Relaxation in homogeneous and non-homogeneous polarized systems. A mesoscopic entropy approach

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Abstract

The dynamics of a degree of freedom associated to an axial vector in contact with a heat bath is described by means of a probability distribution function obeying a Fokker-Planck equation. The equation is derived by using mesoscopic non-equilibrium thermodynamics and permits a formulation of a dynamical theory for the axial degree of freedom (orientation, polarization) and its associated order parameter. The theory is used to describe dielectric relaxation in homogeneous and non-homogeneous systems in the presence of strong electric fields. In the homogeneous case, we obtain the dependence of the relaxation time on the external field as observed in experiments. In the non-homogeneous case, our model accounts for the two observed maxima of the dielectric loss giving a good quantitative description of experimental data at all frequencies, especially for systems with low molecular mass.

Key words: Mesoscopic entropy, Fokker-Planck equations, axial degrees of freedom, dielectric relaxation.

1 Introduction

Orientational dynamics of a nematic director or of a dipole in an applied electric field plays a crucial role in numerous modern technologies. For example, the reorientation of the director vector in nematic liquid-crystals changes...
the electro-optical properties of these materials, making of central interest
the response of these systems to constant and time varying electrical fields
[1]. Liquid crystals, polymer solutions and dielectrics are systems showing
strong anisotropies in their physical properties such as viscosities, transla-
tional and rotational diffusion coefficients, and dielectric or magnetic suscep-
tibilities [1,2,3,4,5,6,7,8,9,10]. This fact together with the interaction of these
systems with their environment, leads to a number of phenomena not ob-
served in isotropic phases, like the dependence of the characteristic relaxation
times of the reorientation of molecules on the intensity of an externally applied
electrical field [11,12].

From a fundamental viewpoint, the interaction with the surroundings and the
orientational relaxation of the system can be modelled in terms of the dynam-
ics of an axial degree of freedom \( \hat{n} \) in contact with a heat bath [1,2]. Due to the
importance of thermal fluctuations in the dynamics of the axial vector, in this
article we begin our analysis by calculating the mesoscopic entropy production
\( \sigma \) of the system using the rules of mesoscopic nonequilibrium thermody
namics [13]. Then, from the entropy production and the probability conservation, we
derive a Fokker-Planck equation for the probability density \( f(\vec{r}, \hat{n}, t) \) which
depends on time \( t \), position \( \vec{r} \), and the axial vector \( \hat{n} \). This Fokker-Planck
equation allows us to formulate evolution equations for the average of the
axial vector and for the associated order parameter in two import-
ant physical situations: i) When the systems can be considered homogeneous and ii)
when non-homogeneities are important. The results we have obtained can be
compared with experiments [12,14] and previous theories based on other ap-
proaches [12,15,16].

The paper is organized as follows. In Sec. 2 we calculate the mesoscopic entropy
production, derive the Fokker-Planck equation for the probability density and
obtain the evolution equations for the axial degree of freedom and its associ-
ated order parameter under the assumption of the system’s homogeneity. In
Sec. 3 we apply our results to the case of dielectric relaxation and in Sec. 4
we compare with experiments and with other theories. In sec. 5 we analyze
the relaxation dynamics in non-homogeneous systems by taking into account
the diffusion of the polarization. Finally, in the last section we summarize our
main results.

2 Mesoscopic entropy and Fokker-Planck dynamics

Consider a system of particles in contact with a heat bath at constant tem-
perature \( T \) and in the presence of an external potential \( U \). The state of the
system is characterized by the position vector \( \vec{r} \) and the axial degree of freedom
\( \hat{n} \) which may be associated to an orientation or a polarization vector.
The mesoscopic dynamics of the system can be described in terms of the single-particle probability density \( f(\vec{r}, \hat{n}, t) \) satisfying the normalization condition \( \int f d\hat{n} d\vec{r} = 1 \). This condition imposes that \( f \) must obey the probability conservation equation \([17]\)

\[
\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \vec{r}} \cdot (f \vec{V}) - \vec{R} \cdot (f \vec{\Omega}),
\]

(1)

where \( \vec{R} = \hat{n} \times \frac{\partial}{\partial \vec{r}} \) is the rotational operator and \( \vec{V} \) is the velocity conjugated to the position vector \( \vec{r} \). Eq. (1) can be obtained by taking into account the corresponding boundary and periodic conditions over \( \vec{r} \) and \( \hat{n} \) after applying the triple product identity and considering that the change in time of the axial vector \( \dot{\hat{n}} \) is perpendicular to \( \hat{n} \): \( \dot{\hat{n}} = \vec{\Omega} \times \hat{n} \), with \( \vec{\Omega} \) the angular velocity \([2]\).

The explicit expressions for the unknown probability currents \( f \vec{V} \) and \( f \vec{\Omega} \) in \((\vec{r}, \hat{n})\)-space, can be found by calculating the entropy production \( \sigma \) of the system during its evolution in time. To this end, we will follow the rules of mesoscopic nonequilibrium thermodynamics which makes use of the Gibbs entropy postulate (GEP) \([13,18]\)

\[
\rho s(t) = -k_B \int f \ln \left( \frac{f}{f_{eq}} \right) d\hat{n} + \rho s_{eq},
\]

(2)

where \( k_B \) is the Boltzmann constant, \( \rho = m \int f d\hat{n} \) is the mass density with \( m \) the mass of a particle and \( s_{eq} \) is the equilibrium entropy. \( f_{eq} \) is the probability density characterizing the equilibrium state of the system, given by \([19,20,21]\)

\[
f_{eq}(\vec{r}, \hat{n}) = f_0 e^{-mU/k_BT},
\]

(3)

where, \( U = U(\vec{r}, \hat{n}) \) is a potential energy field per unit of mass and \( f_0 \) is a normalization constant.

The GEP formulated in (2) is compatible with the Gibbs equation \([18]\)

\[
T \delta s = \delta e + p \delta (\rho^{-1}) - m \int \vec{\mu} \delta \left( \frac{f}{\rho} \right) d\hat{n} d\vec{r},
\]

(4)

where \( s, e, p \) and \( \vec{\mu}(\vec{r}, \hat{n}, t) \) are the non-equilibrium entropy, energy, pressure and chemical potential per unit mass of the system. Taking the variation of Eq. (2) and comparing with (4) keeping constant \( e \) and \( \rho \), we may identify the nonequilibrium chemical potential

\[
\vec{\mu} = \vec{\mu}_{eq} + \frac{k_B T}{m} \ln \frac{f}{f_0} + U,
\]

(5)
where $\bar{\mu}_{eq}$ is the chemical potential in the equilibrium state. The balance equation for the non-equilibrium entropy follows from the Gibbs equation (4) (with $e$ and $\rho$ constant) by taking the time derivative, integrating by parts and using the corresponding boundary and periodic conditions for the currents. We obtain

$$\rho \sigma = -\frac{m}{T} \int \left[ \frac{\partial \bar{\mu}}{\partial \vec{r}} \cdot (f \vec{V}) + \vec{R} \cdot \left( f \vec{\Omega} \right) \right] \, d\hat{n} d\vec{r}. \quad (6)$$

Eq. (6) contains two contributions of the type flux-force pair, each one coming from the diffusion process in $\vec{r}$- and $\hat{n}$-space, respectively. Following nonequilibrium thermodynamics rules, linear phenomenological relationships between currents and thermodynamic forces can be established in the form \[13,18\]

$$\vec{V} = -\mathbb{L}_{rr} \cdot \frac{\partial \bar{\mu}}{\partial \vec{r}} - \mathbb{L}_{rn} \cdot \vec{R} \bar{\mu}, \quad (7)$$

$$\vec{\Omega} = -\mathbb{L}_{nn} \cdot \vec{R} \bar{\mu} - \mathbb{L}_{nr} \cdot \frac{\partial \bar{\mu}}{\partial \vec{r}}. \quad (8)$$

Here, $\mathbb{L}_{rr}$, $\mathbb{L}_{rn}$, $\mathbb{L}_{nr}$ and $\mathbb{L}_{nn}$ are the (tensorial) Onsager coefficients which are, in general, functions of $\vec{r}$, $\hat{n}$, $T$ and $\rho$. \[13,18\]. However, for simplicity we will assume here that the Onsager tensors have constant components. Since $\hat{n}$ is an axial vector and $\vec{r}$ a polar vector, the Onsager-Casimir relationships impose the relation $\mathbb{L}_{nr} = -\mathbb{L}_{rn}$. \[18,22\].

Substituting Eqs. (7) and (8) into (1), we finally arrive at the Fokker-Planck equation

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \vec{r}} \cdot \left[ \frac{k_B T}{m} \mathbb{L}_{rr} \cdot \left( \frac{\partial f}{\partial \vec{r}} + \frac{mf}{k_B T} \frac{\partial U}{\partial \vec{r}} \right) \right] + \vec{R} \cdot \left[ \frac{k_B T}{m} \mathbb{L}_{nn} \cdot \left( \vec{R} f + \frac{mf}{k_B T} \vec{R} U \right) \right]. \quad (9)$$

Eq. (9) constitutes the basis of the mesoscopic description of the system and enables one to derive the evolution equation of the moments of the probability density. A similar equation has been obtained by using hydrodynamic methods in Ref. \[2\] and from a Langevin approach in the case of a mean field approximation describing inhomogeneous nematics \[23\]. The present derivation allows the generalization of Eq. (9) to cases in which inertia effects could be important, \[24\].
2.1 Relaxation equations for the average value of the axial degree of freedom and the order parameter

In order to derive the relaxation equations for the average axial vector $\vec{N}$ and the order parameter $S$, we will assume that the system is homogeneous, that is, the interaction potential of the particles with an external force only depends on $\hat{n}$, $U = U(\hat{n})$. In this case, the translational part of Eq. (9) can be integrated over $\hat{n}$, yielding a free diffusion equation for the center of mass of the particles from which the evolution equation for the second moment of position, $\langle \vec{r}^2 \rangle = \int \vec{r}^2 f(\vec{r}, \hat{n}, t)d\hat{n}d\vec{r}$, is

$$\frac{\partial \langle \vec{r}^2 \rangle}{\partial t} = 2\text{Tr}[D_{tr}].$$  (10)

Here, Tr[D_{tr}] is the trace of the translational diffusion tensor $D_{tr}$ assumed constant for simplicity and which is related to the Onsager coefficient $L_{rr}$ through the expression $D_{tr} = (k_B T/m)L_{rr}$. Eq. (10) implies that the center of mass of the particles performs Brownian motion with second moment $\langle \vec{r}^2 \rangle = 2\text{Tr}[D_{tr}]t$. In the case of solid systems at sufficiently low temperatures, the translational diffusion coefficient can be taken as zero.

Thus, by integrating Eq. (9) over $\vec{r}$ we obtain the following Fokker-Planck equation for the reduced probability distribution $g(\hat{n}, t) = \int f d\vec{r}$

$$\frac{\partial g}{\partial t} = \vec{R} \cdot \left[ \frac{k_B T}{m} L_{mn} \cdot \left( \vec{R} g + \frac{mg}{k_B T} \vec{R} U \right) \right].$$  (11)

In the present case, the Onsager coefficient $L_{mn}$ is related with the matrix of rotational relaxation times $\gamma$ through $L_{mn} = \frac{m}{k_B T} \gamma^{-1}$, which defines the rotational diffusion coefficient. From Eq. (11), we can obtain the relaxation equations for the first and second-order moments of $g(\hat{n}, t)$ corresponding to the average axial vector $\vec{N}$ and the order parameter $S$, defined by [2]

$$\vec{N}(t) = \int \hat{n} g d\hat{n} \quad \text{and} \quad S(t) = \langle S \rangle(t) = (1/2) \int (3\hat{n}\hat{n} - 1) g d\hat{n},$$  (12)

where $\mathbf{1}$ is the unit tensor and $S = (1/2)(3\hat{n}\hat{n} - \mathbf{1})$ is the microscopic order parameter. It is convenient to mention that when $\hat{n}$ represents the orientation vector of a molecule, then $S$ is the orientation tensor [2] that is related to the well known Onsager order parameter characterizing the order-disorder transition in suspensions of rod-like molecules [3]. For polar systems, $\hat{n}$ and $S$ are related to the polar and quadrupolar terms of the corresponding multipolar expansion.
Now, taking the time derivative of equation (12) and using (11), after integrating by parts assuming periodic conditions for the probability current, one obtains the evolution equation

\[
\frac{\partial \vec{N}}{\partial t} = -\tilde{\gamma}^{-1} \cdot \left[ \vec{N} - \frac{2m}{3k_BT} \tilde{\gamma} \cdot \left( \tilde{M}(S) \cdot \frac{\partial U}{\partial \hat{n}} \right) + \frac{m}{3k_BT} \left( \frac{\partial U}{\partial \hat{n}} \right) \right],
\] (13)

where \( \tilde{M}(S) \) is defined by

\[
\tilde{M}(S) = [\tilde{\gamma}^{-1} \cdot S + (\tilde{\gamma}^{-1} : S) \mathbf{1} - \tilde{\gamma}^{-1} \cdot S].
\] (14)

In Eq. (13), the matrix of relaxation times is given by \( \tilde{\gamma}^{-1} = \text{Tr}(\gamma^{-1}) \mathbf{1} - \gamma^{-1} \), implying that, in the general case, the characteristic relaxation times are combinations of the elements of the rotational diffusion tensor. The first term on the right-hand side of Eq. (13) comes from the diffusion term of Eq. (11), whereas the other terms are due to the external force. Eq. (13) is expected to be valid for characteristic values of the interaction energy, \( U \), of the order of the thermal energy \( k_BT \).

Following a similar procedure, Eqs. (11) and (12) yield the evolution equation for \( S \)

\[
\frac{\partial S}{\partial t} = -2\tilde{M}^s(S) - 2(\tilde{\gamma}^{-1} \cdot S)^s + \frac{6m}{5k_BT} \left( \tilde{M}(Q) \cdot \frac{\partial U}{\partial \hat{n}} \right)^s + \frac{3m}{5k_BT} \left[ 2 \left( \tilde{\gamma}^{-1} \cdot \frac{\partial U}{\partial \hat{n}} \right) \hat{n}^s + \left( \tilde{\gamma}^{-1} \cdot \left( \frac{\partial U}{\partial \hat{n}} \right) \right)^s \right] + \frac{3m}{5k_BT} \left[ \left( \tilde{\gamma}^{-1} \cdot \frac{\partial U}{\partial \hat{n}} \right) \cdot \hat{n} + \left( \tilde{\gamma}^{-1} \cdot \hat{n} \right) \frac{\partial U}{\partial \hat{n}} \right]^s,
\] (15)

where the superscript \( s \) stands for the symmetric part of a tensor and \( \tilde{M}(S) \) has the same form as in Eq. (14) but in (15) depends on the averaged order parameter \( S \). In Eq. (15) we have introduced the average tensor \( Q \) defined by

\[
Q(t) = \langle Q \rangle(t) = (1/2) \int [5\hat{n}\hat{n} - (\hat{n}\mathbf{1})^s] gd\hat{n},
\] (16)

and the tensor

\[
\tilde{M}(Q) = [\tilde{\gamma}^{-1} \cdot Q + (\tilde{\gamma}^{-1} : Q) \mathbf{1} - \tilde{\gamma}^{-1} \cdot Q].
\] (17)

Here, \( Q \) is the microscopic octupolar tensor and \( (\hat{n}\mathbf{1})^s_{ijk} = n_i \delta_{jk} + n_j \delta_{ki} + n_k \delta_{ij} \). In Eq. (15), the first three terms come from the diffusion term in Eq. (11)
whereas the others are due to interactions with the external field. Eqs. (13) and (15) constitute the first two evolution equations of the complete hierarchy of moments of the distribution function $g$.

3 Dipole and quadrupole relaxation in a homogeneous system

The relaxation of the polarization vector in dielectrics can be described by means of equations (13) and (15) since $\hat{n}$ can be interpreted as the dipole moment of a molecule through the expression: $\hat{n} = \mu^{-1}\vec{p}$ where $\mu$ is the magnitude of the dipole moment of the molecule. In this form, the polarization $\vec{P}$ and the quadrupolar moment $S_p$ per unit volume are defined by [25]

$$\vec{P} = N\mu\vec{N} \quad \text{and} \quad S_p = N^2\mu^2 \langle S \rangle$$

(18)

where the tensor $S_p$ is the quadrupole moment induced by thermal fluctuations. In first approximation, the potential energy per unit mass of a polar molecule interacting with an external electric field $\vec{E}$ is given by [2]

$$\tilde{U}(\vec{p}) = -\frac{\vec{p} \cdot \vec{E}}{m}.$$  

(19)

From Eqs. (13), (15) and (18), it follows that the evolution equation for $\vec{P}$ is

$$\frac{\partial \vec{P}}{\partial t} = -\tilde{\gamma}^{-1} \cdot \left[ \vec{P} + \frac{2}{3Nk_BT} \tilde{\gamma} \cdot \vec{M}(S_p) \cdot \vec{E} - \frac{N\mu^2}{3k_BT} \tilde{\gamma} \cdot \vec{E} \right],$$

(20)

where $\vec{M}(S_p)$ is defined according to Eq. (14). The evolution equation for $S_p$ takes the form

$$\frac{\partial S_p}{\partial t} = -2\tilde{M}^s(S_p) - 2 \left( \tilde{\gamma}^{-1} \cdot S_p \right)^s - \frac{6}{5Nk_BT} \left[ \tilde{M}(Q_p) \cdot \vec{E} \right]^s$$

$$+ \frac{3N\mu^2}{5k_BT} \left\{ 2 \left( \tilde{\gamma}^{-1} \cdot \vec{E} \right) \cdot \vec{P} \right\}^s + \left[ \tilde{\gamma}^{-1} \left( \vec{P} \cdot \vec{E} \right) \right]^s$$

$$- \frac{3N\mu^2}{5k_BT} \left\{ \left[ \tilde{\gamma}^{-1} \cdot \vec{E} \right] \cdot \vec{P} \right\} + \left[ \tilde{\gamma}^{-1} \cdot \vec{P} \right]^s \vec{E},$$

(21)

where $Q_p = N^3\mu^3Q$ with $\tilde{M}(Q_p)$ defined according to Eq. (17). The contribution of higher order moments will be neglected for convenience. These equations generalize the Debye theory of dielectric relaxation by taking into
account the coupling between the dipolar and quadrupolar moments naturally contained in the distribution function \( g \). Debye’s theory is recovered if quadrupolar contributions are neglected in Eqs. (20) and (21).

A closed set of equations for \( \vec{P} \) and \( S_p \) can be obtained by approximating \( Q_p \) by its equilibrium average, which can be calculated using the equilibrium distribution function

\[
ge_{eq} = Z^{-1}e^{mU/k_BT}.
\]  

Eq. (22) is the stationary solution of (11) and \( Z^{-1} = \int e^{mU/k_BT}d\vec{p} \) is the partition function of the system. Notice that, when the externally applied field is weak, it is usual to take the so-called homogeneous isotropic approximation of (22), given by [2]

\[
ge_{eq} \approx \frac{1}{4\pi}. 
\]

We will use Eqs. (22) and (23) in order to complete the set of equations (20) and (21) and to make comparisons with previous theories.

### 3.1 Dielectric relaxation in the homogeneous-isotropic approximation

By using Eqs. (20) and (21), and the isotropic distribution function (23), the dielectric response of a polar system will be analyzed in terms of the complex dielectric susceptibility \( \chi \).

To proceed, we will now assume that the external electric field is time dependent and given by the sum of a strong constant electric field \( \vec{E}_0 \) applied along the \( z \) axis, and a weak AC probe field \( \vec{E}_1(t) = \vec{E}_1 e^{i\omega t} \) applied in an arbitrary direction, that is: \( \vec{E} = \vec{E}_0 + \vec{E}_1(t) \). In addition, we will assume for simplicity that \( \partial S_p / \partial t \sim 0 \) and solve Eqs. (20) and (21) for \( \vec{P} \). This quasi-stationary assumption leads to a considerable simplification of the obtained formulas and do not modifies considerably the results of our model. Thus, since the average of the octupolar tensor (16) with (23) vanishes \( ([Q_p]_{ijk} = 0) \), from Eq. (21) we obtain the following relation for \( S_p \)

\[
\mathcal{M}^s(S_p) + 2 \left( \tilde{\gamma}^{-1} \cdot S_p \right)^s = \frac{3N\mu^2}{5k_BT} \left\{ 2 \left[ \left( \tilde{\gamma}^{-1} \cdot \vec{E}(t) \right) \vec{P} \right]^s + \left[ \tilde{\gamma}^{-1} (\vec{P} \cdot \vec{E}(t)) \right]^s \right. \\
- \left[ \left( \tilde{\gamma}^{-1} \cdot \vec{E}(t) \right) \vec{P} \right]^s - \left[ \left( \tilde{\gamma}^{-1} \cdot \vec{E}(t) \right) \cdot \vec{P} \right] 1 \right\}. 
\]
From Eqs. (24) and (20), it is possible to obtain two equations for the parallel \( P_\parallel(t) \) and perpendicular \( P_\perp(t) \) components of the polarization vector defined with respect to the constant field \( \vec{E}_0 \). Hence, using the condition \( E_1 \ll E_0 \) in the second term of Eq. (20) and keeping dominant terms, the equation for \( P_\parallel(t) \) becomes

\[
\frac{\partial P_\parallel(t)}{\partial t} = -\tau_\parallel^{-1} \left[ P_\parallel(t) - \epsilon_o \chi_\parallel E_\parallel(t) \right], \tag{25}
\]

where \( E_\parallel = E_0 + E_\parallel_1 \) with \( E_\parallel_1 \) the component of \( \vec{E}_1 \) parallel to \( \vec{E}_0 \), and we have assumed that the matrix of relaxation times \( \gamma \) is diagonal with components \( \gamma_\perp, \gamma_\parallel \). By definition, \( \tilde{\gamma} \) and \( \gamma \) have the same symmetries. The relaxation time \( \tau_\parallel \) and the zero frequency susceptibility \( \chi_\parallel \) in Eq. (25) are given by

\[
\tau_\parallel = \frac{\gamma_\parallel / 2}{1 + \frac{\epsilon_o^2}{30} (4 - \Gamma)} \quad \text{and} \quad \chi_\parallel = \frac{\chi_o}{1 + \frac{\epsilon_o^2}{30} (4 - \Gamma)}. \tag{26}
\]

Here, we have introduced \( \Gamma \equiv \gamma_\perp / \gamma_\parallel \) to simplify the notation and defined \( \chi_o \equiv N \mu^2 / 3 \epsilon_o k_B T \) with \( \epsilon_o = 8.854 \times 10^{-12} \text{F/m} \). It is important to notice the fact that the constant electric field introduces corrections to \( \tau_\parallel \) and \( \chi_\parallel \) through the dimensionless parameter \( \xi = \mu E_0 / k_B T \).

Using Fourier transform techniques, from Eq. (25) one obtains

\[
P_\parallel(t) = \epsilon_o \chi_\parallel E_0 + \epsilon_o \chi_\parallel (\omega_o) E_\parallel_1(t), \tag{27}
\]

where \( \chi_\parallel(\omega_o) = \chi_\parallel(1 + i \omega_o \tau_\parallel)^{-1} \). The evolution equation for the perpendicular component of the polarization vector can be calculated in similar form. One obtains

\[
\frac{\partial P_\perp(t)}{\partial t} = -\gamma_\perp^{-1} \left[ P_\perp(t) - \epsilon_o \chi_\perp E_\perp_1(t) \right], \tag{28}
\]

where \( E_\perp_1 \) is the component of \( \vec{E}_1 \) perpendicular to \( \vec{E}_0 \). Following the same procedure to obtain (26), we find that: \( P_\perp = \epsilon_o \chi_\perp (1 + i \omega_o \tau_\perp)^{-1} E_\perp_1(t) \). In this case, \( \tau_\perp \) and \( \chi_\perp \) take the form

\[
\tau_\perp = \frac{\gamma_\perp / (1 + \Gamma)}{1 + \frac{\epsilon_o^2 (2 - \Gamma)}{10 (1 + \Gamma)}} \quad \text{and} \quad \chi_\perp = \frac{\chi_o}{1 + \frac{\epsilon_o^2 (2 - \Gamma)}{10 (1 + \Gamma)}}. \tag{29}
\]

These results yield the following expressions for the real and imaginary parts of the parallel and perpendicular components of the complex dielectric susceptibility tensor.
where $\chi^\infty_\parallel$ and $\chi^\infty_\perp$ are the high frequency susceptibilities of the system. From Eqs. (26) and (29), it follows that the quadrupole moment induced by thermal fluctuations introduces field dependent corrections in the susceptibility and the relaxation times, as observed in experiments [12].

We have also calculated the expressions for the parallel and perpendicular susceptibilities of the system in the non-stationary case. The expressions for the components of the polarization vector can only be given in Fourier space and, in the isotropic approximation they are given by

\[
P^\text{ns}_\parallel(\omega) = \epsilon_o \frac{\chi^\text{ns}_\parallel(1 + i\omega\tau^\text{ns}_\parallel)\hat{E}_\parallel(\omega)}{1 - i\omega c^\parallel_{\text{ns}}} \quad \text{and} \quad P^\text{ns}_\perp(\omega) = \epsilon_o \frac{\chi^\text{ns}_\perp(1 + i\omega\tau^\text{ns}_\perp)\hat{E}_\perp(\omega)}{1 - i\omega c^\perp_{\text{ns}}}.
\]

(32)

where the superscript $\text{ns}$ indicates the non-stationary case. The relaxation times $\tau^\text{ns}_\parallel$ and $\tau^\text{ns}_\perp$ are now given by

\[
\tau^\text{ns}_\parallel = \frac{\gamma_\perp/2}{1 + \xi^2/30(4-\Gamma)} \quad \text{and} \quad \tau^\text{ns}_\perp = \frac{\gamma_\perp/(1+\Gamma)}{1 + \xi^2/60(1+\Gamma)(1+\omega\tau_\perp/6)^2},
\]

(33)

whereas the susceptibilities $\chi^\text{ns}_\parallel$ and $\chi^\text{ns}_\perp$ in this non-stationary case are defined by

\[
\chi^\text{ns}_\parallel = \frac{\chi_\parallel}{1 + \xi^2/30(1+\omega\tau_\perp/6)^2} \quad \text{and} \quad \chi^\text{ns}_\perp = \frac{\chi_\perp}{1 + \xi^2/60(1+\Gamma)(1+\omega\tau_\perp/6)^2}.
\]

(34)

Finally, the correction factors $c_\parallel$ and $c_\perp$ due to the time derivative in Eq. (21) are respectively given by

\[
c_\parallel = 1 - \frac{\xi^2}{90} \frac{(4-\Gamma)}{1 + (\omega\tau_\perp/6)^2},
\]

\[
c_\perp = 1 - \frac{\xi^2}{60} \frac{(2-\Gamma)}{1 + (\omega\tau_\perp/6)^2}.
\]

(35)

In the following section, the comparison with experiments using the complete set of non-stationary relations for the susceptibilities, Eqs. (32)-(35), or their non-homogeneous versions (see Sec. 5), will show that the quantitative description is very similar to the one given by means of the stationary expressions, that are simpler.
3.2 Relaxation in an homogeneous non-isotropic approximation

Eqs. (26) and (29) for the relaxation times and the susceptibilities have the correct qualitative dependence on the external field $E_0$ as observed in experiments, but they fail quantitatively. This is due to the fact that the isotropic approximation is not adequate when strong electrical fields are applied to the system.

Therefore, the quantitative description can be improved by taking the average (16) in Eqs. (20) and (21) with the non-isotropic probability distribution (22). In this case, the components of the tensor $Q_p$ do not vanish and more complicated formulas are obtained for $S_p$ and $\vec{P}$. Thus, following a procedure similar to that of subsection 3.1, it is possible to derive the following expressions for the zero frequency parallel and perpendicular susceptibilities

\[ \tilde{\chi}_\parallel = \frac{\chi_o \left\{ 1 + \frac{2}{3} (3 - 2\Gamma) \left[ (1 + \frac{15}{2} L[\xi] - \frac{5}{2}) \right] \right\}}{1 + \frac{\xi^2}{30} (4 - \Gamma)}, \]
\[ \tilde{\chi}_\perp = \frac{\chi_o \left[ 1 + \frac{\xi}{5} \left( \frac{2 - \Gamma}{1 + \Gamma} \right) \left\{ L[\xi] - 2\Gamma \left[ (1 + \frac{15}{2} L[\xi] - \frac{5}{2}) \right] \right\} \right]}{1 + \frac{\xi^2}{30} (2 - 1)}]. \] (36)

Here, the tilde stands for the non-isotropic case. The expression for the relaxation times do not change and are given by the corresponding expressions in (26) and (29). If we approximate our description by decoupling Eqs. (20) and (21) by taking the average of $S_p$ with (22), then the expressions for the components of the susceptibility reduce to

\[ \tilde{\chi}^{bh}_\parallel = \frac{3\chi_o L[\xi]}{\xi} \quad \text{and} \quad \tilde{\chi}^{bh}_\perp = \chi_o \left[ 1 + \left( \frac{2 - \Gamma}{1 + \Gamma} \right) \left( 1 - \frac{3L[\xi]}{\xi} \right) \right], \] (37)

where the parallel component $\tilde{\chi}^{bh}_\parallel$ is equal to the one reported in Ref. [12]. In this approximation, the parallel and perpendicular relaxation times become: $\tau_\parallel = \gamma_\perp / 2$ and $\tau_\perp = \gamma_\perp/[1 + \Gamma]$.

In this section we have shown that the field dependent corrections of the relaxation times and susceptibilities of a dielectric are due to the coupling between the evolution equations for the dipolar, quadrupolar and, in general, higher order moments of the distribution. The results obtained agree with previous theories (see, for instance, [16]) and, when $\xi \sim 0$, reduce to the ones derived by means of Debye’s theory.

When considering the non-stationary dynamics of the quadrupole, we obtain that in the present case the susceptibilities entering in the corresponding Eqs.
Fig. 1. Comparison of the experimental data of the critical frequency \( f_c(E) \) (symbols) taken from Ref. [12] with the theoretical results for a strong DC field (lines) for a dilute solution of PBLG molecules with molecular weights \( M_w \) of \( 1.1 \times 10^5 \) (romboids), \( 2.6 \times 10^5 \) (circles) and \( 4.6 \times 10^5 \) (squares).

The relaxation times and the correction factors \( c_\parallel, c_\perp \) are still given by Eqs. (33) and (35). In the case when there is no coupling we have \( c_\parallel = c_\perp = 1 \), and therefore the relaxation times and the susceptibilities are given reduce to the form Eq. (37), as expected.

4 Comparison with experiments

In this section, we use Eq. (26) for the relaxation time to estimate the value of the dipolar moment of PBLG molecules with different molecular masses [12]. In similar form, the susceptibilities given in (36) are used to fit the experimental data for the dielectric loss of \( \text{cis-PI} \) polymers in solution reported in Ref. [26].

4.1 Determination of the dipolar moment using the field dependent relaxation time

The magnitude of the dipolar moment \( \mu \) of a molecule can be estimated by using the critical frequency \( f_c \), defined as the value of the frequency at which
The maximum of the dielectric loss occurs. Since the value of $f_c$ depends on the magnitude of the applied field, see Fig. 1, then $\mu$ can be determined by using the relation \[ f_c = (2\pi \tau_\parallel)^{-1}. \] (39)

The open symbols in Fig. 1 show isothermal (298 K) data of the critical frequency $f_c$, reported from experiments with dilute solutions of PBLG having different molecular masses $M_w$. The data were obtained by applying a strong DC electric field ($0 - 9 \times 10^5$ V/m) on the system and can be fitted using Eq. (26) by assuming that the energy of a dipole in the DC field is of the order of the thermal energy ($\xi \approx 1$), and that $\gamma_\perp \sim \gamma_\parallel = \gamma$. In this case the relaxation time takes the form $\tau_\parallel = (\gamma/2)/[1 + (\xi^2/10)]$.

Table 1 shows a comparison of the values of $\mu$ obtained by using different theories. The values estimated with the Debye and the Block and Hayes model 1 (BH-1), were obtained in the weak-field approximation. For the system with the largest molecular mass in the strong-field approximation, the magnitude of the dipolar moment obtained with the Block and Hayes model 2 (BH-2) is very similar to those obtained by means of a theory based on the Langevin equation (WKC) and a classical result reported by Ullman in Ref. [15]. The last column in Table 1 shows that the results obtained with our model (FP) in the non-isotropic (strong field) approximation are in good agreement with the experimental results.

4.2 Normal and $\alpha$ relaxations in type-C polymers

Highly concentrated solutions of cis-polyisoprene (cis-PI) show a dielectric relaxation that involves both normal and $\alpha$-relaxations characterized by two absorption peaks of the imaginary part of the dielectric susceptibility; see Fig. 2 and Ref. [26]. The first maximum of the dielectric loss is usually attributed to the dipolar moment aligned with the chain contour, and is associated to the normal relaxation characteristic of Type-A polymers. The second maxi-
Fig. 2. Experimental data (symbols) [26] of the dielectric loss of highly concentrated solution of cis-PI chains at 273 K as a function of frequency for different mass weights $M_w$. The average molecular mass in kg-mol$^{-1}$ are: a) 2; b) 14 and c) 32. The dotted lines correspond to the best fit obtained with Eqs. (30) and (31) under the assumption of an homogeneous system. The solid lines correspond to the best fit using Eqs. (43) and (44) for the non-homogeneous approximation where we have used dispersion relations of the form $k^2(\omega) = (\omega_0/\omega^*)^\alpha$ for the parallel and perpendicular components of the translational diffusion coefficient. Here, $\alpha \neq 1$ and $\omega^*$ is a characteristic frequency associated with the viscoelastic nature of the medium (see details in Sec. 5). The dashed lines correspond to the non-stationary and non-homogeneous approximation given by Eqs. (45) and (46).

The polarization $\vec{p}$ can be interpreted as a local degree of freedom in contact with a heat bath, and therefore its dielectric relaxation can be described by using Eqs. (30)-(36) only after assuming that the system is homogeneous (the translational diffusion of the polarization is neglected).

The comparison between experiments (symbols) and theory (lines) shown in Fig. 2 was performed by taking the total imaginary part of the susceptibility as the sum of the parallel $\chi''_\parallel(\omega_0)$ and perpendicular $\chi''_{\perp}(\omega_0)$ contributions given in (30) and (31), respectively. The low frequency maximum of $\chi''$ was used to obtain the values of $\xi$, $\chi_0$ and $\tau_\parallel$ as was done in section 4.1. Then, after determining the characteristic frequency $(\tau_{\perp}^{-1})$ at which the high frequency maximum appears, Eqs. (30) and (31) were used to fit the whole set of experimental data. From the dotted line in Fig. 2 it is clear that our model gives an
Table 2

Values of the parameters obtained with Eqs. (30) and (31) in the homogeneous approximation (see dotted lines in Fig. 2). \( \chi_0 \) and \( \xi \) are dimensionless quantities.

5 Diffusion effects in dielectric relaxation

The previous description of dielectric relaxation in \( cis \)-PI solutions can be improved by considering the effects of non-homogeneities of the dipolar and the quadrupolar moments. Therefore, it is relevant to consider the local definitions

\[
\tilde{P}(\vec{r}, t) = N \int \tilde{p}(\vec{p}, \vec{r}, t) d\vec{p}, \quad S_p(\vec{r}, t) = \frac{N^2}{2} \int (3\tilde{p}\tilde{p} - \mu^2 \mathbf{1}) f(\vec{p}, \vec{r}, t) d\vec{p},
\]

where we have assumed that the distribution function depends on the polarization vector

Similarly as in section 2, the evolution equations for \( \tilde{P}(\vec{r}, t) \) and \( S_p(\vec{r}, t) \) can be calculated by taking the time derivative of Eqs. (40), substituting (9) in the resulting expression and integrating by parts assuming the corresponding boundary conditions. The resulting diffusion equation for \( \tilde{P}(\vec{r}, t) \) is

\[
\frac{\partial \tilde{P}}{\partial t} = (\mathbb{D}_r : \nabla \nabla) \tilde{P} - \tilde{\gamma}^{-1} \cdot \left[ \tilde{P} + \frac{2}{3Nk_BT} \tilde{\gamma} \cdot \mathbb{M}(S_p) \cdot \vec{E} - \frac{N\mu^2}{3k_BT} \vec{E} \right],
\]

whereas for \( S_p(\vec{r}, t) \) the diffusion equation is

\[
\frac{\partial S_p}{\partial t} = (\mathbb{D}_r : \nabla \nabla) S_p - \frac{6}{5Nk_BT} \left[ \mathbb{M}(Q_p) \cdot \vec{E} \right]^s - 2M^s(S_p) - 2 \left( \tilde{\gamma}^{-1} \cdot S_p \right)^s
\]
The numerical values are obtained with nonlinear regression with Eqs. (43) and (44) in the non-homogeneous approximation (dashed lines in Fig. 2). $\chi_0$, $\xi$, $\alpha$ and $\beta$ are dimensionless quantities. The values of the relaxation times $\tau$ can be obtained by using Eqs. (26) and (29).

The first term on the right-hand side of equations (41) and (42) accounts for the translational diffusion, $\nabla \equiv \partial / \partial \vec{r}$ is the gradient operator and we have assumed that the interaction potential only depends on the externally applied electric field: $U = -\vec{p} \cdot \vec{E}_0$. Eqs. (41) and (42) are coupled through the term containing the tensor $\mathbb{M}(S_p)$.

The expressions for the parallel and perpendicular contributions of the dielectric susceptibility tensor can be obtained by following a procedure similar to that of Sec. 3. That is, by substituting the components of $S_p$ obtained from Eq. (42) into (41), in the quasi-stationary approximation one finds

\[
\chi_\parallel(\vec{k}, \omega_0) = \frac{\tilde{\chi}_\parallel}{1 + D_{tr\parallel} k^2 \tau_\parallel + i \omega_0 \tau_\parallel},
\]

(43)

\[
\chi_\perp(\vec{k}, \omega_0) = \frac{\tilde{\chi}_\perp}{1 + D_{tr\perp} k^2 \tau_\perp + i \omega_0 \tau_\perp}.
\]

(44)

The expressions for the relaxation times $\tau_\parallel$ and $\tau_\perp$ are given through Eqs. (26) and (29). The relation for the parallel and perpendicular components of the susceptibility $\tilde{\chi}_\parallel$ and $\tilde{\chi}_\perp$ are still given by (36).

Comparison with experiments can be performed by using the previous expressions and assuming that the parallel and perpendicular components of the diffusion tensor are of the form: $D_{tr\parallel} k^2 = (\omega_0 / \omega_\parallel)^\alpha$ and $D_{tr\perp} k^2 = (\omega_0 / \omega_\perp)^\beta$. This dependence on frequency has been suggested in the literature and is related to the viscoelastic nature of the system [27], and discussed in relation to the problem of liquid-crystal like relaxing amphiphilic systems such as lipid membrane. In these last systems, it was shown that the non-Debye relaxation manifests a memory feeling submesoscopic dynamics that may arise due to a reduced system’s dimensionality that can be accessed phenomenologically [28].

| Polymer | $\chi_0$ | $\xi$ | $\gamma_\parallel(s)$ | $\gamma_\perp(s)$ | $\alpha$ | $\beta$ | $\omega_\parallel(\text{Hz})$ | $\omega_\perp(\text{Hz})$ |
|---------|---------|-------|----------------------|------------------|---------|-------|----------------|------------------|
| PI02    | 1.48    | 2.51  | $4.10 \times 10^{-6}$ | $5.75 \times 10^{-8}$ | 1.03    | 0.65  | $2.03 \times 10^{-1}$ | $3.39 \times 10^{-6}$ |
| PI14    | 8.14    | 2.15  | $2.93 \times 10^{-4}$ | $1.00 \times 10^{-8}$ | 0.79    | 0.71  | $2.19 \times 10^{-3}$ | $3.38 \times 10^{-6}$ |
| PI32    | 3.69    | 1.87  | $9.79 \times 10^{-2}$ | $3.73 \times 10^{-8}$ | 0.80    | 0.65  | $1.10 \times 10^{-2}$ | $1.12 \times 10^{-6}$ |
In the non-stationary case, the expressions obtained for the susceptibilities are

\[ \chi_{ns}^{\parallel}(\vec{k}, \omega) = \frac{\tilde{\chi}_{ns}^{\parallel}}{1 + D_{tr} k^2 \tau_{ns}^{\parallel} - i \omega c_{ns}^{\parallel}}; \] (45)

\[ \chi_{ns}^{\perp}(\vec{k}, \omega) = \frac{\tilde{\chi}_{ns}^{\perp}}{1 + D_{tr} k^2 \tau_{ns}^{\perp} - i \omega c_{ns}^{\perp}}; \] (46)

where all the field dependent factors (\(\tau_{ns}^{\parallel}, \tau_{ns}^{\perp}, c_{\parallel}, c_{\perp}, \tilde{\chi}_{ns}^{\parallel}\) and \(\tilde{\chi}_{ns}^{\perp}\)) are given by Eqs. (33), (35) and (38).

The solid line in Fig. 2 shows the theoretical results in the non-homogeneous case. The effect of diffusion is to make the peaks broader due to the power law relation between the wave number and the frequency. They also introduce two relaxation times associated to \(\omega_{\parallel}^{-1}\) and \(\omega_{\perp}^{-1}\). Fig. 2 shows that our approach is more appropriate for describing systems made up of particles with low molecular mass, although both maxima are well described even for systems of particles having large molecular masses. Table 3 shows the values of the parameters obtained in the present approximation after using a nonlinear regression of Eqs. (43) and (44) to the experimental data. Calculations in progress indicate that the description offered here could be improved by incorporating the effects of mass dispersion.

The results obtained in this section suggest that the coupled relaxation equations for the dipolar \(\vec{P}\) and quadrupolar \(S_p\) fields constitute a minimal model to describe the dielectric relaxation of solutions of Type-C polymers.

6 Conclusions

We have formulated a mesoscopic model describing the dynamics of systems characterized by an axial degree of freedom in contact with a heat bath. The description of the dynamics of this degree of freedom is performed by means of a Fokker-Planck equation for the nonequilibrium probability distribution function. The equation, derived by calculating the mesoscopic entropy production, allows one to formulate a nonequilibrium description of the system in terms of relaxation equations for the multipoles, related to the moments of the distribution function.

Applications of the theory to describe dielectric relaxation in homogeneous and non-homogeneous systems in different approximations allowed us to compare with previous theories and better elucidate the new contributions of our model. In the case of dilute polymer suspensions, we found that our theory accounts for the dependence of the relaxation time on the strong applied electrical field.
and gives values for the dipolar moment of the particles which agree with previous ones.

We used our model to describe the normal and $\alpha$ relaxations in Type-C polymer solutions. Our results clearly show that, in order to correctly account for the amplitude of the second maximum of the dielectric loss (associated to the $\alpha$ relaxation), the minimal model has to take into account the coupled diffusion equations for the dipolar and quadrupolar fields. The anisotropic diffusion of these quantities introduces new characteristic times leading to a better description of the experiments. In particular, we found that our theory is very useful in describing dielectric relaxation of solutions of molecules having low molecular masses.

The general model describing the dynamics of systems characterized by axial degrees of freedom presented here can be generalized and applied to other systems such as suspensions of rod-like particles or liquid crystals through an adequate choice of the interaction energy. This will be done in future work.

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