

Polarization-diffusion effect on the dispersion of N- and α -dielectric relaxation modes

S.I. Hernández, L.F. del Castillo*

Departamento de Polímeros, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, Coyoacán 04510, México D.F., Mexico

Received 11 October 2006; received in revised form 6 November 2006

Available online 4 December 2006

Abstract

In this paper, the contribution of polarization diffusion on the dispersion of the electric susceptibility in polymeric materials, that exhibits normal (N-) relaxation at low frequencies and segmental or alpha (α -) relaxation at high frequencies, is studied. Polarization diffusion is locally established when the viscoelastic relaxation couples to the relaxation of a dipolar system. In order to formulate this diffusion process, it was proposed a physical description based on a system of two coupled equations to express the viscoelastic and dielectric relaxations, and the coupling between them is introduced by considering spatial inhomogeneities. The complex polarization-diffusion coefficient and the wave number as frequency function are obtained considering two parameters, which were evaluated using a diffusive model for the N- and α -dielectric modes, respectively, for several polymeric systems.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Polarization diffusion; Normal relaxation; Alpha relaxation; Polymers

0. Introduction

In order to explain and figure out the results obtained using dielectric spectroscopy, the Debye theory of dielectric relaxation has been successful [1–4]. However, it is limited in the attempt to describe the total frequency spectrum, as it has been pointed out by many authors [5–8]. Therefore, the problem has been how to modify this theory to involve molecular-dipolar liberation from microscopic formalism [9,10], as well as macroscopic one. In this paper it is considered the latter point of view, and particularly the coupling between the polarization evolution and the local stress relaxation as it was treated by Onsager et al. and Hubbard et al. [11–14]. The main assumption to this approach consists on the validity of superposition of the Maxwell tensor and the viscous-stress tensor in a locality of a material, and therefore, the momentum balance equation of the hydrodynamics was modified in order to include this sum [15,16]. This gives us a generalized Debye's relaxation equation where the polarization relaxation is a result of two channels in series. One of them is the rotational diffusion as presented by Debye, and the other is the polarization diffusion, which describes a polarization transport produced when dipole particles move from one point to another.

*Corresponding author. Tel.: + 52 5622 4723; fax: + 52 5616 1201.

E-mail address: lfelipe@servidor.unam.mx (L.F. del Castillo).

In this paper, the polarization diffusion effect is formulated as a coupling between stress relaxation and the excess polarization decaying. This kind of coupling effect was reported before as the flexoelectric contribution by de Gennes [17], and now this flexoelectric effect can be described in terms of the inclusion of the polarization inhomogeneities, which are induced by the action of the total stress tensor given by the superposition of local stresses of the material and the Maxwell stress tensor. With this aim in mind, a set of two partial differential equations are proposed, one being the Debye equation, and the other one the Oldroyd's type-mechanical-relaxation equation. Both equations have been modified in order to couple each other by introducing spatial inhomogeneities [18] in the polarization. These sort of couplings have been previously identified elsewhere [19–21]. In order to improve the formulation of the coupling terms, a hierarchy of coupling equations of internal variables, which represent different contribution produced by the spatial inhomogeneities, was proposed. This way, it was obtained a model with two parameters, which are the polarization-diffusion coefficient and the characteristic length. We report those values for several polymeric samples with the N- and α -dielectric bands, reported previously by other authors (see Refs. [22,23]). Applying this model, the characteristic time of the polarization diffusion, the complex polarization-diffusion coefficient and the dispersion relation $k = k(\omega)$ for those substances, were obtained.

Finally, a discussion about the difference of the characteristics of the wave number between N- and α -dielectric bands was also included.

1. The polarization-diffusion coupling and the generalized Debye equation

Debye's relaxation equation describes the relaxation of orientational polarization per unit of volume (\vec{P}), produced when an external electric field (\vec{E}) is applied to the material sample. In this theory, it is considered that the mechanical equilibrium prevails, without the presence of any acceleration effect, in such a way that the electric torque produced by the electric field on the dipole particle is equilibrated by the friction produced by the rotational movement of the dipole particle on surrounding particles. The evolution of the polarization is not instantaneous, and a delay response is accounted into the characteristic relaxation time (τ_D). Debye's result is given by the equation

$$\left(\frac{d\vec{P}}{dt}\right)_{rot} = -\frac{1}{\tau_D}(\vec{P} - \chi_0\vec{E}), \quad (1)$$

where χ_0 is the static electric susceptibility.

To generalize this result, the translational contribution is considered as a long-range effect. The first contribution along this line was done by Onsager and Hubbard [12], who extended the momentum balance equation to include the superposition of the electromagnetic Maxwell tensor and the local stress tensor. In that sense, the net force acting on a fluid particle is due to this superposition, and a coupling effect is produced in the resulting velocity.

In terms of Stiles and Hubbard [24,25] the translational diffusion is independent of the rotational one, and it can be written in separated form

$$\frac{d\vec{P}}{dt} = \left(\frac{d\vec{P}}{dt}\right)_{rot} + \left(\frac{d\vec{P}}{dt}\right)_{tran}, \quad (2)$$

where

$$\left(\frac{d\vec{P}}{dt}\right)_{tran} = -\nabla \cdot \mathbf{J}, \quad (3)$$

and \mathbf{J} is the polarization flux tensor, which can be established by three different parts: the symmetric traceless, the antisymmetric, and the diagonal tensorial contributions, namely

$$J_{\alpha\beta} = \left(D^l - \frac{2}{3}D^s\right) \frac{dP_\alpha}{dx_\beta} \delta_{\alpha\beta} + D^s \left[\frac{dP_\beta}{dx_\alpha} + \frac{dP_\alpha}{dx_\beta}\right] + D^a \left[\frac{dP_\beta}{dx_\alpha} - \frac{dP_\alpha}{dx_\beta}\right], \quad (4)$$

where D^s , D^a and D^l are diffusion coefficients.

In Hubbard and Stiles and van der Zwan [26,27], these tensors represent the hydrodynamic coupling, produced by the hydrodynamic flow evolution affecting the dipolar movement.

In dielectric relaxation, each of these terms make independent contribution to the total diffusion process and they are different kinds of polarization diffusion according to the symmetric character. The first one (D^s), corresponds to the translational diffusion and it is due to the coupling to the symmetric stress tensor, which is related to the N-relaxation mode present in type-A polymers, following Stockmayer's classification [28]. The second one (D^a), corresponds to the axial coupling with the antisymmetric stress tensor and it produces polarization propagation involved in the α -dielectric relaxation mode, present in type-B polymer, following Stockmayer's classification. The third one is the charge polarization diffusion related to longitudinal relaxation mode, which contributes far away from the dielectric relaxation frequency domain, and for this reason it will not be considered here.

Here, it is presented a description in which Eq. (2) keeps valid, according to Hubbard and Stiles formulation, as discussed elsewhere [29]. Furthermore, concerning to the polarization flux in dielectric relaxation for solid or static liquids, the coupling between local polarization and local stress-strain occurs similarly to the flexoelectric effect, named by de Gennes [17].

2. Formulation of the polarization-diffusion coupling in the generalized-fluctuating Debye equation

As well as to show an expression for dielectric susceptibility, the aim of this section is to obtain a complete set of constitutive equations corresponding to the evolution of the fluctuation of the polarization vector, given by the generalized-fluctuating Debye equation, and the evolution of the fluctuation of the stress tensor (whereas symmetric and antisymmetric) in viscoelastic Oldroyd's form, with a coupling term which expresses the polarization gradient as traceless tensor. The evolution equation for the fluctuation of the polarization is given by

$$\tau_D \frac{d\delta\vec{P}}{dt} = -\delta\vec{P} - \chi_0 \nabla \delta\phi + \alpha_0 \nabla \cdot \delta\mathbf{Q}, \quad (5)$$

where $\delta\phi(\vec{r}, t)$ is the fluctuation of the local electric potential, $\delta\vec{P}$ is the fluctuation of the polarization vector and α_0 is a coupling parameter. $\delta\mathbf{Q}$ is the fluctuation of the total stress tensor and represents the superposition of the viscous ($\delta\tau^v$) and electromagnetic ($\delta\mathbf{T}$) stress tensors, namely

$$\delta\mathbf{Q} = \delta\tau^v - \delta\mathbf{T}. \quad (6)$$

The $\delta\mathbf{Q}$ value is a fluctuating quantity during the relaxation process, since the $\delta\tau^v$ tensor also is time dependent. The evolution equation for $\delta\mathbf{Q}$ is assumed to be of Oldroyd's form, given by

$$\left(1 + \tau_1 \frac{d}{dt}\right) \delta\mathbf{Q} = \alpha_1 \nabla \cdot \delta\mathbf{Q}^{(2)} + \gamma_1 \nabla \delta\vec{P}, \quad (7)$$

here α_1 and γ_1 are coupling parameters, $\delta\mathbf{Q}^{(2)}$ is a third-order tensor, and τ_1 is a relaxation time.

In those equations, the response of the material to the external and internal stresses is represented. On the other hand, the evolution of this tensor is governed by the gradient of the fluctuation of the polarization and the contributions of tensors of high order, to consider all the effects induced by the spatial inhomogeneities. The proposed evolution equation for $\delta\mathbf{Q}^{(n)}$ defines a hierarchy of equations according to

$$\left(1 + \tau_n \frac{d}{dt}\right) \delta\mathbf{Q}^{(n)} = \alpha_n \nabla \cdot \delta\mathbf{Q}^{(n+1)} + \gamma_n \nabla \delta\mathbf{Q}^{(n-1)}, \quad n = 2, 3, \dots \quad (8)$$

Here $\delta\mathbf{Q}^{(n)}$ is a traceless tensor of $n + 1$ order. Diagonal or longitudinal components are not included, since they represent the polarization diffusion produced by the polarization charges, which contributes to the high frequency spectrum far from the frequency interval of the α - and N-dielectric relaxation modes. Therefore, the longitudinal relaxation mode will not be considered in the present work, and we will only treat the diffusion in the transversal N- and α -relaxation modes.

All the $\delta\mathbf{Q}^{(n)}$ ($n = 2, 3, \dots$) define a set of variables considered as internal in the irreversible thermodynamical formalism (including the extended and the mesoscopic theories [30,31]), which are

convenient to introduce to take into account local electrical effects that cannot be formulated directly within the external variable or measurement ones [32]. One of the thermodynamical schemes back of this formalism has been discussed in terms of a hierarchy of variables in Jou et al. work [30], and with a coupled hierarchy of hydrodynamic equations [33]. They found that the inclusion of higher order time derivatives was necessary to describe high frequency processes, and spatial derivatives are necessary to describe processes at short length.

Now, taking the Fourier–Laplace transformation of Eqs. (5)–(8) and using the relation for the transformed fluctuating-polarization vector

$$\delta\tilde{P}(\omega, k) = -ik \cdot \chi(\omega, k) \delta\tilde{\phi}(\omega, k), \quad (9)$$

where $\chi(\omega, k)$ is the susceptibility tensor, it is found that

$$\chi(\omega, k) = \frac{\chi_0}{1 + i\omega\tau_D + \alpha_0\gamma_1 k^2 / (1 + i\omega\tau_1 + H_n(\omega, k))}. \quad (10)$$

Here $H_n(\omega, k)$ is defined in the following form:

$$H_n(\omega, k) = \frac{l_n^2 k^2}{1 + i\omega\tau_2 + l_2^2 k^2 / (1 + i\omega\tau_3 + \dots)}, \quad (11)$$

where the relationship $l_n = \alpha_n \gamma_{n+1}$ was used for $n = 2, 3, \dots$.

It is noted that electric susceptibility expressed by Eq. (10) fulfills the limit for each tensorial component $\chi(\omega, k) = \chi_0$ when ω and $k \rightarrow 0$.

Now, it is considered the following scheme. It is defined $H_n(\omega, k) = \chi_n(\omega, k) / \chi_0$, where $\chi_n(\omega, k)$ is the n th order function, which approximate to $\chi(\omega, k)$ in the asymptotic limit. Then it is found that

$$\Rightarrow H_\infty(\omega, k) = \frac{l_c^2 k^2}{1 + i\omega\tau_1 + H_\infty(\omega, k)},$$

where l_c is interpreted as the characteristic length.

The solution of $H_\infty(\omega, k)$ is given by

$$H_{\infty(1,2)} = \frac{-(1 + i\omega\tau_1) \pm \sqrt{(1 + i\omega\tau_1)^2 + 4l_c^2 k^2}}{2}, \quad (12)$$

here, it is taken the positive sign before the square root, since $H_\infty(\omega, k) \geq 0$ and $H_\infty(\omega, k) = 0$ is obtained if $l_c = 0$.

3. The complex polarization-diffusion coefficient

Identification of the diffusion coefficient can be done in the following way. Consider $\alpha_1 = 0$ into Eq. (7), and then replace this result into Eq. (5). This gives the Debye's equation with a Laplace operator and their coefficient is identified as $D_0 = \alpha_0 \gamma_1 \tau_D^{-1}$. When $\alpha_1 \neq 0$, other terms appear, making the diffusion coefficient a frequency and wave number dependent function.

On the other hand, the electric susceptibility is a diagonal tensor with two independent components, namely the longitudinal and the transversal. For the normal mode (symmetric one), the polarization diffusion contribution appears in the two components, and for the α -relaxation mode (antisymmetric one) appears only the transversal component. However, due to the way in which dielectric-relaxation experiment is usually done, only the transversal component is necessary to take into account. Therefore,

$$\frac{\chi_T(\omega, k)}{\chi_0} = \frac{1}{1 + i\omega\tau_D + \tau_D D^*(\omega, k) k^2}, \quad (13)$$

where the complex polarization-diffusion coefficient is defined by

$$D^*(\omega, k) = D' - iD'' = \frac{2D_0}{1 + i\omega\tau_1 + \sqrt{(1 + i\omega\tau_1)^2 + 4l_c^2 k^2}}. \quad (14)$$

In this result, the selection of the positive sign before the square root is corroborated, because the negative sign leads diffusion coefficient to a divergence for the low wave-number limit.

The physical meaning of the complex polarization-diffusion coefficient is as follows. The real part is the frequency-dependent-diffusion coefficient involved in the local polarization transport in the material. It was assumed that the origin of this process is due to density fluctuations, which produce local spatial inhomogeneities in the dipole distribution that induces polarization diffusion. The regression of the fluctuations occurs via the translational diffusion of the dipolar molecules to relax the spatial inhomogeneities, including those of the local polarization field. On the other hand, the imaginary part represents the dissipative property involved in the polarization-diffusion process.

4. Evaluation of the polarization-diffusion coefficient and the characteristic length

Up to this point, it is necessary to stress that the dielectric relaxation description given before is a two free parameter model, namely D_0 and l_c . Next, we carry on with their identification and their evaluation.

As Hubbard and Stiles pointed out, the polarization-diffusion coefficient at $\omega = 0$, might be considered equal to the self-diffusion coefficient [34].

For the N-relaxation mode, in the case of linear polymers, the diffusion coefficient is proportional to the square of the end to end distance (λ_0), and inversely proportional to the Rouse or reptational time [35],

$$D_0 = \frac{\lambda_0^2}{\tau_1}. \quad (15)$$

It should be noted that for the normal mode the characteristic time τ_1 for mechanical response is equal to τ_D .

The diffusion coefficient D_0 is a molecular weight (M_w) dependent quantity, and it scales like

$$D_0 = C(M_w)^{-(m-1)}, \quad (16)$$

where m is the scaling power of the molecular weight in the relationship for the characteristic time and C is a proportionality constant.

For the α -relaxation mode, in the case of any glass forming system, this coefficient is proportional to the square of the mean value of the spatial inhomogeneities, l_c , and inversely proportional to the Debye relaxation time [36],

$$D_0 = \frac{l_c^2}{\tau_D}. \quad (17)$$

The characteristic length is estimated considering the minimum separation between molecular planes in the amorphous state. The characteristic length data for the molecule's polymer by X-ray is given by $l_c \approx 5 \text{ \AA}$ [37]. For concentrated polymeric solutions, it was assumed $l_c \approx 15 \text{ \AA}$, according to the cooperative rearranging region of the mechanical relaxation mechanism.

The values of τ_1 were calculated using the $\tau_1 = 1.8\tau_D$ relation, which gives a representative number in order to obtain consistent results, as it is stated in the next section. It was assumed that the ratio between mechanical and dielectric times keeps constant for amorphous polymers, because alpha loss peak is shifted to higher frequencies less than a decade, in the shear mechanical spectrum compared to the dielectric spectrum at the log–log plot [38,39].

The D_0 and l_c obtained values for the N- as well as for α -dielectric modes, for *cis*-polyisoprene (PI) [22], and for poly(2, 6-dichloro-1, 4-phenylene oxide) (PDCPO) in chlorobenzene [23], are given in Tables 1 and 2.

5. Calculation of the dispersion relation

From the complex dielectric constant experimental data, and using Eq. (13), it was calculated the complex polarization diffusion coefficient times squared wave vector, by using the following algorithm, which

Table 1

Parameters of the model for N-relaxation mode for *cis*-polyisoprene (PI) [22], and for poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO) in chlorobenzene [23]

Polymer code	$10^{-3} M_w$	τ_D (s)	D_0 (cm ² /s)	l_c (cm)
PI-02	1.56	3.10×10^{-6}	3.63×10^{-8}	3.36×10^{-7}
PI-03	2.64	1.91×10^{-5}	9.98×10^{-9}	4.37×10^{-7}
PI-05	4.84	1.83×10^{-4}	1.92×10^{-9}	5.92×10^{-7}
PI-14	13.50	1.05×10^{-3}	9.30×10^{-10}	9.90×10^{-7}
PI-32	31.6	2.15×10^{-2}	1.07×10^{-10}	1.51×10^{-6}
PI-53	52.9	2.70×10^{-1}	1.42×10^{-11}	1.96×10^{-6}
PDCPO 21.5%	380	4.00×10^{-4}	6.89×10^{-8}	5.25×10^{-6}
PDCPO 31.2%	380	1.95×10^{-4}	1.41×10^{-7}	5.25×10^{-6}

Table 2

Parameters of the model for α -relaxation mode in *cis*-polyisoprene (PI) [22], and poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO) in chlorobenzene [23]

Polymer code	$10^{-3} M_w$	τ_D (s)	D_0 (cm ² /s)
PI-02	1.56	1.18×10^{-8}	2.12×10^{-7}
PI-03	2.64	1.87×10^{-8}	1.34×10^{-7}
PI-05	4.84	2.35×10^{-8}	1.06×10^{-7}
PI-14	13.50	3.03×10^{-8}	8.24×10^{-8}
PI-32	31.6	3.33×10^{-8}	7.52×10^{-8}
PI-53	52.9	2.64×10^{-8}	9.46×10^{-8}
PDCPO 21.5%	380	1.54×10^{-7}	1.46×10^{-7}
PDCPO 31.2%	380	1.51×10^{-6}	1.49×10^{-8}

Here $l_c = 5.00 \times 10^{-8}$ cm for PI, and $l_c = 15.00 \times 10^{-8}$ cm for PDCPO.

constitutes a novel way to show dielectric-relaxation data:

$$[D^*(\omega)k^2]_{\text{exp}} = \frac{R'}{\tau_D[(R')^2 + (R'')^2]} - \frac{1}{\tau_D} + i \left\{ \frac{R''}{\tau_D(R')^2 + \tau_D(R'')^2} - \omega \right\}, \quad (18)$$

where

$$R^*(\omega) = R'(\omega) - iR''(\omega) = \frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{\chi_T^*(\omega)}{\chi_0}. \quad (19)$$

The $[D^*(\omega)k^2]_{\text{exp}}$ behavior for *cis*-polyisoprene is shown in Figs. 1 and 2, for N- and α -relaxation modes, respectively. On the other hand, the inverse of this quantity is the polarization-diffusion time. It can be selected, as a characteristic value of this time, the value on the plot in which the slop changes. It should be noted that this time is bigger than τ_D . It might reflect the required time for the long-range evolution in the polarization-diffusion process (see $\tau_{\text{diffusive}}$ in Tables 3 and 4). Particularly, for the N-relaxation mode, diffusion time is one order of magnitude larger than the rotational one.

The dispersion relation $k = k(\omega)$ as a complex number is obtained considering Eq. (14). To this end, the values of the experimental data given by $[D^*(\omega)k^2]_{\text{exp}}$ and the corresponding theoretical expression are made the same, i.e.,

$$[D^*(\omega)k^2]_{\text{exp}} = \frac{2D_0k^2(\omega)}{1 + i\omega\tau_1 + \sqrt{(1 + i\omega\tau_1)^2 + 4l_c^2k^2(\omega)}}, \quad (20)$$

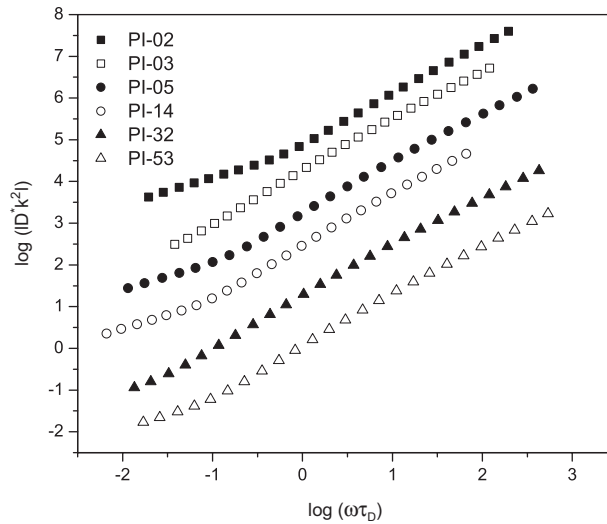


Fig. 1. The logarithm of the absolute value of $[D^*(\omega)k^2]_{\text{exp}}$ from experimental data, is plotted against logarithm of the product frequency times τ_D , for the N-relaxation mode in *cis*-polyisoprene. The code number indicates the weight average molecular weight in kg mol^{-1} .

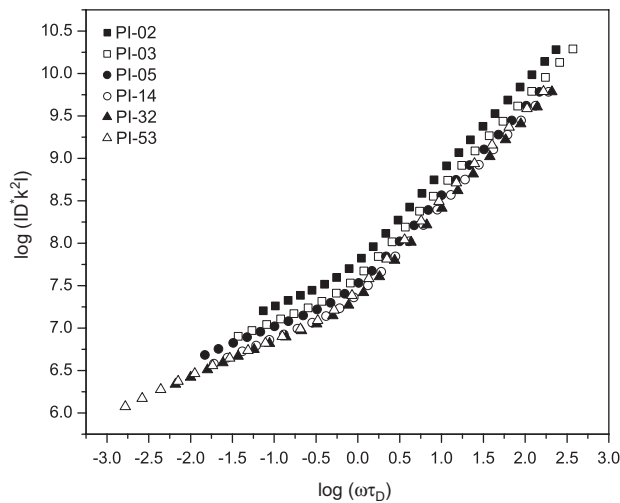


Fig. 2. The logarithm of the absolute value of $[D^*(\omega)k^2]_{\text{exp}}$ from experimental data, is plotted against logarithm of the product frequency times τ_D , for α -mode in *cis*-polyisoprene. The code number indicates the weight average molecular weight in kg mol^{-1} .

where all the quantities involved are known, except for $k = k(\omega)$, which represents a complex and implicit expression, as it can be seen by the fact that k^2 is in the numerator, and also in the square root term of Eq. (20). So, it is necessary to proceed using numerical evaluation for each frequency in order to obtain a numerical representation of the complex function $k^2(\omega) = \text{Re}\{k^2\} + i \text{Im}\{k^2\}$.

Now, considering the real part of the dispersion relation, it can be expressed according to the following form:

$$\text{Re}\{k^2(\omega)\} = A\omega^{2r}, \tag{21}$$

where A and r are quantities obtained by fitting the result of $\text{Re}\{k\} = k(\omega)$ from Eq. (20). Usually $r = 1$ is related to the propagation of mechanical waves in a medium. On the other hand, from the theoretical point of view, the solutions $k = k(\omega)$, of a closed differential-equations system, given in the generalized hydrodynamic formalism, have $r = 1$ as a particular case.

Table 3
Characteristic times for N-relaxation mode in *cis*-polyisoprene

Polymer code	τ_D (s)	$\tau_{diffusive}$ (s)	$\tau_{dissipative}$ (s)
PI-02	3.10×10^{-6}	4.60×10^{-6}	2.91×10^{-6}
PI-03	1.91×10^{-5}	2.43×10^{-4}	1.40×10^{-5}
PI-05	1.83×10^{-4}	1.42×10^{-3}	1.43×10^{-4}
PI-14	1.05×10^{-3}	1.19×10^{-2}	8.69×10^{-3}
PI-32	2.15×10^{-2}	5.54×10^{-1}	1.59×10^{-2}
PI-53	2.70×10^{-1}	2.77	2.18×10^{-1}

Table 4
Characteristic times for α -relaxation mode in *cis*-polyisoprene

Polymer code	$10^8 \tau_D$ (s)	$10^8 \tau_{diffusive}$ (s)	$10^8 \tau_{dissipative}$ (s)
PI-02	1.18	1.50	1.63
PI-03	1.87	2.48	2.34
PI-05	2.35	2.82	2.91
PI-14	3.03	3.51	3.85
PI-32	3.33	3.75	4.08
PI-53	2.64	3.94	2.98

It was found that, for N-relaxation mode in PI, $r = 0.93$, and in PDCPO $r = 0.64$. Instead, for α -relaxation mode, $r = 1$ in both PI and PDCPO samples.

The results for the dispersion relation according to Eq. (21) are shown in Figs. 3 and 4. In these plots, it is represented the logarithm of the real part of the product $l_c^2 k^2$ versus the logarithm of the product $\omega \tau_D$. It should be noted that, in each figure there is only one curve, and it represents a superposition of several data in a master curve. This means that the product $l_c^2 k^2$ is a constant for any frequency, independently of the properties of the sample and it is a characteristic of Eq. (20).

Also, in Figs. 3 and 4 a transition frequency is defined as $\omega_D = \tau_D^{-1}$ which separates two regions. The high-frequency wing ($\omega > \omega_D$) and the low-frequency wing ($\omega < \omega_D$).

For the α -mode (Fig. 4), in the high-frequency region it has $r = 1$, which could implied the propagation of the mechanical perturbation in the material with the v velocity. The nature of this wave phenomenon can be analyzed considering the evolution equation for the stress–stress correlation. This equation defines the propagation of the stress self-correlations, according to the velocity expression given in Eq. (25) in the Appendix. Since this relation comes from stress-evolution equation, the nature of this propagation effect does not have an electromagnetic origin, but a mechanical one. This fact is consistent with the two following points of the present development, i.e.:

- From the electromagnetic point of view there is no wave in the material, since there is no retardation effect in the propagation of electromagnetic perturbation, due to that the wave velocity inside of the material can be considered infinite (electrostatic limit).
- The diffusion-polarization coefficient as defined in Eq. (14) considers a characteristic length associated to an arrangement of the medium, induced by the behavior of the local stress. The propagation of these fluctuations is a result of the elastic properties of the medium, and it does not come from the diffusive mechanism.

Therefore, considering the propagation of the fluctuations as a mechanical effect and the dispersion relation of k , proportional to the angular frequency, then v might be identified as the sound velocity, and this phenomenon might be properly identified as a Fisher-like mode [40,41]. This effect might be considered as an electroacoustic one.

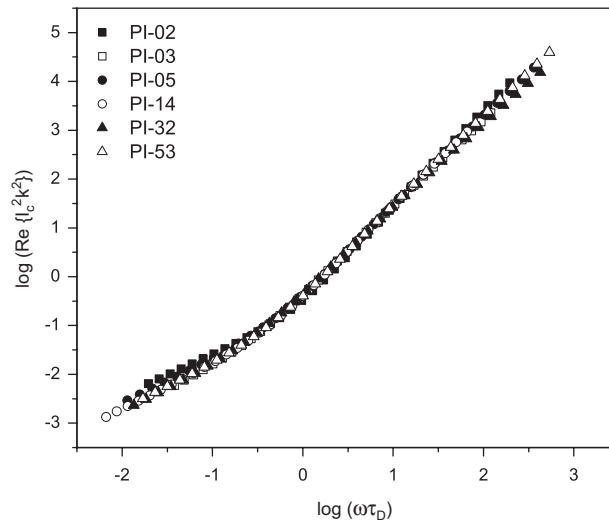


Fig. 3. A master curve is shown when the logarithm of the real part of the product $l_c^2 k^2$ is plotted against logarithm of the product frequency times τ_D , for the N-relaxation mode in *cis*-polyisoprene. It was obtained from the numerical evaluation indicated in Eq. (20).

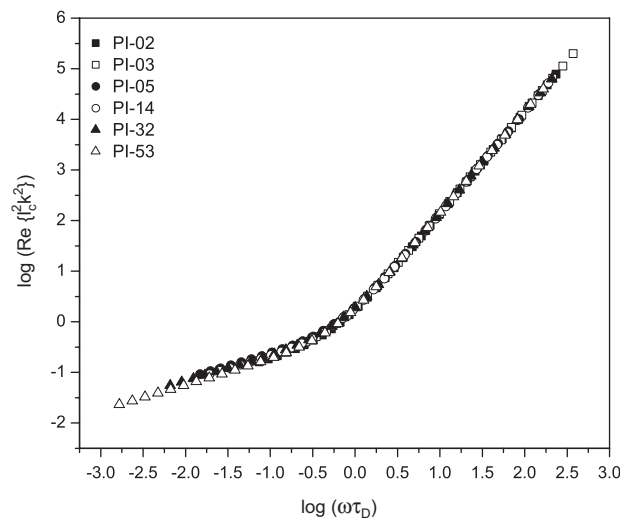


Fig. 4. A master curve is shown when the logarithm of the real part of the product $l_c^2 k^2$ is plotted against logarithm of the product frequency times τ_D , for the α -relaxation mode in *cis*-polyisoprene. It was obtained from the numerical evaluation indicated in Eq. (20).

On the other hand, in the low-frequency wing for the α -mode ($\omega < \omega_D$) in Fig. 4 this effect is not present since r starts from zero and, near the transition frequency, ω_D , changes rapidly to one. This region seems as a transition to the Fisher-like mode.

The N-relaxation mode (Fig. 3) in the low-frequency wing, shows identical behavior, and it could imply that no propagation of the mechanical perturbations is present in this region.

For the high-frequency wing ($\omega > \omega_D$) in Fig. 3 for N-relaxation mode, the resulting dispersion relation is a fractional-power exponent and the interpretation is not so direct as in the α -case. Consequently, the velocity of propagation of the fluctuations is not defined. This case could be interpreted as one of non-propagative fluctuations, perhaps related to the sublinear character of the diffusion on the normal mode, as it can be seen in Eq. (16) with $n \geq 3$.

Regarding to the value of the sound velocity in the α -relaxation mode, that is defined by the value of A on Eq. (21) when $r = 1$. Comparing this result with that obtained using Eq. (25) of the Appendix, there is a difference of at most 20%. This difference is not so bad when considering internal consistence in the prediction of the two-parameter model. Also, this point is consistent with the resulting values of the wave number given by Sills et al. [42], who states that long-range processes—the Fischer modes—may couple with α -relaxation, producing energy dissipation in domains of tens of nanometers.

Finally, from the mathematical point of view, k^2 cannot be a complex number, consequently the imaginary part of this number is a meaningless quantity. However, making a restriction for the τ_1 values between the range $1.4 \leq \tau_1/\tau_D \leq 2.2$ and admitting 6% deviation error in solving Eq. (21), we can obtain a solution for k^2 real.

6. Calculation of the complex polarization-diffusion coefficient

Up to this point, it is known the dispersion relation $k^2(\omega)$, the diffusion coefficient D_0 and the characteristic length l_c . Therefore, it can be used Eq. (14) to obtain the real and the imaginary parts of the complex polarization-diffusion coefficient. The real and the imaginary parts are plotted in Figs. 5 and 7 for N-relaxation mode. Similarly, the real and the imaginary parts are plotted in Figs. 6 and 8 for α -relaxation mode. These figures show the general characteristic of the real and the imaginary parts of an electric or viscoelastic modulus. The real part starts with a plateau and the change of the slop or transition, coincides with the maximum of the imaginary part. This property is verified for the N- as well as the α -relaxation mode.

Particularly, in Figs. 5–8 the experimental and theoretical data are given by means of the symbol points and the continuous lines, respectively. The values of $[D'(\omega)]_{\text{exp}}$ and $[D''(\omega)]_{\text{exp}}$ are given considering them as experimental data. Their definition was estimated using the following relations:

$$[D^*(\omega)k^2]_{\text{exp}} = [D^*(\omega)]_{\text{exp}}k^2,$$

$$[D^*(\omega)]_{\text{exp}} = [D'(\omega)]_{\text{exp}} - i[D''(\omega)]_{\text{exp}}.$$

The theoretical results were obtained using Eq. (14), which expresses the two parameter model. The correspondence between them is apparent.

On the other hand, in Figs. 5–8 dashed lines are included to represent the theoretical cases for $l_c = 0$. The difference between the dashed and continuous lines shows that the dispersion effect observed in the

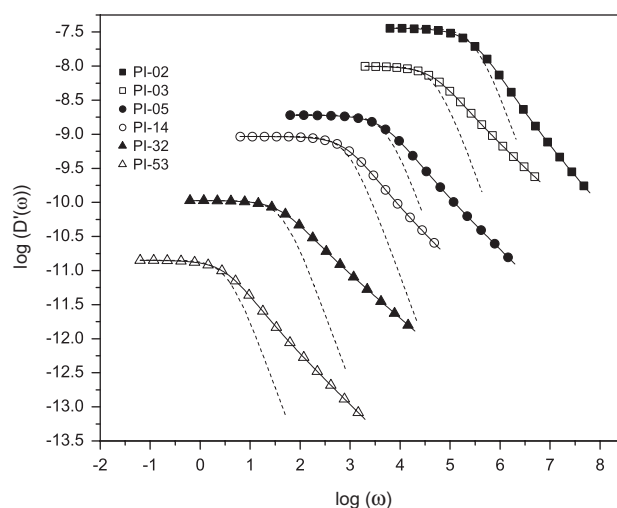


Fig. 5. Real part of the complex polarization-diffusion coefficient for N-relaxation mode in *cis*-polyisoprene. The separation of the curves denotes the variation of the molecular weight of different samples. Experimental data (symbols) are compared with theoretical model, Eq. (14) (continuous line), and with theoretical model considering $l_c = 0$ (dashed line).

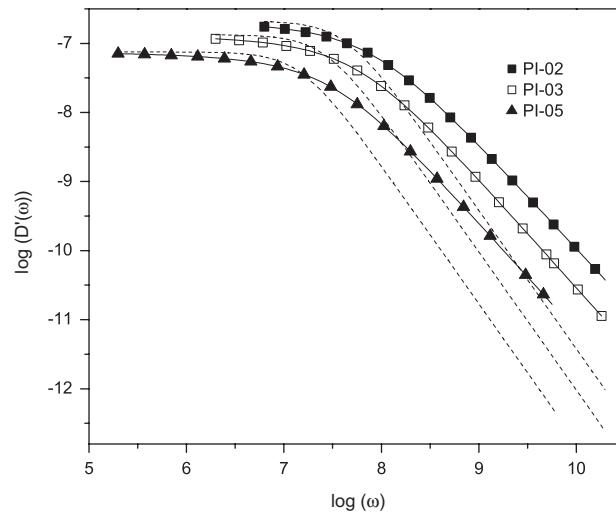


Fig. 6. Real part of the complex polarization-diffusion coefficient for α -relaxation mode in *cis*-polyisoprene. Experimental data (symbols) are compared with theoretical model, Eq. (14) (continuous line), and with theoretical model considering $l_c = 0$ (dashed line).

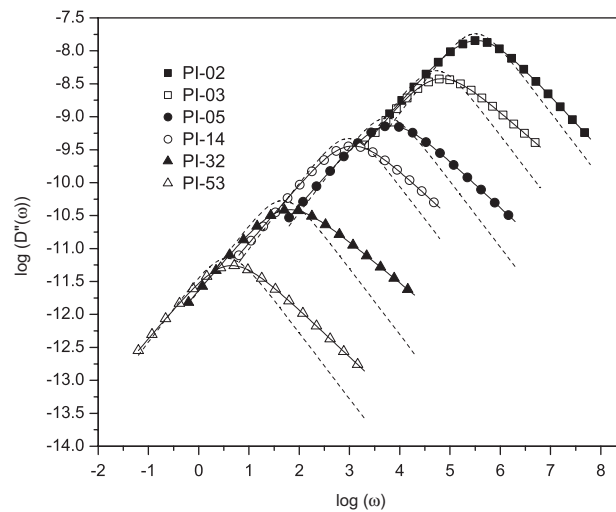


Fig. 7. Imaginary part of the complex polarization-diffusion coefficient for N-relaxation mode in *cis*-polyisoprene. The separation of the curves denotes the variation of the molecular weight of different samples. Experimental data (symbols) are compared with theoretical model, Eq. (14) (continuous line), and with theoretical model considering $l_c = 0$ (dashed line).

experimental electric susceptibility is originated from the viscoelastic coupling, which determines the polarization diffusion.

The dependence on the molecular weight of the real and imaginary parts of the polarization diffusion appears in the N-mode, which acts as a parameter separating the curves.

In the α -relaxation mode the separation of the curves is due to the chemical structure which influences the polarization diffusion.

Also in Tables 3 and 4, the characteristic time for the polarization-diffusion modulus ($\tau_{dissipative}$) is given. It represents the position of the maximum of the imaginary part of polarization-diffusion coefficient, such as for N- as well as for α -relaxation modes.

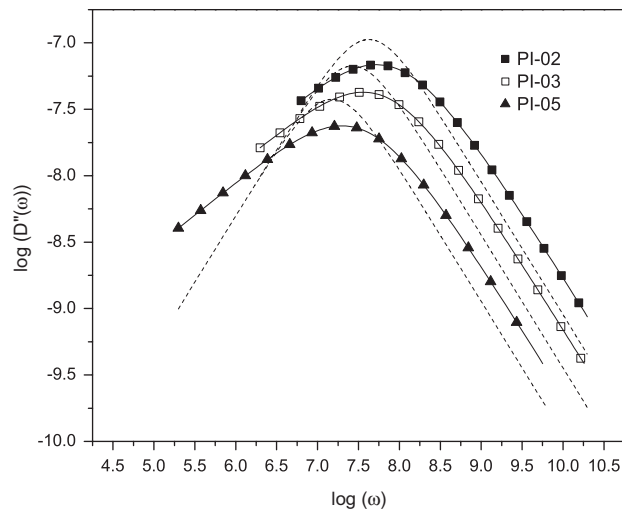


Fig. 8. Imaginary part of the complex polarization-diffusion coefficient for α -relaxation mode in *cis*-polyisoprene. Experimental data (symbols) are compared with theoretical model, Eq. (14) (continuous line), and with theoretical model considering $l_c = 0$ (dashed line).

7. Discussion

Polarization-diffusion contribution into the N- and α -dielectric relaxation modes, arose by considering the coupling between the polarization relaxation and the stress relaxation of the material. The diffusion contribution in the polarization dynamics has been proposed as a long-range interaction mechanism, which is an additional contribution to the Debye relaxation, accounted for the short-range mechanism. This effect was formulated considering a hierarchy of high order tensorial differential equations, coupled to the polarization differential equation. The hierarchy takes into account all the contributions of the spatial inhomogeneities, which modify the effect of the stress tensor on the polarization dynamics. The resulting theory from the two-coupled equations leads to an explicit $\chi_T(\omega, k)$ form, in terms of two unknown parameters which are given by D_0 and l_c . A diffusional model was considered in order to obtain the values of these parameters. Therefore, a diffusion-polarization-two-parameter model was proposed, which is consistent with the measurement of the complex-dielectric constant.

It should be noted the role played by the parameter l_c . It represents the effect of the hierarchy introduced to account the spatial inhomogeneities, which ultimately determined the dispersion effect in the electric susceptibility.

The other result presented here is the wave number as frequency function, which was obtained by comparison between the model and the experimental data. Considering this two-parameter model for the case of α -relaxation mode, we find that the Fischer-type relation might be associated to the propagation of fluctuations. However, for the N-mode relaxation, such conclusion was not reach.

So far within the approximation we settled, the two-parameter model for polarization diffusion gives us a proper physical description basis for the understanding of the electric susceptibility.

Acknowledgments

This work was supported by the CONACYT under Grant SEP-2004-C01-47070 and by DGAPA-UNAM under Grant IN-119606, S.I.H. acknowledges the support of the CONACYT under Grant 43596-F and by DGAPA-UNAM under Grant IN-110103. We thank María Teresa Vázquez Mejía, Sara Jiménez Cortés and Raúl Reyes Ortíz.

Appendix

It was consider that the polarization-diffusion phenomenon is a result of a coupling between the polarization equation and the viscoelastic ones, which represents a mechanical evolution of the stress tensor in

the material. When the polarization vector is replaced into the equation for the stress tensor then propagation of the fluctuation is produced, and from it we could know the propagation velocity of the perturbation, which is a product of the coupling between the mechanical and the electric character (electroacoustic effect). The most simple model of this effect can be established considering Eqs. (5) and (7) when $\alpha_1 = 0$.

Defining the autocorrelation function for fluctuations of stress tensor as,

$$\Phi_Q = \langle \delta Q_{ij}(t, k) \delta Q_{ij}(0, k) \rangle, \quad (22)$$

and polarization-stress correlation function for fluctuations as,

$$\Phi_i = \langle \delta P_j(t, k) \delta Q_{ij}(0, k) \rangle, \quad (23)$$

the resulting equation for the Φ_Q is given by

$$\tau_1 \frac{\partial^2 \Phi_Q}{\partial t^2} + \left(\frac{\tau_1}{\tau_D} + 1 \right) \frac{\partial \Phi_Q}{\partial t} + \frac{1}{\tau_D} \Phi_Q = D_0 \nabla^2 \Phi_Q. \quad (24)$$

The propagation of the perturbation was assured by the appearance of the second time derivative of the auto-stress correlation function and by the Laplacian of the same quantity. Therefore, the squared velocity of the perturbation is given by the coefficient of the Laplacian operator divided by τ_1 ,

$$v^2 = \frac{D_0}{\tau_1}. \quad (25)$$

References

- [1] R. Díaz-Calleja, V. Compañ, E. Riande, *Physica B* 349 (2004) 37.
- [2] R. Díaz-Calleja, E. Riande, *Mater. Sci. Eng. A-Struct.* 370 (2004) 21.
- [3] W.T. Coffey, D.S.F. Crothers, Yu.P. Kalmykov, J.T. Waldron, *Physica A* 213 (1995) 551.
- [4] W.T. Coffey, Yu P. Kalmykov, B. Ouari, S.V. Titov, *Physica A* 368 (2006) 362.
- [5] G. Williams, D.C. Watts, *Trans. Faraday Soc.* 66 (1970) 80.
- [6] W.T. Coffey, Yu P. Kalmykov, S.V. Titov, *J. Chem. Phys.* 116 (2002) 6422.
- [7] U. Buchenau, M. Ohl, A. Wischnewski, *J. Chem. Phys.* 124 (2006) 094505.
- [8] Ya E. Ryabov, Y. Feldman, *Physica A* 314 (2002) 370.
- [9] P. Madden, D. Kivelson, *Adv. Chem. Phys.* 56 (1984) 467.
- [10] O.S. Jenkins, K.L.C. Hunt, *Theochem-J. Mol. Struct.* 633 (2003) 145.
- [11] L. Onsager, L.K. Runnels, *J. Chem. Phys.* 50 (1969) 1089.
- [12] J. Hubbard, L. Onsager, *J. Chem. Phys.* 67 (1977) 4850.
- [13] J.B. Hubbard, *J. Chem. Phys.* 68 (1978) 1649.
- [14] J.B. Hubbard, R.F. Kayser, P.J. Stiles, *Chem. Phys. Lett.* 95 (1983) 399.
- [15] B.U. Felderhof, *Mol. Phys.* 48 (1983) 1003;
B.U. Felderhof, *Mol. Phys.* 49 (1983) 449.
- [16] H.J. Kroh, B.U. Felderhof, *Z. Phys. B—Condens. Matter* 66 (1987) 1.
- [17] P.G. de Gennes, *The Physics of Liquids Crystals*, Clarendon Press, Oxford, 1974.
- [18] J. Casas-Vázquez, M. Criado-Sancho, D. Jou, *Physica A* 311 (2002) 353.
- [19] L.F. del Castillo, S.I. Hernández, A. García-Zavala, R. Díaz-Calleja, *J. Non-Cryst. Solids* 235–237 (1998) 677.
- [20] L.F. del Castillo, R. Díaz-Calleja, *Physica A* 268 (1999) 469.
- [21] V.S. Volkov, A.I. Leonov, *J. Chem. Phys.* 104 (1996) 5922.
- [22] Y. Imanishi, K. Adachi, T. Kotaka, *J. Chem. Phys.* 89 (1988) 7585.
- [23] K. Adachi, T. Kotaka, *Polym. J.* 18 (1986) 315.
- [24] P.J. Stiles, J.B. Hubbard, *Chem. Phys.* 84 (1984) 431.
- [25] P.J. Stiles, J.B. Hubbard, *Chem. Phys.* 94 (1985) 7.
- [26] J.B. Hubbard, P.J. Stiles, *J. Chem. Phys.* 84 (1986) 6955.
- [27] G. van der Zwan, J.T. Hynes, *Physica A* 121 (1983) 227.
- [28] W.H. Stockmayer, *Pure Appl. Chem.* 15 (1967) 539.
- [29] L.A. Dávalos-Orozco, L.F. del Castillo, *J. Chem. Phys.* 96 (1992) 9102.
- [30] D. Jou, J. Casas-Vázquez, G. Lebon, *Extended Irreversible Thermodynamics*, third ed., Springer, Berlin, 2001.
- [31] D. Reguera, J.M. Rubí, J.M.G. Vilar, *J. Phys. Chem. B* 109 (2005) 21502.
- [32] L.F. del Castillo, A. Estrada-Flores, *Physica A* 209 (2001) 131.
- [33] I. Santamaría-Holek, D. Reguera, J.M. Rubí, *Phys. Rev. E* 63 (2001) 051106.
- [34] J.B. Hubbard, P.J. Stiles, *Chem. Phys. Lett.* 114 (1985) 121.

- [35] P.G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, 1979.
- [36] C.A. Angell, C.T. Moynihan, M. Hemmati, *J. Non-Cryst. Solids* 274 (2000) 319.
- [37] S.G. Charati, A.Y. Houde, S.S. Kulkarni, M.G. Kulkarni, *J. Polym. Sci. Part B* 29 (1991) 921.
- [38] D. Ferri, L. Castellani, *Macromolecules* 34 (2001) 3973.
- [39] Bo Jakobsen, K. Niss, N.B. Olsen, *J. Chem. Phys.* 123 (2005) 234511.
- [40] E.W. Fischer, *Physica A* 201 (1993) 183.
- [41] G. Floudas, T. Pakula, W.E. Fisher, *Macromolecules* 27 (1994) 917.
- [42] S. Sills, T. Gray, R.M. Overney, *J. Chem. Phys.* 123 (2005) 134902.