J. Phys. D: Appl. Phys., 18 (1985) 137–143. Printed in Great Britain

Limitations of the one-body approach to dielectric relaxation: comparison with rise transients from computer simulation

Myron W Evans† and Fabio Marchesoni‡§
† Department of Physics, University College of North Wales, Bangor, Gwynedd LL57 1UT, UK
‡ Dublin Institute for Advanced Studies, 10 Burlington Road, Dublin-4, Ireland

Received 10 May 1984, in final form 23 July 1984

Abstract. The approximate analytical solution by Morita of the standard Debye diffusion equation is extended for the purpose of comparison with the rise transients produced by 3D, asymmetric top, computer simulation. The analysis and computation produce a similar qualitative dependence of rise-transient characteristic time on electric field strength, but quantitative differences call for a more realistic analytical theory of the molecular dynamics.

The liquid phase of matter is usually isotropic at equilibrium. This ceases to be the case when the sample is treated with a more or less intense field of force applied in an axis of the laboratory frame of reference. It is well known that birefringence is observable (Bottcher and Bordewijk 1978) in a liquid treated with an intense electric field (the Kerr effect), magnetic field (the Faraday or Cotton/Mouton effect) or laser field (the Buckingham effect). The theory of molecular diffusion in anisotropic liquids is based on the equations which govern the evolution with time of probability density functions under the influence of an applied force or torque (Evans *et al* 1982). Bénoit (1951) first based his treatment on Debye's theory of rotational diffusion, with the basic assumption that in energetic terms the external perturbation is much smaller than the thermal kT. Some authors (Morita 1978a, b, Morita and Watanabe 1979, Watanabe and Morita 1980a, Ullman 1972) have more recently extended the theory to deal with an arbitrarily strong applied torque. In general, the standard theoretical approach is based on a stochastic differential equation, diffusional in nature (Morita 1978a, Sack 1956, Debye 1929):

$$\frac{\partial}{\partial t}\rho(\theta,t)=\Gamma\rho(\theta,t)=\frac{D}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\left[\frac{\partial}{\partial\theta}+\frac{1}{kT}\left(\frac{\partial}{\partial\theta}V\right)\right]\rho(\theta,t)\qquad(1)$$

where D is the rotational diffusional constant, k is the Boltzmann constant, T is the absolute temperature, and $V(\theta,t)$ is the perturbation potential affecting the orientation θ of the molecule. For a symmetrical body which has a permanent electric dipole μ along the axis of symmetry and which is optically polarisable both along the axis of symmetry and the orthogonal axes with electric polarisabilities $\alpha_\parallel$ and $\alpha_\perp$ respectively, the potential

---

§ Permanent address: Dipartimento di Fisica, Università di Perugia, I-06100-Perugia, Italy.

0022-3727/85/010137 + 07 $02.25 © 1985 The Institute of Physics

energy $V(\theta, t)$ is given by

$$V(\theta, t) = -\mu E(t) \cos\theta - \tfrac{1}{2}(\alpha_{\parallel} - \alpha_{\perp}) E^2(t) \cos^2\theta \tag{2}$$

where $E(t)$ is an applied electric field.

Recently Evans (1982a, b, c, 1983a, b) initiated a project of molecular dynamics simulation of anisotropic liquids. The assembly of dipolar molecules is simulated in the presence of a constant homogeneous electric field E_0 under the type of conditions assumed by Morita (1978a, b) in his analytical work. In particular, the results of Evans' numerical simulation (Evans 1982b) should be taken into account on solving equations (1) and (2) with $\alpha_{\parallel} = \alpha_{\perp}$ (Evans 1982a). These equations can then be rewritten as follows:

$$\frac{\partial}{\partial\tau}\rho(\theta, \tau) = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\left(\frac{\partial}{\partial\theta} + e_0 \sin\theta\right)\rho(\theta, \tau) \tag{3}$$

where $e_0 = \mu E_0/kT$ and $\tau \equiv Dt$. Equation (3) is studied later in some more detail by Watanabe and Morita (1980b).

The present paper is aimed at comparing the results of Evans' microscopic scale numerical simulations with some predictions of Morita's microscopic scale one-body diffusion model. In particular we focus on the so-called *rise transient time* (RTT) of the orientational correlation functions. The analytical calculations based on equation (3) and the simulations of Evans (1982b) are shown to differ markedly. In order to make such a comparison as faithful as possible, Morita's RTT approximation is worked out thoroughly and compared with alternative characterisations. The slight improvements to Morita's original calculation so far obtained in this way do not explain the pronounced discrepancy detected in this paper between theoretical modelling and 'numerical' experiments, i.e. 'molecular dynamics' computer simulation.

In order to calculate the time dependence of the electric polarisation and electric birefringence of an ensemble of molecules, we need to obtain the averages (Peterlin and Stuart 1939)

$$\langle P_i(\cos\theta, t)\rangle = \int_0^{2\pi} \rho(\theta, t) P_i(\cos\theta) \sin\theta \, d\theta \tag{4}$$

where $P_i(x)$ are the Legendre polynomials of degree i. Let us focus our attention on $\langle P_1(\cos\theta, t)\rangle \equiv \langle\cos\theta(t)\rangle$. Expressing $\rho(\theta, \tau)$ in terms of the Legendre polynomials $P_i(x)$, Morita (1978b) obtains for the Laplace transform of $\langle\cos\theta(\tau)\rangle$ the following continued fraction:

$$\mathcal{L}\{\langle\cos\theta(\tau)\rangle\} = \tfrac{2}{3} e_0 \Lambda(s, e_0)/s, \tag{5}$$

where

$$\Lambda(s, e_0) = \cfrac{1}{s + \lambda_0 + \cfrac{\Delta_1^2}{s + \lambda_2 + \dots \cfrac{\Delta_n^2}{s + \lambda_n + \dots}}} \tag{6}$$

in which

$$\lambda_n = (n+1)(n+2) \tag{7}$$

$$\Delta_n^2 = \frac{n(n+1)^2(n+2)}{(2n+3)(2n+1)} e_0^2. \tag{8}$$

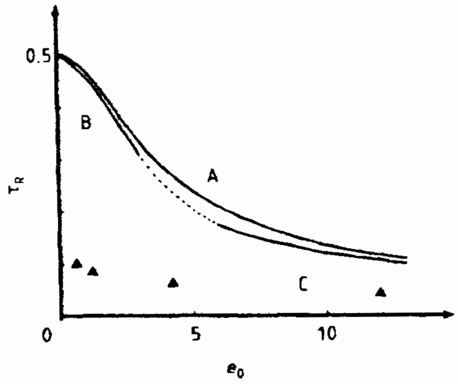

Figure 1. τ_R against e_0 in dimensionless units $D\tau$. Curve A: τ_R^M of equation (12); curve B: $\tau_R^{(1)}$ of equation (17); curve C: $\tau_R^{(2)}$ of equation (23); (▲) simulation results from figure 3 of Evans (1982b).

In passing we note that the same expansion can be recovered by adopting the Mori expansion (Grosso and Pastori-Parravicini 1985). From equation (5) it follows that

$$\lim_{\tau\to\infty} \langle \cos\theta(\tau)\rangle = \lim_{s\to 0} \tfrac{2}{3} e_0 \Lambda(s, e_0) = L(e_0) \tag{9}$$

where $L(e_0)$ is the Langevin function defined by $L(z) = \coth(z) - 1/z$. The saturation values of $\langle P_l(\cos\theta, \tau)\rangle$ are correctly reproduced by simulation (Evans 1982b).

From now on let us consider the observable

$$A_1(\tau) \equiv 1 - \langle \cos\theta(\tau)\rangle / \langle \cos\theta(\infty)\rangle \tag{10}$$

whose Laplace transform $\hat{A}_1(s)$ reads (see equations (5) and (9))

$$\hat{A}_1(s) = [\Lambda(0, e_0) - \Lambda(s, e_0)]/s\Lambda(0, e_0). \tag{11}$$

Morita (1978b) introduces a characteristic RTT τ_R by fitting $A_1(\tau)$ with an exponential function, $\exp(-\tau/\tau_R)$. Such an exponential fit is obtained by putting $s = 0$ in all the fractions of equation (6) except the first one, so that

$$\tau_R^M \equiv \Lambda(0, e_0) = \tfrac{3}{2} L(e_0)/e_0. \tag{12}$$

This is a rough estimate of τ_R, and a good agreement with the 'numerical' experiment of Evans (1982b) is not expected (Morita and Watanabe 1979) (see figure 1). In the following we retain Morita's definition of the RTT, using an exponential fit, but we work out two different characterisations of τ_R which are likely to be more appropriate for small and large fields, respectively.

(*a*) Small e_0-RTT, $\tau_R^{(1)}$. A widely accepted definition of relaxation time (see e.g. Marchesoni and Grigolini 1983) takes this as the area below the appropriate normalised autocorrelation function. This can be calculated by taking the $s = 0$ value of the corresponding Laplace transform. Our first alternative characterisation of $\langle \cos\theta(\tau)\rangle$ RTT, $\tau_R^{(1)}$, therefore reads

$$\tau_R^{(1)} \equiv \lim_{s\to 0} \hat{A}_1(s) = -\frac{\Lambda'(0, e_0)}{\Lambda(0, e_0)} \tag{13}$$

where $\Lambda'(0, e_0)$ is the derivative of $\Lambda(s, e_0)$ with respect to s at $s = 0$. We can compute $\tau_R^{(1)}$ by means of a suitable expansion for $\Lambda'(0, e_0)$. By writing the continued fraction (6) as

$$\Lambda_n(s, e_0) = \frac{\Delta_n^2}{s + \lambda_n + \Lambda_{n+1}(s, e_0)} \qquad n \in \mathbb{N} \tag{14}$$

where

$$\Lambda_0(s, e_0) = \Lambda(s, e_0)$$

we can easily recast $\Lambda'(0, e_0)$ as follows:

$$\Lambda'(0, e_0) = -\frac{1}{(\lambda_0 + \Delta_1^2)^2}\left[1 - \frac{\Delta_1^2}{(\lambda_1 + \Lambda_2)^2} \cdots \left(1 - \frac{\Delta_{n-1}^2}{(\lambda_{n-1} + \Lambda_n)^2} \cdots\right) \cdots\right] \tag{15}$$

Furthermore, from equation (14), we have the recursive relation

$$\Lambda_n(0, e_0) = \frac{\Delta_{n-1}^2}{\Lambda_{n-1}(0, e_0)} - \lambda_{n-1}. \tag{16}$$

Equations (15) and (16) allow us to give $\tau_R^{(1)}$ a more convenient form for computer calculation

$$\tau_R^{(1)} = \tau_R^M \left[1 + \frac{\Lambda_1^2(0, e_0)}{\Delta_1^2} \cdots \left(1 - \frac{\Lambda_n^2(0, e_0)}{\Delta_n^2} \cdots\right) \cdots\right] \tag{17}$$

where τ_R^M is defined in equation (12). The convergence of such an expansion is slow for large values of e_0, while for small e_0, $\tau_R^{(1)}$ can be readily approximated with

$$\tau_R^{(1)} \simeq \tau_R^M \left(1 - \frac{\Delta_1^2}{\lambda_1^2}\right) \simeq \frac{1}{\lambda_0}\left(1 - \frac{\Delta_1^2}{\lambda_0 \lambda_1} - \frac{\Delta_1^2}{\lambda_1^2}\right) + O(e_0^4). \tag{18}$$

By using equations (7) and (8), equation (18) is shown to imply only a slight negative correction to Morita's estimate (figure 1). In particular, the overshoot of the curve τ_R^M against e_0 at small e_0 (Morita and Watanabe 1979) can be explained in terms of the actual shape of $A_1(\tau)$. Indeed in view of a theorem concerning Laplace transformation we have

$$\lim_{s \to \infty} s^2 \hat{A}_1(s) - sA(0) = A_1'(0) = -1. \tag{19}$$

This means that $A_1(\tau)$ cuts the $\tau = 0$ axis with a negative slope smaller than $(\tau_R^M)^{-1}$ and the exponential fit, $\exp(-\tau/\tau_R)$, reproduces it more and more badly as e_0 tends to zero.

(*b*) Large e_0-RTT, $\tau_R^{(2)}$. An alternative characterisation of the RTT can be given as follows. The Laplace transform of the time derivative of $\langle \cos\theta(\tau)\rangle$ can be expressed as

$$\mathscr{L}\left\{\frac{\mathrm{d}}{\mathrm{d}\tau}\langle \cos\theta(\tau)\rangle\right\} = s\mathscr{L}\{\langle \cos\theta(\tau)\rangle\} - \langle \cos\theta(0)\rangle = \tfrac{1}{3}e_0 \Lambda(s, e_0)$$

where equation (15) and the usual initial conditions $\langle \cos\theta(0)\rangle = 0$ have been taken into account. For that reason $\langle \cos\theta(\tau)\rangle$ is obtained explicitly by integrating the inverse Laplace transform of the continued fraction $\Lambda(s, e_0)$, equation (6), with respect to time. Such an inversion can be carried out by having recourse to a diagonalisation procedure (Marchesoni and Grigolini 1983) which yields

$$\mathscr{L}^{-1}\{\Lambda(s, e_0)\} = \sum_{i\in\mathbb{N}} c_i \exp(-\gamma_i\tau). \tag{20}$$

On integrating equation (20) with respect to τ and employing the definition (10), we thus determine

$$A_1(\tau) = \sum_{i\in\mathbb{N}} \frac{c_i}{\gamma_i} \exp(-\gamma_i\tau) \Big/ \sum_{i\in\mathbb{N}} \frac{c_i}{\gamma_i}. \tag{21}$$

In the present case $c_i \in \mathbb{R}$ and $\gamma_i \in \mathbb{R}_+$ for any $i \in \mathbb{N}$ (Grosso and Pastori-Parravicini 1984). In the presence of diffusional behaviour such as that exhibited by the model under study, the relaxational time $\tau_{\mathrm{R}}^{(2)}$ is commonly identified with the inverse of the smallest eigenvalue $\{\gamma_i\}_{i\in\mathbb{N}}$, i.e.

$$\tau_{\mathrm{R}}^{(2)} = \left(\min_{i\in\mathbb{N}} \{\gamma_i\}\right)^{-1}. \tag{22}$$

Avoiding complex numerical procedures of continued fraction diagonalisation (Grosso and Pastori-Parravicini 1984), we can recover the smallest (positive) eigenvalue in equation (20) by applying an equivalent recurrence relation proved by Guàrdia *et al* (1984) and Risken (1984). For brevity we just report the corresponding explicit expression for $\tau_{\mathrm{R}}^{(2)}$:

$$\tau_{\mathrm{R}}^{(2)} = \frac{3}{2e_0} \lim_{i\to\infty} \frac{1}{z_i} \tag{23}$$

where

$$z_{i+1} = \frac{3}{2e_0} \Big/ \Lambda(z_i, e_0) \tag{24}$$

and $z_0 = 0$ (Guàrdia *et al* 1984). This second definition of the RTT is better founded from a mathematical point of view than those introduced above. A fast numerical convergence of the recurrence relation (24) can be achieved at large e_0 (figure 1). In passing we remark that Morita's estimate, equation (12), coincides with z_1^{-1} of equation (24).

We are now in a position to compare the predictions of the diffusional models like that of equation (1) with Evans' (1982b) findings. Let us note that equation (1) contains only one parameter, D, which can be obtained with the numerical results. Let us consider the behaviour with time of the torque-off $\langle\cos\theta(0)\cos\theta(t)\rangle$. From equation (1) it can be easily proved that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\cos\theta(0)\cos\theta(t)\rangle = \langle\cos\theta(0)\mathbb{F}^{+}\cos\theta(t)\rangle = -2D\langle\cos\theta(0)\cos\theta(t)\rangle \tag{25}$$

where $\mathbb{F}^{+}$ is the self-adjoint of the Fokker–Planck operator $\mathbb{F}$. $(2D)^{-1}$ is then the (Debye) relaxation time τ_{D} of the autocorrelation function $\langle\cos\theta(0)\cos\theta(t)\rangle$ simulated by Evans (1982a) in his figure 3: $\tau_{\mathrm{D}} = 4.5$ ps. The result of our comparison is shown in figure 1 where the RTT are all given in dimensionless units $\tau = Dt$. Inaccuracies in the reported simulation data (obtained *via a numerical exponential fit*) are mainly due to the oscillations that the curves of figure 10 by Evans (1982b) exhibit. These are artifacts of the numerical algorithm (caused by temperature rescaling) and must be smoothed for a theoretical analysis.

Our conclusion is that, after extending the validity of the analytical solution of equation (1) for detailed comparison with the numerical analysis of the simulation by Evans (1982b), large discrepancies remain when we try to interpret the relaxation dynamics of an actual assembly of polar molecules in terms of a one-body diffusional model. In particular, we note that the picture of equation (1) assumes as a starting point that the interaction between the tagged molecule and its environment can be mimicked by means of a stochastic torque with the following properties: (i) Fluctuations are introduced as an equilibrium stochastic process. Moreover a time-varying electric field $E(t)$ is supposed not to affect the environment of the polar molecule but only the torque acting on the molecule itself. (ii) The rest of the sample is depicted as a Markovian heat bath which means that no feedback reaction occurs as a consequence of the movement of the symmetrical top even if at $t = 0$ it is far from its statistical equilibrium. In other words, the stochastic torque has no memory of the molecule–environment interaction. (iii) Such interaction is assumed to be Gaussian, which seems to suggest a *linear* coupling between the tagged molecule and the nearest neighbours (Maeckawa and Wada 1980). Now these three assumptions have been refuted by studying both equilibrium and non-equilibrium properties of an assembly of ideal molecules (Balucani *et al* 1982. Evans *et al* 1983a, b, Praestgaard and van Kampen 1981, van der Zwan and Hynes 1983). Our conclusions agree with the remarks of these authors: a satisfactory explanation of the simulation results would involve something more than the one-body picture of equation (1)—even if inertial effects were implemented (Evans *et al* 1983a, b). Two-body *nonlinear* models like those of Coffey *et al* (1982) and of Risken and Vollmer (1982) seem at the moment to be better candidates for accounting for the non-Gaussian and non-Markovian transient statistics of molecular dynamics in the liquid state.

Finally we mention that dielectric relaxation is necessarily a *many-body* problem, but a problem that usually is still tackled in the dielectric literature by the one-particle diffusive theory described above—originally that of Debye. The technique of molecular dynamics computer simulation allows an approach to the same problem that is more sensible, in the sense that the details of *the intermolecular pair potential* can be modelled approximately but more realistically. The formidable problem remains of relating the microscopic properties, dealt with in this paper, to macroscopic observables such as the complex permittivity. This problem involves a detailed investigation of the time dependence of the internal field. However, in this paper, we have been concerned specifically and exclusively with comparing the results of a diffusional microscopic model with a well defined, microscopic, computer simulation.

It is not possible to relate one-body models (such as Debye's) to the actual many-body dynamics simply by rescaling the applied electric field, using a static (time-independent) model for the internal field effect. Some of the most striking evidence for this is the following.

(i) This procedure cannot explain some recent numerical and experimental results, for instance the newly discovered fall-transient acceleration (Evans *et al* 1983a, b, Marchesoni 1984).

(ii) Two-body models can account for most of the known properties of many-body systems owing to the key role played by *nonlinearity*. The classical papers of Zwanzig, Mori, van Kampen and others in this area are reviewed by Evans *et al* (1982, ch 9, 10, on reduction techniques). These provide good descriptions of the available numerical and experimental data in many fields of condensed matter dynamics, notably molecular dynamics in liquids. A special issue of Advances in Chemical Physics (see Grosso and Pastori-Parravicini 1984) is devoted both to the philosophy and application of these new techniques.

Acknowledgment

The University of Wales is thanked for a fellowship for MWE, and the Nuffield Foundation for a bursary.

References

Balucani U, Tognetti V, Vallauri R, Grigolini P and Marin P 1982 *Z. Phys.* **B 49** 181
Bénoit H 1951 *J. Chem. Phys.* **49** 517
Bottcher C J F and Bordewijk P 1978 *Theory of Electric Polarization* (Amsterdam: Elsevier)
Coffey W T, Rysbarsh C and Schroer W 1982 *Chem. Phys. Lett.* **92** 245
Debye P 1929 *Polar Molecules* (New York: Dover)
Evans M W 1982a *J. Chem. Phys.* **76** 5473
—— 1982b *J. Chem. Phys.* **76** 5480
—— 1982c *J. Chem. Phys.* **77** 4632
—— 1983a *J. Chem. Phys.* **78** 925
—— 1983b *J. Chem. Phys.* **78** 5403
Evans M W, Coffey W T, Evans G T and Grigolini P 1982 *Molecular Dynamics* (New York: Wiley)
Evans M W, Grigolini P and Marchesoni F 1983a *Chem. Phys. Lett.* **95** 544
—— 1983b *Chem. Phys. Lett.* **95** 548
Grosso G and Pastori-Parravicini G 1985 *Adv. Chem. Phys.* to be published
Guàrdia E, Marchesoni F and San Miguel M 1984 *Phys. Lett.* **100A** 15
Maeckawa M and Wada K 1980 *Phys. Lett.* **80A** 293
Marchesoni F 1984 *Phys. Scr.* **30** 19
Marchesoni F and Grigolini P 1983 *J. Chem. Phys.* **78** 6287
Morita A 1978a *J. Phys. D: Appl. Phys.* **11** L9
—— 1978b *J. Phys. D: Appl. Phys.* **11** 1357
Morita A and Watanabe H 1979 *J. Chem. Phys.* **70** 4708
Peterlin A and Stuart H A 1939 *Z. Phys.* **112** 129
Praestgaard E and van Kampen 1981 *Molec. Phys.* **43** 33
Risken H 1984 *The Fokker Planck Equation. The Methods of Solution and Applications* (Berlin: Springer) ch 9
Risken H and Vollmer H D 1982 *Molec. Phys.* **46** 555
Sack R A 1956 *Physica* **22** 917
Ullman R 1972 *J. Chem. Phys.* 1869
Watanabe H and Morita A 1980a *J. Chem. Phys.* **73** 5884
—— 1980b *J. Phys. D: Appl. Phys.* **13** L153
van der Zwan G and Hynes J T 1983 *Physica* **121A** 227