

A NOVEL MODEL FOR NON-DEBYE DIELECTRIC RELAXATION

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Introduction

Relaxation processes in complex systems such as liquid crystals, polymeric melts or glass-forming liquids is a very active area of research, see Refs. [1,2,3] and references therein. These systems have been studied using different techniques ranging from nuclear magnetic resonance and Brillouin light scattering to dielectric spectroscopy [1,2]. The variety of relaxation phenomena occurring in these systems are non-Debye and therefore they cannot be characterized by a single relaxation time [2,3]. The multiscale time relaxations involved in systems' relaxation suggest an accumulative effect of different elemental relaxation processes that can be associated with collective motions in the system [2,3].

In this work we show that a mesoscopic nonequilibrium thermodynamic approach can be used to formulate a powerful model describing the relaxation of a system of non-interacting polar molecules immersed in a time-dependent external electric field [3]. The model accounts for memory and cooperative effects and improves previous descriptions by incorporating in the effects due to inhomogeneities and related to the so-called diffusion of polarization effect.

The system of our interest is an ensemble of N noninteracting particles whose center of mass is located at \mathbf{r} and having a constant dipolar moment \mathbf{q} , which constitutes an axial degree of freedom. The ensemble is assumed to be in thermal equilibrium with a heat bath at constant temperature T . We will consider the case when an external time-dependent electric field $\mathbf{E}(t)$ is applied. In the general case, this electric field can be composed by the superposition of a static strong component \mathbf{E}_0 and a weak time-dependent component $\mathbf{E}_1(t)$ corresponding to the usual configuration of dielectric spectroscopy experiments [4,5].

The mesoscopic variable \mathbf{q} is assumed to perform fluctuations and therefore it can be adequately described through a probability density $f=f(\mathbf{q},t)$. This quantity contains all the information related the dynamics of the elemental dipoles and therefore constitutes the central quantity of the theory. From it we can evaluate all the moments of the distribution which contain information about the mean polarization vector of the system as well as the information of the quadrupolar, octupolar and higher order multipolar moments. These multipolar moments contain the macroscopic information of the system and their dynamics is related to the so-called dielectric susceptibility $\chi(\omega, \mathbf{k})$, which is in general a

function of the frequency ω and the wave number \mathbf{k} . This susceptibility is currently measured in dielectric spectroscopy experiments because it characterizes the response of a given material to an applied electric field. We show how $\chi(\omega, \mathbf{k})$ can be deduced from a powerful nonequilibrium thermodynamic model for dielectric relaxation.

Mesoscopic description

A way to find the evolution equation for the moments of $f(\mathbf{q},t)$ is to calculate first the evolution equation for $f(\mathbf{q},t)$ which, in view of the normalization condition satisfies the continuity equation [3]

$$\partial_t f(\mathbf{r}, \mathbf{q}, t) = \partial_r (f V_r) + p \otimes \partial_p (f \Omega), \quad (1)$$

where ∂_r is the gradient operator and $p \otimes \partial_p$ is the rotational operator. The unknown currents $f V_r$ and $f \Omega$ can be determined explicitly by using mesoscopic nonequilibrium thermodynamics, that makes use of the Gibbs entropy postulate

$$S(t) = S_{leq} - k_B \int f \ln f / f_{leq} dq dr. \quad (2)$$

Here, $S(t)$ and $S_{leq}(t)$ are the non-equilibrium and local equilibrium entropies, k_B is Boltzmann's constant. Thus, the time derivative of $S(t)$ is related to the entropy produced by the system during its relaxation to equilibrium. Finally, f_{leq} the local equilibrium probability density given by

$$f_{leq} = Z^{-1} \exp[U(\mathbf{q}, t) / kT], \quad (3)$$

where Z is the partition function corresponding to the Boltzmann factor that contains the interaction energy

$$U(\mathbf{q}, t) = -\mathbf{q} \cdot \mathbf{E}(t). \quad (4)$$

With the ingredients stated in Eqs. (1)-(4) and the rules of nonequilibrium thermodynamics it can be shown that $f(\mathbf{r}, \mathbf{q}, t)$ satisfies a Fokker-Planck equation (see Ref. 3 for details) from which evolution equations for the moments of the distribution can be deduced.

Macroscopic equations for the multipoles

Using the definitions of the average dipole field

$$P(\mathbf{r}, t) = N \int p f dq, \quad (5)$$

and the quadrupolar field

$$Q(\mathbf{r}, t) = (N^2 / 2) \int (3 pp - p^2 1) f dq, \quad (6)$$

the evolution equations can be obtained by taking the time derivative and using the Fokker-Planck equation for $f(\mathbf{r}, \mathbf{q}, t)$. The resulting equations are diffusion like equations for the dipolar moment

$$\partial_t P(\mathbf{r}, t) = D_0 \partial_{r,r} P - \gamma \left[P + M(Q) - (N p^2 / 3 k_0 B T) E(t) \right]$$

and for the quadrupolar moment

$$\partial_t Q(r,t) = D_0 \partial_{r,r} Q - \gamma Q + F(R, Q, P; E), \quad (7)$$

where D_0 is the translational diffusion coefficient and γ is a matrix of relaxation times. The matrices $\mathbf{M}(\mathbf{S})$ and $\mathbf{F}(\mathbf{R}, \mathbf{Q}, \mathbf{P}; E)$ have complicated forms. \mathbf{R} is the octupolar moment. The first term in the rhs of these equations comes from the effect of thermal agitation and indicates that both the dipolar and quadrupolar moments undergo macroscopic diffusion. The second term at the rhs reflects the effect of thermal agitation on reorientation of the molecules thus implying that γ is related to the rotational diffusion coefficient.

Using Fourier transform techniques, it is possible to obtain the following simple expression for the dipolar moment

$$P(\omega, k) = \chi(\omega, k) E(\omega), \quad (8)$$

where the complex dielectric susceptibility has a general form

$$\chi(\omega, k) = \chi_0(E_0) / (1 + i\omega\tau(E_0) + D_0 k^2). \quad (9)$$

Here, the equilibrium susceptibility $\chi(E_0)$ and the relaxation time $\tau(E_0)$ are nonlinear functions of the static field E_0 thus implying nonlinear material relations between the polarization field and the electric field, which in general also takes into account memory effects.

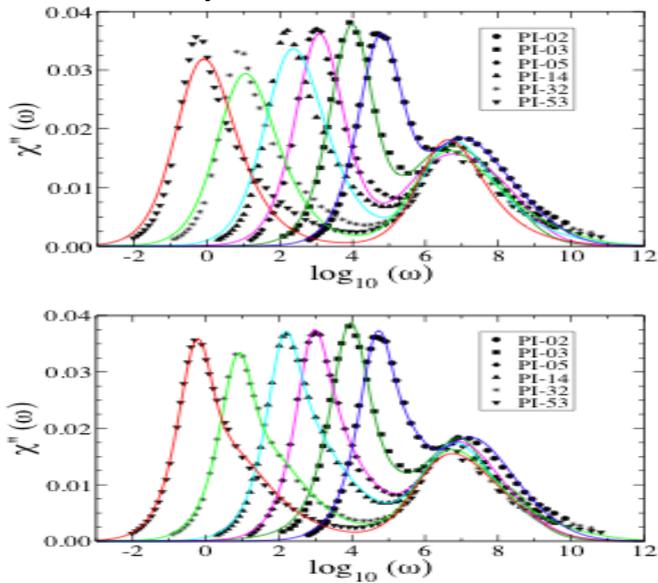


Fig.1: Top panel: Experimental data (symbols) taken from Ref. [4] of the dielectric loss of highly concentrated solution of cis-PI chains at 273K as a function of frequency for different mass weights M . The average molecular mass in kgmol^{-1} go from 2 to 53 as indicated in the figure. Solid lines are fits using Eq. (9) with the dispersion relation $k^2(w) = (w/w_0)^\alpha$. Bottom panel: The same experimental data. The solid lines correspond to a susceptibility obtained with the present formalism in a superposition approximation [3].

Comparison with experiments

Equation (9) together with the dispersion relation $k^2(w) = (w/w_0)^\alpha$ for the diffusion of polarization contri-

bution, allow to formulate very general models able to cope with the phenomenology and which, in different limiting cases, reduce to well come function as Cole-Cole, Cole-Davidson and others. The top panel in Figure 1 shows a comparison between experiments [4] and theory (9) and [3] for concentrated solutions of cis-PI with different molecular masses. The comparison has been performed by fitting the first maximum at low frequencies and giving the characteristic absorption frequency for the second one. The expressions obtained automatically give the amplitude of the second maximum. The bottom panel of Fig. 1 shows the same data but fitted with a sum of Eqs. (9) having different amplitudes and characteristic relaxation times. In this superposition approximation each amplitude and relaxation time correspond to different number of polar elements, thus suggesting that the overall relaxation is a consequence of cooperative effects. Figure 2 shows a comparison between experiments and theory for the dielectric loss of glycerol-water samples at 160 K in the presence of myoglobin with different levels of hydration.

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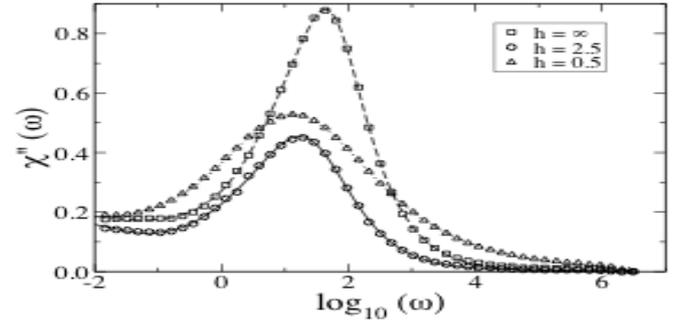


Fig. 3. Normalized dielectric loss of glycerol/water samples at 160 K in the presence of myoglobin with different levels of hydration. The symbols represent experimental results taken from Ref. [5] whereas the lines are the fits from [3].

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