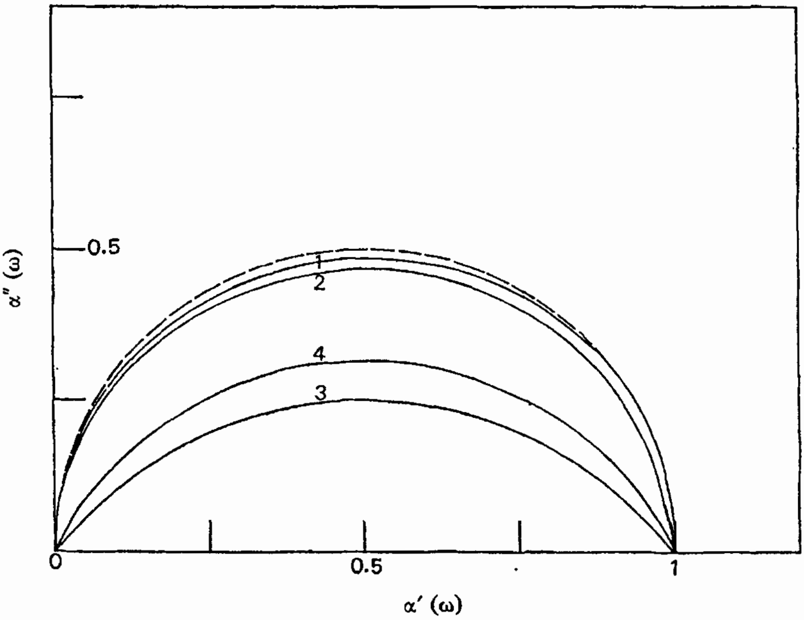

FIG. 2.—Argand diagram for $\alpha^*(\omega)/\alpha(0)$, the complex microscopic polarisability. (- - -) Semicircle. (1) Pair interaction model $(\mu/\mu_v)/n_2^2 = 1$. (2) Pair interaction model $(\mu/\mu_v)/\mu$ = Brot/Darmon value. (3) Experimental, TCTMB solid, 186 K. (4) Monte Carlo simulation,[5] 170 K.

Runge–Kutta formula devised by Merson, with automatic control of local error. The computed values of λ have a mixed absolute/relative error, those in table 1 being set accurate to 1 part in $\approx 10^8$ or 10^9. The eigenvalue part of the algorithm will soon become available as Numerical Algorithm Group (mark 7) DO2KDF.

The eigenfunctions are evaluated by a method which relies on the construction of a miss–distance function which for given trial values of the parameters measures how far the conditions of the problem are being met. The problem is then reduced to one of finding the values of the parameters for which the miss–distance function is zero, *i.e.*, to a root-finding process. Numerical solution is actually effected by shooting forward from the left hand boundary condition and backward from the right to a matching point. In common with the Mathieu and Hill equations, eqn (20) is such that the periodicity of $V(2\eta)$ is that of $z(2\eta)$. The boundary conditions are therefore $z'(0) = z'(\pi) = 0$.

TABLE 1.—λ AND I_λ FOR VARIOUS VALUES OF $x = (\mu/\mu_v)(1/n_2^2)$

x	n	λ_n	$I^\lambda(\mu_1 \pm \mu_2)^2 \pm \approx 0.001$
1	0	0.000 000 ± 0.000 000 6	0.071
	1	0.023 70 ± 0.000 000 6	0.887
	2	8.923 0 ± 0.000 005 6	0.180
	3	14.350 2 ± 0.000 010	0.000
	4	20.304 6 ± 0.000 013	0.021
	5	29.108 1 ± 0.000 18	0.0039
	6	40.085 6 ± 0.000 025	0.005
	7	53.043 0 ± 0.000 033	0.006
	8	68.013 8 ± 0.000 043	0.001
*	0	0.000 000 ± 0.000 000 6	0.090
	1	0.052 71 ± 0.000 000 8	0.857
	2	7.370 14 ± 0.000 004 6	0.029
	3	12.499 53 ± 0.000 007 8	0.000
	4	18.855 65 ± 0.000 011 8	0.021
	5	27.751 79 ± 0.000 017 3	0.003
	6	38.726 75 ± 0.000 024 2	0.004
	7	51.700 79 ± 0.000 032 3	0.006
	8	66.683 64 ± 0.000 052 4	0.001

* Value used by Brot and Darmon for x.

Each eigenfunction $Z_\lambda(\eta)$ is stored on file at a series of unequally spaced integration mesh points. The values of I_λ for each λ (table 1) are then evaluated using N.A.G. DO1GAA for the quadratures, keeping error bounds of one part in 10^5 or better. In checking the accuracy of the overall computation note that:

$$\frac{\beta E}{3(\mu_1 \pm \mu_2)^2} \sum_\lambda I_\lambda = 1. \tag{21}$$

The I_λ series is rapidly convergent and by summing up the first half dozen or so terms eqn (21) is satisfied to within ± 0.5 %. This could easily be improved at the cost of more computer time. The deviation from semicircularity in fig. 2 is not, therefore, due to local numerical uncertainties. In fact it is due to an infinite distribution of relaxation times quite closely spaced, determined by an approximately quadratic progression in the eigenvalues λ of table 1. The smaller the separation R_0 the slightly greater is the deviation from the semi-circular in fig. 2.

DISCUSSION

The final step of relating $\alpha^*(\omega)$ to the complex permittivity $\varepsilon^*(\omega)$ is the one about which least is known theoretically, there being too many theories. The step involves, of course, an internal field estimation which is dependent on our first solving the electrodynamic/kinematic problem set out briefly in the introduction. Our predicament is therefore circular. The problem is present even in relating the results of Monte Carlo simulation to $\varepsilon^*(\omega)$, which is that of relating $\varepsilon^*(\omega)$ to a microscopic correlation function, involving cross-correlation. In this paper we assume that the Argand diagrams of $\varepsilon^*(\omega)$ and $\alpha^*(\omega)$ are similar, Darmon and Brot having checked already that the many and complicated internal field corrections do not yield very different results. In comparing $\alpha^*(\omega)$ from the Sturm–Liouville equation with that from the Monte Carlo simulation, the internal field is not a problem, since both approaches are already microscopic.

The essential difference between the simulation and pair-interaction approach is that the former takes account of all charge–charge interactions in a block of 240 molecules with edges $6a$, $10b$ and $2c$, where a, b and c are the parameters of the monoclinic unit cell in the high temperature phase (300 K). The equivalent of the friction constant ζ_1 is introduced in the Monte Carlo simulation by setting up a potential barrier to hinder orientational jumps between one molecular site and the next, barriers of essentially repulsive origin. For a given molecular site in a given surrounding, the electrostatic interaction produces a slight variation of the six barrier heights. In this picture, at high temperatures, due to the amount of orientational disorder in the neighbouring molecules, the differences in depth of the potential wells tend to cancel out and to be smaller than kT, producing a constant probability of jump and thus a near semicircular Cole–Cole plot. At low temperatures the few disoriented molecular dipoles produce around themselves potential differences of opposite signs for different neighbours, hence a greater variability of the potential wells. This makes for a wide distribution of jump probabilities and a flattened Cole–Cole arc.

In the model developed in this paper the friction coefficient at 300 K is many orders of magnitude less than that at low temperature but the variation in electrodynamic potential energy is small. This is of course well-known from the calculations of Kitaigorodskii *et al.*[13] on the variation of the electrodynamic energy in compact dipolar and quadrupolar lattices, which varies slowly with the structural parameters (in our case R_0, to a close approximation the lattice constant b at 300 K).

At the 300 K the experimental data, simulation and model produce results in close accord (a slightly flattened Cole–Cole arc, fig. 2). However, as the temperature is lowered (as R_0 becomes progressively a little smaller and ζ_1 increases enormously) the TCTMB lattice undergoes a more or less continuous transition and potential barriers of repulsive origin separate wells whose levels evolve cooperatively, as a result of electrostatic interaction, so that near the low temperature end of the transition region the superstructure exists in the form of domains. The flattening of the Cole–

Cole arc is obviously not followed (fig. 2) by the pair interaction model, even when the lattice spacing is reduced to $R_0 = 2.50$ Å (unrealistically small in practice). Electrostatic interaction as represented in a pair approximation is therefore not a good representation of the overall molecular dynamical process of TCTMB which relies on cooperative phenomena, especially at low temperatures. In fact the Monte Carlo simulations were performed with a constant R_0, so that in both high and low temperature configurations the Brownian model plus pair interactions would yield the same type of slightly flattened Cole–Cole arc. The order–disorder transition cannot, therefore, be followed by pairwise electrodynamics alone.

The self-consistent approach to the problem of rotational diffusion recently suggested by Berne [14] has many interesting consequences, especially were his equations modified to take into account inertial effects and memory effects, so that the far infrared region could also be described satisfactorily. Berne's results have recently been extended to spheroids by Warchol and Vaughan [15] and the Budó theory generalised in this context by these authors and by G. T. Evans,[16] using a truncated Mori approximant to the initial stochastic Liouville equation governing the system.

However, Berne's results are essentially based on the Cole method of treating the Zwanzig lattice and none of these treatments is capable of producing the symmetric broadening of the Cole–Cole arc observed experimentally in disordered solids such as TCTMB and successfully simulated by the semi-stochastic Monte Carlo methods of Darmon and Brot. They all tend to produce a series of shorter relaxation times and a Cole–Davidson type of skewed Argand diagram. Symmetric broadening is often, of course, observed also in liquids. It seems, therefore, that this is an area where computer simulation is more informative than the analytical approach, provided the problem of long-range interactions on boundary conditions can be overcome.

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[1] *Faraday Disc. Chem. Soc.*, 1978, **66.**

[2] V. M. Titulaer and J. M. Deutch, *J. Chem. Phys.*, 1974, **60**, 1502.

[3] R. W. Zwanzig, *J. Chem. Phys.*, 1963, **38**, 2776.

[4] R. H. Cole, *Mol. Phys.*, 1974, **27**, 1.

[5] C. Brot and I. Darmon, *J. Chem. Phys.*, 1970, **53**, 2271.

[6] W. T. Coffey, *Mol. Phys.*, 1979, **37**, 473.

[7] A. Budó, *Phys. Z.*, 1938, **39**, 706; *J. Chem. Phys.*, 1949, **17**, 686.

[8] J. H. Calderwood and W. T. Coffey, *Proc. Roy. Soc. A*, 1977, **356**, 269.

[9] R. A. Sack, *Proc. Phys. Soc.*, 1957, **70B**, 414.

[10] S. Kielich, *Dielectric and Related Molecular Processes* (Chem. Soc. Specialist Periodical Report, London, 1973), vol. 1.

[11] J. D. Pryce, *Inst. Maths. Applics.*, *Numerical Analysis Newsletter*, vol. 1, No. 3, 1977.

[12] B. Hargrave and J. D. Pryce, NPARAM: Report on a programme to solve multiparameter Sturm–Liouville problems. Bristol University, Computer Department, 1977.

[13] A. I. Kitaigorodskii, *Acta, Cryst.*, 1965, **18**, 585; A. I. Kitaigorodskii and K. V. Mivskaja, *Kristallografia*, 1964, **9**, 634.

[14] B. J. Berne, *J. Chem. Phys.*, 1975, **62**, 1154.

[15] M. K. Warchol and W. E. Vaughan, *J. Chem. Phys.*, 1976, **65**, 1374; 1977, **67**, 486.

[16] G. T. Evans, *Mol. Phys.*, 1968, **36**, 49, 65.

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