Theory of anomalous dielectric relaxation

D J Byrne1,2,5, W T Coffey1, Yu P Kalmykov3 and S V Titov1,4

1Department of Electronic and Electrical Engineering, Trinity College, Dublin 2, Ireland
2Electricity Supply Board, Dublin 3, Ireland
3Laboratoire de Mathématiques et Physique, Université de Perpignan Via Domitia, 54, Avenue Paul Alduy, F-66860 Perpignan, France
4Kotel’nikov Institute of Radio Engineering and Electronics of the Russian Academy of Sciences, Vvedenskii Square 1, Fryazino, Moscow Region, 141190, Russian Federation

wcoffey@mee.tcd.ie

Abstract. Anomalous dielectric relaxation in a double-well potential is reviewed showing that it explains the dielectric spectrum of CH2Cl2 decalin glass.

1. Debye models of relaxation

Debye [1], following Errera’s [2] finding that solids which after melting yield polar liquids show dispersion even in the solid state, proposed a microscopic model consisting of an ensemble of polar molecules each of permanent dipole moment $\mu$ and situated, e.g., at the intersection points of a space lattice. He [1] further supposed if a constant field $F$ acts on $\mu$ that $\mu$ can point only in two definite directions viz. $F$ and its opposite. Hence this model (elaborated on by Fröhlich [3]) is known as discrete orientation in contrast to his better known continuous distribution of orientations model of noninteracting polar molecules representing a polar liquid which was initially based [4] on a fixed axis rotator version of Einstein’s theory of Brownian movement [5,6] then extended to rotation in space, the only difference being the trivial one [6] of their respective Debye relaxation times characterizing relaxation towards the Boltzmann equilibrium distribution of orientations. Now, in the discrete orientation model the essential difference between it and the free rotational diffusion one is that the latter predicts dispersion and absorption in the microwave region while typically the former roughly explains dispersion and absorption in ice which occurs at km wavelengths. Thus, a solid like ice behaves as if it were a polar liquid [1] with very high internal friction hence a very long relaxation time, in essence leading Maier et al. [6] to generalize the discrete orientation model to a continuous distribution (with the bath represented by Brownian movement) to explain dielectric relaxation in nematic liquid crystals. This mesophase has [6] the simplest dielectric behaviour with the advantage that quantitative results for nematics also provide a basis for understanding the molecular dynamics of other mesophases, e.g. ferroelectric smectics. For details v. [6], where the rotational Brownian motion of a rod-like molecule $\mu$ in a uniaxial nematic potential is exactly treated leading to a clear physical understanding of the dielectric relaxation of nematics also meaning that the low frequency relaxation over the nematic

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potential barrier is effectively governed by a single Debye-like formula with Arrhenius-like relaxation time given by the inverse $\lambda_1^{-1}$ of the smallest nonvanishing eigenvalue of the Smoluchowski (noninertial Fokker-Planck (FPE)) equation for the rotational diffusion of the dipole in the nematic potential. The time so-calculated corresponds to the inverse escape rate over the barrier and so is exponentially large, justifying the hypothesis that a solid like ice behaves as if it were a polar liquid with very high internal friction. An essentially similar result was obtained for the longitudinal relaxation of a single domain ferromagnetic nanoparticle in a magnetocrystalline anisotropy potential. The statistical mechanical approach for the magnetization relaxation time was initiated by Néel [6,7] who suggested that the reversal of the magnetization of such particles over an internal magnetocrystalline anisotropy-Zeeman energy barrier was governed by an Arrhenius-like process (discrete orientation model). His approach was later refined by Brown [6,8]. He formulated from the magnetic Langevin equation [6] the FPE for the surface probability distribution of magnetic moment orientations on the unit sphere and ignoring the gyromagnetic term (as is valid for longitudinal relaxation in circularly-symmetric potentials) one is left with an FPE formally equivalent to that of Debye [1]. Thus Brown’s [6,8] treatment constitutes a replica of the Maier et al. theory.

2. Anomalous dielectric relaxation

Notwithstanding its outstanding success in explaining the molecular mechanisms underlying dielectric relaxation, one of the most noteworthy failures of the Debye theory in either discrete or free rotation guises is that it cannot explain low frequency relaxation of disordered materials, e.g., we have the empirical Cole-Cole [6,9,10] expression for the normalized complex susceptibility, namely

$$\chi'(\omega) = \frac{1}{1 + (i\omega \tau)^\sigma}, \quad 0 < \sigma < 1,$$

where $\omega$ is the angular frequency of the imposed ac field, $\tau$ is a characteristic relaxation time and $\sigma$ is a fractional parameter. Furthermore $\sigma = 1$ is the Debye result while materials with $\sigma \neq 1$ exhibit anomalous dielectric relaxation. However, in [10] extending the Debye model of noninteracting dipoles to fractional diffusion leads to the ac stationary response ($f = F_0/|F_0|$)

$$\langle \mathbf{u} \cdot \mathbf{f} \rangle(t) = \frac{\mu^2 F_0}{2kT} \frac{e^{i\omega t}}{1 + (i\omega \tau)^\sigma}, \quad \chi'(\omega) = \frac{1}{1 + (i\omega \tau)^\sigma},$$

where $\tau$ is identified with the Debye relaxation time $\xi/kT$, $\xi$ is the friction coefficient, $k$ is the Boltzmann constant and $T$ is the absolute temperature. Assuming linear response theory [6,10] is still valid for fractional relaxation, equation (2) corresponds to the after-effect solution

$$\langle \mathbf{u} \cdot \mathbf{f} \rangle(t) = \frac{\mu^2 F_0}{2kT} E_\sigma \left[-(t/\tau)^\sigma \right],$$

where $E_\sigma(z)$ denotes the Mittag-Leffler function [10] interpolating between initial stretched exponential form and long-time inverse power law behaviour and becomes a decaying exponential for $\sigma = 1$.

Hence the Debye theory for noninteracting polar molecules based on normal diffusion in a regular space may be extended to anomalous diffusion, i.e., diffusion in disordered fractal structures and so may heuristically explain equation (1) in a microscopic way. However, in view of comments of Debye [1] concerning the discrete orientation model and the lengthy discussion of relaxation in a mean field potential given in [6] and also fractional relaxation, a more realistic treatment comprises generalizing the discrete orientation model to fractional diffusion and a continuous distribution of orientations and also to include the inertia of the dipoles [6,10].
3. Continuous distribution of orientations fixed axis rotation model for normal diffusion

The simplest model of dielectric relaxation in a potential is an assembly of rigid dipoles each of moment \( \mu \) rotating about a fixed axis through its centre, \( \mu \) has moment of inertia \( I \) and angular coordinate \( \theta \) constituting a system of one rotational degree of freedom. The continuous distribution of orientations model then obeys the evolution equation (FPE) (cf. equation 10.1.2 of [6]) in phase space \((\theta, \dot{\theta})\)

\[
\frac{\partial W}{\partial t} = -\theta \frac{\partial W}{\partial \theta} + \frac{1}{I} \frac{\partial V}{\partial \theta} \frac{\partial W}{\partial \theta} + \frac{\zeta}{I} \frac{\partial}{\partial \theta} \left( \theta \frac{\partial W}{\partial \theta} \right) + \frac{kT}{I} \frac{\partial^2 W}{\partial \theta^2},
\]

i.e., \( \frac{\partial W}{\partial t} = L_{FP}W \). \( \tag{4} \)

The first two terms on the right comprise the Liouville term describing the undamped streaming motion along the energy trajectories in phase space, corresponding to Hamilton’s equations. The others represent the interchange of energy with the bath. We represent the internal field arising from molecular interactions by \( V(\theta) = -V_c \cos N \theta \). Next suppose that a weak uniform electric field \( F \) (applied to the assembly at a time \( t = -\infty \), so that equilibrium conditions prevail at \( t = 0 \)) is switched off. For \( t \leq 0 \) and \( t \to \infty \), the relevant linearized distribution functions are

\[
W_{s\theta} = W_0(\theta, \dot{\theta}) \left[ 1 + \xi \cos(\theta - \Theta) - \zeta \langle \cos(\theta - \Theta) \rangle_0 \right], \quad W_{r\rightarrow} = W_0(\theta, \dot{\theta}) = Z_0^\dagger \exp \left[ -(\dot{\eta} \dot{\theta})^2 + \xi_v \cos N \theta \right]. \tag{5} \]

Here \( Z_0 \) is the partition function, \( \Theta \) is the angle between \( F \) and the \( Z \)-axis in the plane \( Z-X \), \( \xi = \mu F / kT \) and \( \xi_v = V_c / kT \) are field and barrier height parameters respectively, \( \langle \cdot \rangle_0 \) denotes the equilibrium statistical averages over \( W_0 \), and \( \eta = \sqrt{I/(2kT)} \) is a characteristic time of the free inertial motion. Choosing \( N = 2 \) equations (4)-(5) yield the exact after effect solution by matrix continued fractions (MCF) [6,11] and thus \( \chi(\omega) \) and \( \epsilon^*(f) \) (cf. curve 2 in figure 1 below). In general, three distinct peaks appear. One broad absorption peak dominates the low frequency (LF) spectrum corresponding to the slow overbarrier relaxation in the double-well potential. Another occurs in the mid-frequency (MF) region due to fast near degenerate exponential decays in the wells (without crossing the barrier) called intrawell modes, existing even in the noninertial limit. Finally sharp resonance appears at very high frequencies (VHF) due to fast inertial librations in the wells. The characteristic frequency \( \omega_k \) of the LF peak is given [6] by the Kramers escape rate, \( \omega_k \tau_D \approx 8\xi_v \exp(-2\xi_v) / \pi \), and the characteristic frequency of the fast internal librations \( \omega_v \) increases as \(- (kT \xi_v / I)^{1/2} \). These are associated with the Poley (THz) absorption while \( \beta' = \zeta_v / I \). Despite the elaborate MCF calculations the low and mid frequency behaviour may be accurately described by

\[
\frac{\chi(\omega)}{\chi(0)} = \frac{\Delta_1}{1 + i\omega \lambda_1^\dagger} + \frac{1 - \Delta_1}{1 + i\omega \tau_w}, \tag{6} \]

where \( \Delta_1 \) and \( \tau_w \) are parameters characteristic of the chosen \( V(\theta) \), \( \lambda_1 \) is the smallest nonvanishing eigenvalue of the FPE operator \( L_{FP} \) yielding an exponentially great relaxation time coinciding with \( \omega_k^{-1} \) of the LF peak, and \( \Delta_1 \) and \( \tau_w \) may be calculated analytically from equation 2.13.6 of [6]. However, figure 1 indicates that the normal diffusion model curve 2 fails to describe the LF loss spectrum. Therefore, we seek an explanation in anomalous diffusion.

4. Continuous distribution of orientations double-well model for anomalous diffusion

The fractional diffusion equation used is equation (12.6.1) of [6]

\[
\frac{\partial W}{\partial t} = -\theta \frac{\partial W}{\partial \theta} + \frac{1}{I} \frac{\partial V}{\partial \theta} \frac{\partial W}{\partial \theta} + \sigma D_{1-a}^\dagger \tau^{1-a} \beta \left[ \frac{\partial}{\partial \theta} \left( \theta \frac{\partial W}{\partial \theta} \right) + \frac{kT}{I} \frac{\partial^2 W}{\partial \theta^2} \right], \tag{7} \]
where $\beta = \xi / \gamma$, $D_t^{\alpha} = \partial_t \mathcal{D}_{t}^{\alpha}$ and the Riemann-Liouville fractional derivative is [6]

$$D_t^{\alpha} f(x,t \mid x_0) = \frac{1}{\Gamma(\alpha)} \int_0^t \frac{f(x,t' \mid x_0)}{(t-t')^{1+\alpha}} dt', \quad (8)$$

$\Gamma$ denotes the gamma function, $0<\alpha<1$ means subdiffusion, $1<\alpha<2$ means enhanced diffusion; normal diffusion occurs when $\alpha=1$. Now, equation (7) was originally proposed for subdiffusion in velocity space [6] which yields enhanced diffusion in configuration space. However if we suppose enhanced diffusion in velocity space then equation (7) leads to subdiffusion in configuration space [6], i.e., essentially the Cole-Cole equation (1) with $\sigma = 2 - \alpha$. The MCF solution of equation (7) subject to equation (5) then shows that $\chi(\omega)$ as calculated from equation (7) with $\tau = \tau_D$ accurately reproduces the loss spectrum of CH$_2$Cl$_2$ in glass decalin. Moreover, the formula

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{\Delta_1}{1 + (i\omega / \omega_H)^\beta} + \frac{1 - \Delta_1}{1 + (i\omega / \omega_\alpha)^\beta}, \quad \omega_H = \tau_D^{-1}(\tau_D^{-1} \chi_\alpha)^{\beta/\gamma}, \quad \omega_\alpha = \tau_D^{-1}(\tau_D^{-1} / \tau_\alpha)^{\beta/\gamma} \quad (9)$$

accurately reproduces the LF and MF features of the spectra. Also including $I$ reproduces the VHF spectrum, e.g., return to transparency at the Poley absorption peak. Thus the Debye model as adapted in equation (7) is a viable one for CH$_2$Cl$_2$-decalin.

**Figure 1.** Broad-band (0–THz) dielectric loss spectrum of 10% v/v solution of probe molecule CH$_2$Cl$_2$ in glassy decalin at 110K. Symbols are the experimental data [12]. Curve 1 is the best fit for the anomalous diffusion in the double-well cosine potential ($\alpha = 1.5$, $\xi'_v = 8$, and $\beta' = 0.003$); curve 2 is the best fit for the normal diffusion ($\alpha = 1$, $\xi'_v = 7$, and $\beta' = 0.001$). Dashed line is the Cole-Cole equation (9).

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