J.C.S. Faraday II, 1980, 76, 217–220

Diffusion Equation for the Nematic Phase Dielectric Loss

BY ALUN H. PRICE AND MYRON W. EVANS*

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

Received 17*th May*, 1979

The loss features up to 18 GHz of the nematic and isotropic phases of n-heptyl-4-cyanobiphenyl are described with a model of Brownian motion with a superimposed potential. This is pairwise additive and is ultimately responsible for the formation of the nematic phase. The model reproduces the results better in the isotropic phase, since the initial Smoluchowski equation refers to istotropic reorientation, but could easily be extended to tensor properties.

A recent dielectric study by Price and co-workers [1] up to 18 GHz of the nematic and isotropic phases of n-heptyl and n-heptoxycyanobiphenyl has revealed an extra high frequency loss peak in both the nematic phase (parallel alignment) and in the isotropic phase. The purpose of this note is to describe a mechanism by which this high frequency shoulder may be followed analytically without using the concept of a director pseudo-potential.[2] Both the nematic and to some extent the isotropic phases [3] are characterised by a persistent rotational ordering and relative translational disorder.[4] The two types of motion evolve on very different scales of time but are mutually interrelated. On the time scale characterising the observable dielectric loss (that of the orientational correlation function), the angular velocity is a fast-decaying variable. In other words, it is valid to describe the high frequency rotational molecular dynamics approximately in terms of a lattice with fixed molecular centres of mass.

The molecular motion and interaction may then be modelled on Brownian motion with an extra superposed potential, pairwise additive. This extra potential energy may be regarded as being (for example) electrodynamic in origin, in the simplest case dipole–dipole energy would be appropriate. The positive (repulsion) forces caused by shape anisotropy may be accounted for through the friction coefficient (tensor) and stochastic part of the Langevin equation governing the Brownian motion. The fictional nematic director can now be replaced in molecular terms by imagining a typical parallel ordering built up on this pairwise basis. The dynamics of each interacting pair would be describable in terms of the well-known Budó model [5] developed for intramolecular dipole interaction. The tensor properties of the nematic phase dielectric permittivity may be treated by restricting the isotropy of the pair reorientation, *i.e.*, by assuming that the diagonalised friction tensor (ζ) does not have identical elements. However, for scalar ζ_1 the Smoluchowski equation governing the Brownian motion is, for $t > 0$,

$$\frac{\partial f}{\partial t} = \frac{kT}{\zeta}\left[\frac{\partial^2 f}{\partial \theta^2} + \cot\theta\,\frac{\partial f}{\partial \theta} + (1+\cot^2\theta)\left(\frac{\partial^2 f}{\partial \phi_1^2} + \frac{\partial^2 f}{\partial \phi_2^2}\right) + 2\cot^2\theta\,\frac{\partial^2 f}{\partial \phi_1\,\partial \phi_2}\right] + \frac{\partial}{\partial \phi_1}\left(\frac{f\sin\theta}{\zeta_1}\,\frac{\partial V}{\partial \phi_1}\right) + \frac{\partial}{\partial \phi_2}\left(\frac{f\sin\theta}{\zeta_1}\,\frac{\partial V}{\partial \phi_2}\right). \tag{1}$$

In eqn (1) θ and ψ are the polar angles which specify the orientation of the interacting pair of molecules relative to that of the external measuring field $\boldsymbol{E}$. μ_1 and μ_2 denote the dipole vector in each molecule and ϕ_1 and ϕ_2 their azimuthal angles measured from the plane containing $\boldsymbol{E}$ and an axis fixed in the rotating coordinate frame of the pair. The form of eqn (1) implies that each molecule experiences a frictional drag ζ_1 which is in general a tensor quantity, becoming strongly anisotropic in the nematic phase giving rise to observable $D_{\parallel}$ and $D_{\perp}$ diffusion coefficients in the presence of very weak aligning external magnetic or electric fields. Eqn (1) governs the evolution in configuration space of the probability density function $f(\theta, \phi_1, \phi_2, t)$ in the presence of the extra potential V. Upon the oversimplified framework of eqn (1) it is not rational to hang an elaborate functional for V and it is sufficient to use the form

$$V = -\frac{V_0}{kT}\cos(\phi_1 - \phi_2) \tag{2}$$

to reproduce the main features of the experimental results in both nematic and isotropic phases.

The solution of eqn (1) subject to eqn (2) has been discussed very fully by Budó and lately by Coffey [6] and G. T. Evans,[7] who have extracted analytically the complex microscopic polarisability $\alpha^*(\omega)$, which is a sum of Debye-like terms. The usual internal field corrections must be applied in relating this to the complex permittivity $\varepsilon^*(\omega)$, which is a multi-molecule property.

We have recently developed [8] a numerical method for solving eqn (1) and (2) based on an algorithm of Hargrave and Pryce.[9] This makes it possible to use a more realistic form for V in the Sturm–Liouville equation whose eigenvalues and eigenfunctions go to make up the theoretical $\alpha^*(\omega)$. Using numerical methods it is possible also to solve eqn (1) directly for f and also to solve similar but more realistic and more complicated diffusion equations which are tensorial in nature.

DISCUSSION

The results of our calculations using eqn (1) and (2) are illustrated in fig. 1 and 2 and compared with the loss curves of Price and co-workers. Not surprisingly [in view of the scalar nature of eqn (1)] the result is better in the isotropic phase. However, it is clear that the loss features can be roughly reproduced without recourse to a director pseudo-potential. The further high frequency (far infrared) loss can be accommodated by considering inertial and memory effects in eqn (1), *i.e.*, by making ζ_1 time-dependent.[10] A complete analytical treatment would be multi-particle in nature and inclusive of translation/rotation coupling as discussed recently by, among others, Wolynes and Deutch.[11] With the rapid development in computer software and hardware it is now possible to handle equations more realistic than those in this note and it might be expected, therefore, that the nature of the isotropic–nematic " transition " might be classified on the molecular scale by judicious use of dielectric spectroscopy and computer-aided analysis.

It is, therefore, possible to explain the presence of the two absorptions observed in both the nematic and isotropic phases of liquid crystals using the one theory. The only requirement is the persistence of short-range (or pre-transitional) effects in the isotropic phase. Such a phenomenon is now well established [3] above the nematic-to-isotropic transition temperature and this appears to be the first direct demonstration using the dielectric relaxation technique.

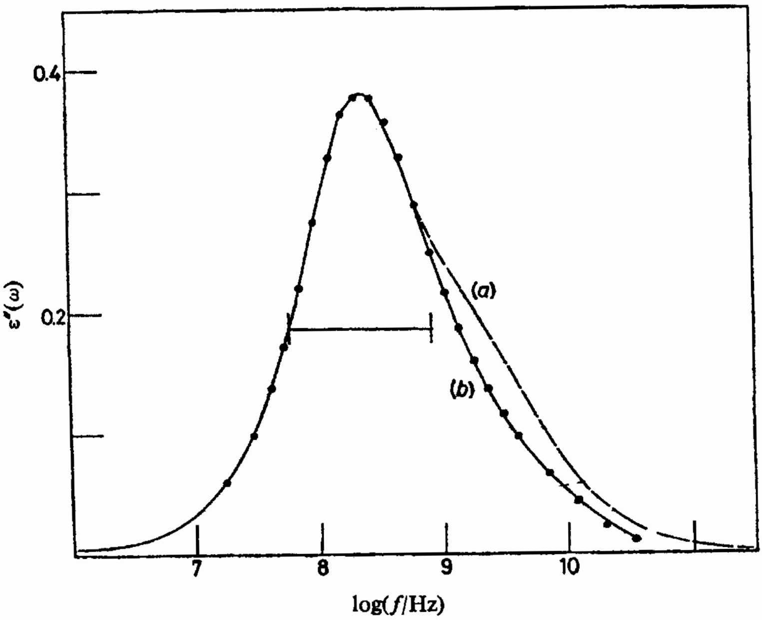

FIG. 1.—Measured dielectric loss of 4-n-heptyl-4′-cyanobiphenyl in the isotropic liquid state at 321 K. (*a*) Eqn (1) and (2), $V_0/kT = 2.0$. (*b*) ●, Eqn (1) and (2), $V_0/kT = 2.5$.

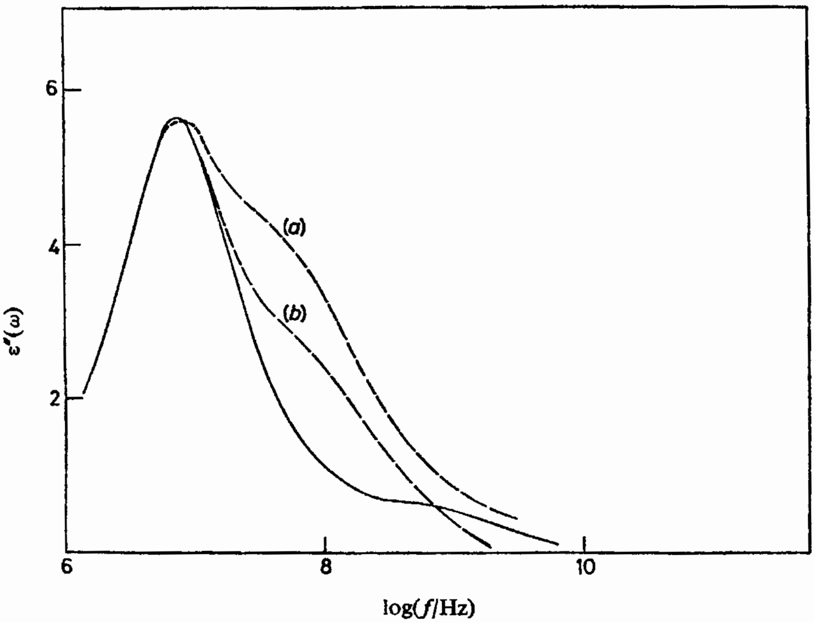

FIG. 2.—Measured dielectric loss of 4-n-heptyl-4′-cyanobiphenyl in the nematic state at 313 K (parallel alignment). (*a*) $V_0/kT = 1.0$; (*b*) $V_0/kT = 2.0$.

In the far infrared (at frequencies still higher than the microwave) there appear spectral features due to inertial and memory effects. A computer program for a fully comprehensive analysis is being written to round off this preliminary theoretical analysis. The experimental findings reported here mean that the accepted theories of nematic phase molecular behaviour must be extended to account for the extra microwave detail. The whole of the frequency region from static to THz must be considered when dealing comprehensively with the molecular dynamical evolution.

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

[1] A. Buka, P. G. Owen and A. H. Price, *J.C.S. Faraday II*, in press.

[2] P. L. Nordio, G. Rigatti and U. Segre, *Mol. Phys.*, 1973, **25**, 129.

[3] M. Davies, R. Moutran, A. H. Price, M. S. Beevers and G. Williams, *J.C.S. Faraday II*, 1976, **72**, 1447.

[4] J. Kushick and B. J. Berne, *J. Chem. Phys.*, 1976, **64**, 1362.

[5] A. Budó, *Phys. Z.*, 1938, **37**, 706: *J. Chem. Phys.*, 1949, **17**, 686.

[6] W. T. Coffey, *Mol. Phys.*, 1979, **37**, 000.

[7] G. T. Evans, *Mol. Phys.*, 1978, **36**, 1199.

[8] M. W. Evans, W. T. Coffey and J. D. Pryce, *Chem. Phys. Letters*, in press.

[9] B. Hargrave and J. D. Pryce, NPARAM; Report on a programme to solve multiparameter Sturm–Liouville problems. Bristol Univ., Computer Dept., 1977.

[10] M. W. Evans, G. J. Evans and A. R. Davies, *Adv. Chem. Phys.*, to be published.

[11] P. Wolynes and J. M. Deutch, *J. Chem. Phys.*, 1977, **67**, 733.

(PAPER 9/770)