



Effects of symmetric and antisymmetric stress tensors on N- and α -dielectric relaxations

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Abstract

We present a generalized hydrodynamic model for dielectric relaxation to describe the effect of spatial inhomogeneities in the polarization fluctuations in viscoelastic fluids. The model is a generalization of the simple Debye relaxation equation with the addition of the gradient of the total stress tensor. The two known modes of relaxation, N- and α -absorption can be incorporated in the model semiquantitatively, since we do not know the actual parameters involved. The comparison between our results and the experimental response reported for the N- and α -modes in polymers, shows that the predicted intensities of the loss peaks are well represented. However, at lower and higher frequencies the predicted curves deviate from the experimental ones. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Molecular motions in dense amorphous polymers or polymeric solutions control the rate of the dielectric relaxation. Therefore, the response of the material can be observed in several frequency domains depending on the number of molecules involved. The low frequency region has a normal mode relaxation, in which fluctuation dynamics of the long polymeric chains takes place [1]. The intermediate region of the dielectric relaxation frequency range has Brownian fluctuations of segment of the chains. This relaxation is identified as the α -relaxation [2]. In the high frequency region the dielectric relaxation response involves internal rotations of side groups attached to the polymeric chains, the β -relaxation,

and by the motion of subunit chains, the γ -relaxation [3].

In this paper, we consider that related to the molecular fluctuations of the normal and α -relaxations there is the effect of the polarization diffusion, produced by local spatial variations in the polarization caused by the dipole–dipole interaction. Consequently, the diffusion of the polarization is an additional macroscopic mechanism of the system towards the equilibrium state [4].

Along these lines, we will consider a polarization–diffusion model to explain some characteristic details of the normal mode relaxation.

2. Contribution of the polarization diffusion effect to the dielectric normal relaxation

From the macroscopic point of view, we consider the following proposed equations [4–6] for the polarization vector (\vec{P}) and the symmetric stress tensor (\mathbf{Q}^s), which are given respectively by:

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$$-\frac{d\vec{P}}{dt} = \frac{1}{\tau_1} (\vec{P} - \chi_0 \vec{E}) + \delta_2 \nabla \cdot \mathbf{Q}^s, \quad (1)$$

$$\left(1 + \tau_2 \frac{d}{dt}\right) \mathbf{Q}^s = -\eta_0 (\nabla \vec{v})^s + \delta_1 \left(1 + \tau_3 \frac{d}{dt}\right) (\nabla \vec{P})^s. \quad (2)$$

where η_0 is the shear viscosity and χ_0 the electric susceptibility at equilibrium. The terms δ_1 and δ_2 are coupling parameters. Eqs. (1) and (2) represent a set of coupled equations. For the normal mode relaxation, \vec{P} is the component of the polarization aligned along of the backbone of the polymeric chains [2]. We consider that the baricentric velocity, \vec{v} , is zero everywhere and that the system is incompressible. The Debye relaxation time, τ_1 , is given by the position of the maximum value of the loss peak, τ_2 is the viscoelastic relaxation time and is of the same order of magnitude as that given by molecular models, as by Rouse or the reptational models [7–9]. Regarding the retardation time, τ_3 , we assume that the corresponding effect does not have an affect on the viscoelastic relaxation, and it can be dropped from Eq. (2).

By considering the Laplace–Fourier transformation of Eqs. (1) and (2) and the relation for transformed vectors $\vec{P} = \chi^*(\vec{k}, \omega) \vec{E}$, we obtain the following result for the complex dielectric constant:

$$\frac{\chi^*(\omega, \vec{k})}{\chi_0} = \frac{\varepsilon^*(\omega, \vec{k}) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 - i\omega\tau_1 - \frac{A_1\tau_1 k^2}{1 - i\omega\tau_2}}, \quad (3)$$

where ω and \vec{k} are, respectively, the frequency and the wave number. The presence of the term, $A_1 = \delta_1\delta_2$, in Eq. (3) is responsible for the contribution of the polarization–diffusion effect. When the parameter $A_1 = 0$ expression (3) reduces to the well known Debye relaxation equation.

3. Contribution of the polarization–diffusion effect to the dielectric α -relaxation

The proposed constitutive equations for the antisymmetric stress tensor (\mathbf{Q}^a) and for the polarization vector are given respectively by [6]

$$\left(1 + \tau_4 \frac{d}{dt}\right) \mathbf{Q}^a = -\zeta_0 \vec{\omega} + \delta_3 \left(1 + \tau_5 \frac{d}{dt}\right) (\nabla \vec{P})^a, \quad (4)$$

$$-\frac{d\vec{P}}{dt} = \frac{1}{\tau_6} (\vec{P} - \chi_0 \vec{E}) + \delta_4 \nabla \cdot \mathbf{Q}^a, \quad (5)$$

where $\vec{\omega}$ is the angular velocity and ζ_0 is the rotational viscosity. Up to this point, we stress that the nature of the above equations involves macroscopic quantities, and the angular velocity vector, in Eq. (4), represents the angular movement of a group of molecules produced by external mechanical effects, which twists the material. Nevertheless, we consider that, under actual experimental conditions for dielectric tests, the simultaneous application of any mechanical perturbation is absent, and for the sake of simplicity this term will be considered equal to zero ($\vec{\omega} = 0$). For a further discussion of this sort of contributions see Ref. [10].

Taking the Laplace–Fourier transformation of Eqs. (4) and (5), one obtains

$$\frac{\varepsilon^*(\omega, \vec{k}) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 - i\omega\tau_6 - \frac{A_2\tau_6 k^2}{1 - i\omega\tau_4}}, \quad (6)$$

where $A_2 = \delta_3\delta_4$ represents the polarization–diffusion parameter. Again, if $A_2 = 0$, we obtain the Debye expression. A comparison of Eq. (6) with experimental data for the α -relaxation has been reported elsewhere [10].

4. A general expression for dielectric α and normal mode relaxation

The frequency of the loss peak of the α -relaxation is usually separated from the loss peak of the normal-mode relaxation by two or three frequency decades [11]. To describe these two polarization processes in a unique expression, we assume that the effect of each stress tensor is independent of the other, and the change of polarization is produced by the contribution of the two processes with a new characteristic time given by

$$\frac{1}{\tau_e} = \frac{1}{\tau_1} + \frac{1}{\tau_6}. \quad (7)$$

Therefore, the global constitutive equation for the polarization is given by

$$-\frac{d\vec{P}}{dt} = \frac{1}{\tau_e} (\vec{P} - \chi_0 \vec{E}) + \delta_2 \nabla \cdot \mathbf{Q}^s + \delta_4 \nabla \cdot \mathbf{Q}^a. \quad (8)$$

Considering the equations for \mathbf{Q}^s and \mathbf{Q}^a , the new expression for the complex dielectric constant is then

$$\frac{\epsilon^*(\omega, \vec{k}) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 - i\omega\tau_e \left[1 - \frac{A_2 k^2}{i\omega(1 - i\omega\tau_4)} \right] - \frac{A_1 \tau_e k^2}{1 - i\omega\tau_2}}. \quad (9)$$

It should be noted that Eq. (6) is a particular case of Eq. (9) when $A_1 = 0$ and $\tau_e = \tau_6$, and Eq. (3) is also obtained when $A_2 = 0$ and $\tau_e = \tau_1$.

5. Results

Fig. 1 shows the presence of two peaks, one at the right associated with the dielectric α -relaxation. The one at the left is related to the dielectric normal-mode relaxation. The position of the former peak is given by the parameter τ_e when $A_2 = 0$ in Eq. (9). The position of the left peak is provided by the inverse of the Rouse relaxation time τ_2 , and is molecular weight dependent.

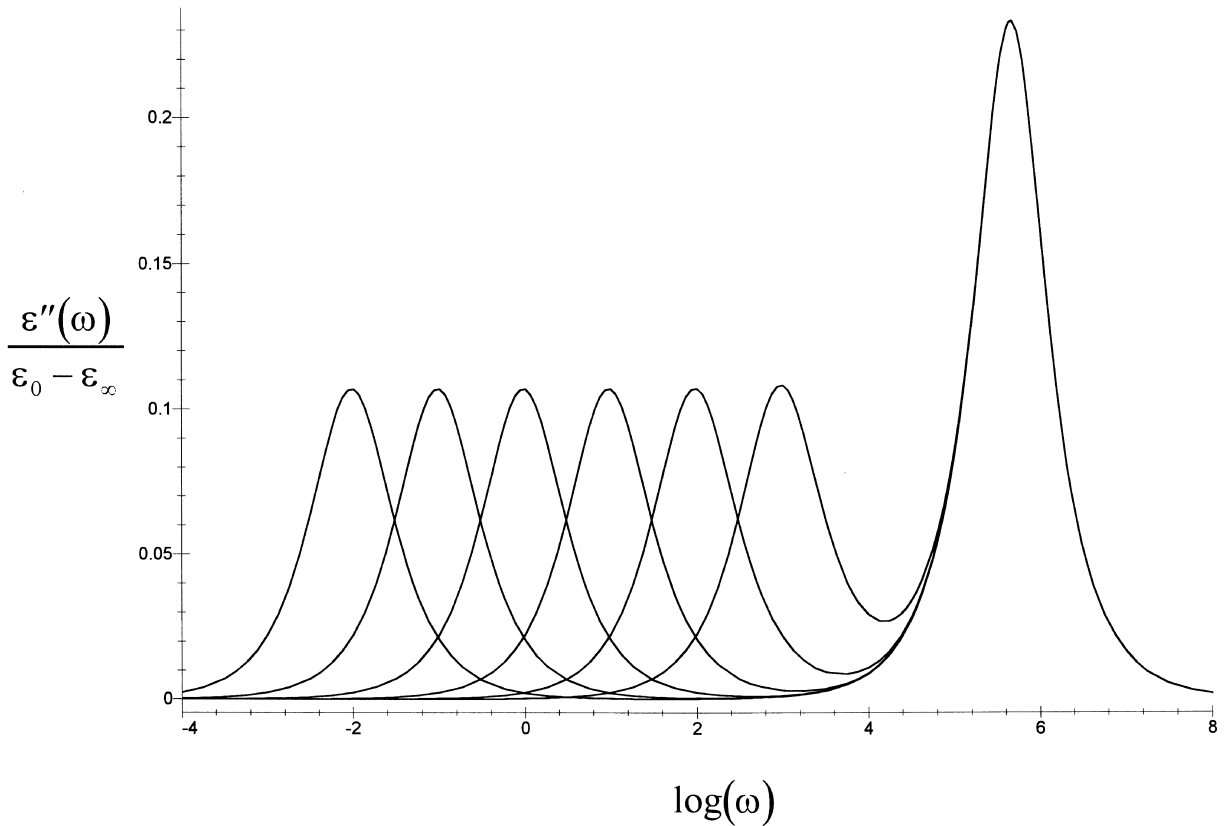


Fig. 1. Imaginary part of the complex dielectric constant versus $\log(\omega)$. The right-hand peak is the Debye description of the α -relaxation and is represented by Eq. (9) with $A_1 k_2 = 0.8 \text{ s}^{-1}$, $A_2 k_2 = 2.21 \times 10^5 \text{ s}^{-1}$, $\tau_2 = \{7 \times 10^{-4} \text{ s}, 7 \times 10^{-3} \text{ s}, 7 \times 10^{-2} \text{ s}, 7 \times 10^{-1} \text{ s}, 7 \text{ s}, 7 \times 10 \text{ s}\}$, $\tau_4 = 9.86 \times 10^{-7} \text{ s}$ and $\tau_e = 6.22 \times 10^{-6} \text{ s}$. The position of the normal-mode relaxation moves toward the left when Rouse's parameter τ_2 increases. According to the Rouse or tube models, this parameter is molecular weight dependent.

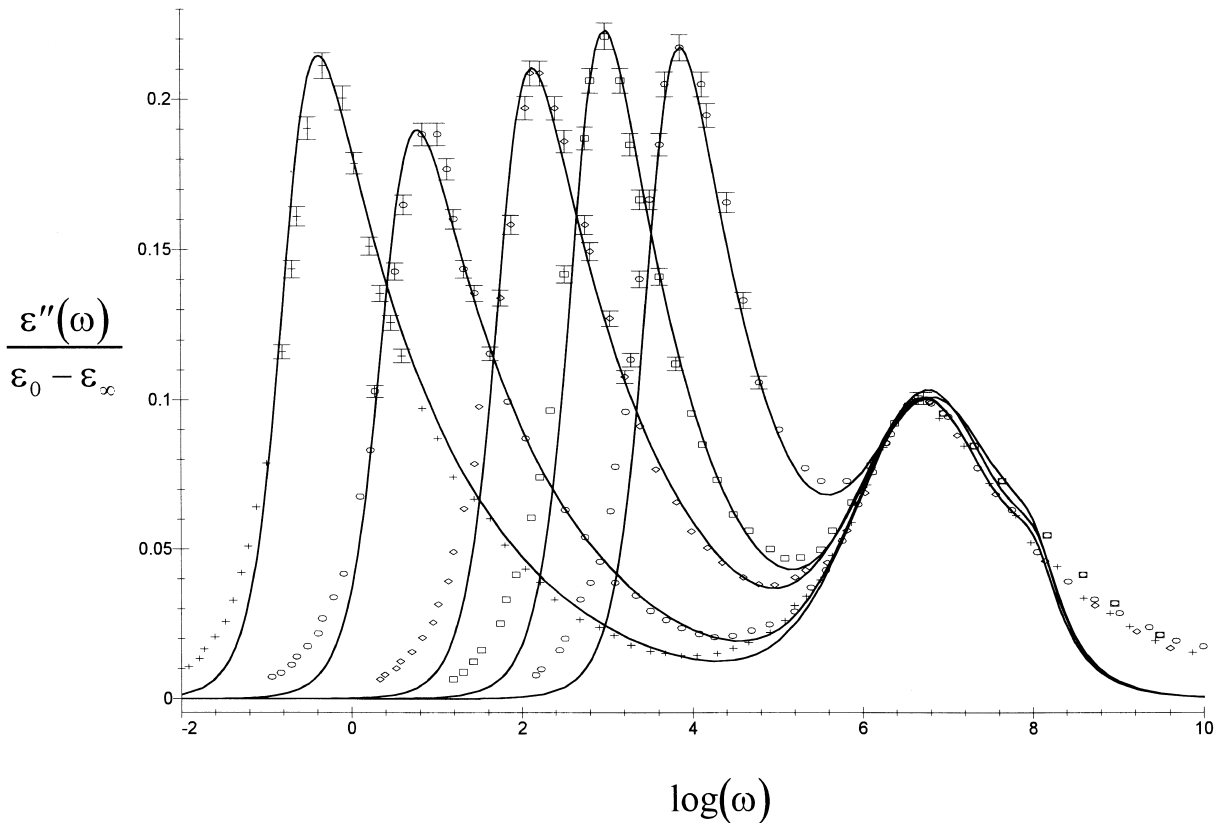


Fig. 2. The imaginary part of the complex dielectric constant versus $\log(\omega)$. The experimental data is from Adachi and Kotaka [8]. The continuous lines were obtained using Eq. (9). The error bars have been obtained considering an estimated error of $\pm 2\%$, as reported by the same authors in Ref. [12].

Fig. 2 shows the fitting of the experimental data of liquid *cis*-polyisoprene at 273 K for different molecular weights, from Ref. [1]. In the fitting procedure a dispersion relation of the type $k^2 = k_0^2(\omega/\omega_0)^n$ was considered, therefore $A_1 k^2 = A_{10}(\omega/\omega_1)^{n_1}$ and $A_2 k^2 = A_{20}(\omega/\omega_2)^{n_2}$, where ω_1 , ω_2 , n_1 and n_2 are unknown constants. The values of the parameters used in Eq. (9) are given in Table 1. In Fig. 2, the deviations of the fitting curves from the experimental data shows the range of validity of the present model.

6. Discussion

We have separated two contributions in the dielectric relaxation expression, into translational and rotational, according to the molecular move-

Table 1

Parameters used in Eq. (9) to fit the experimental data from Adachi and Kotaka [1]^a

Curve	A_{10} (cm ² /s)	τ_1 (s)	ω_1 (Hz)	n_1
PI-53	0.29	4.22	0.29	0.71
PI-32	0.09	0.30	0.76	0.70
PI-14	0.06	0.01	7.77	0.69
PI-05	0.04	1.50×10^{-3}	20.14	0.59
PI-03	0.02	2.03×10^{-4}	63.06	0.64

^a $A_{20} = 16.95 \times 10^6$ cm²/s, $\tau_4 = 8.64 \times 10^{-9}$ s, $\tau_c = 189.57 \times 10^{-9}$ s, $\omega_2 = 12.37 \times 10^6$ Hz, $n_2 = 0.63$

ment of the particle dipoles involved. The translation one, according to Rouse, is related to the diffusion of polymeric chains and the relaxation of the symmetric stress tensor. The rotational one, according to Stockmayer is due to the Brownian fluctuations of the segments of the polymeric chains and is related to the relaxation of the

antisymmetric stress tensor. These contributions are respectively, in the normal and alpha modes.

To take into account the two polarization processes in a unique expression, Eq. (9) is given in terms of several unknown parameters, which may be determined by a molecular model or by a comparison with experimental data. In the particular comparison of Eq. (9) with measurement for the *cis*-polyisoprene, we show that the use of Eq. (9), with adequate values of these parameters, allows the determination of the intensity and the position of the maximum of the loss peaks (see Fig. 2). However, the fitting procedure fails to correctly predict the bandwidths of the respective peaks.

7. Conclusions

A comparison of the proposed model with experimental data, suggests that the polarization–diffusion formulation presented here may be a good alternative description for the dielectric relaxation theory. In the near future, it may be possible to improve the model to provide a full description of the dielectric relaxation response in polymers.

Acknowledgements

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