

# Role of the second-order memory function on the dielectric relaxation

R. Díaz-Calleja and M. J. Sanchis

*Departamento de termodinámica aplicada, Universidad Politécnica de Valencia, Valencia E-46071, Spain*

L. F. del Castillo<sup>a)</sup>

*Instituto de Investigaciones en Materiales, UNAM. Ap. Postal 70-360, Coyoacan, México D.F. 04510, México*

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In this paper the use of the second-order memory function to represent experimental results of dielectric relaxation data of amorphous and glass forming materials is presented, and particularly, its interpretation in terms of the frequency dependence of the complex shear modulus, shear viscosity, and diffusion coefficient is pointed out. The method used for its evaluation is applied to consider the experimental results for three ester substances, and their particular features are discussed. © 1998 American Institute of Physics. [S0021-9606(98)50843-4]

## I. INTRODUCTION

The role played by the memory function in the formalism of Mori–Zwanzig<sup>1</sup> applied to the dielectric relaxation has been discussed in several papers considering rotational Brownian particles<sup>2,3</sup> and the fluctuation of the interacting torques acting on dipole particles.<sup>4,5</sup> The relevant paper of Nee–Zwanzig<sup>6</sup> studied the theory of dielectric relaxation on the basis of Kubo's technique to derive response coefficients. Nee–Zwanzig found an expression for the dielectric friction and its relation with the energy dissipation mechanism in the interaction between the electric field and the molecular dipoles. Another paper by Fulton<sup>7</sup> described the long-range character of the dipolar interactions, from which the anisotropy character of the dielectric constant is derived. In the frame of the three variable model, the dielectric response is accounted using the first- and second-order memory functions related to the evolution of the angular velocity correlation function and the torque–torque correlation function, respectively.<sup>8–10</sup> Hubbard and Wolynes<sup>11</sup> introduced the rotational Smoluchowski equation with fluctuating dipole-torques and derived from it a generalized friction coefficient. Sparling *et al.*<sup>12</sup> showed that the hydrodynamic memory function is related to the generalized Stokes friction coefficient for rotational polar molecules, and how this friction coefficient determines the form of the memory and affects the response of the dielectric material.

In the present paper, we first consider that both the hydrodynamic and the interaction dipole–dipole contributions to the total friction are nonseparable from the dynamic friction coefficient, which determines the dielectric response complex coefficient. In the second place, we consider that within the frequency domain of the  $\alpha$  relaxation, there is no contribution of any resonance process to the complex dielectric constant. Under these considerations, the generalized friction coefficient is in fact the second-order memory function in the Mori–Zwanzig formalism, and it allows us to discuss properly the properties of this memory kernel within

the context of the experimental data and model representation. One of the direct antecedents of the present paper is the work by Douglas and Hubbard<sup>13</sup> where they have considered a two-parameter model to describe the first memory function in the formalism of Mori–Zwanzig. They showed that the width of the loss peak of the  $\alpha$  relaxation is a result of the material inhomogeneity and cooperative molecular motion, and they modeled these effects in the memory function. Furthermore, the mode–mode coupling theory<sup>14,15</sup> represents an interesting model for the  $\alpha$  relaxation in terms of the second-order memory function (SOMF) which assures the correct width of the loss modulus of the complex dielectric constant.<sup>16</sup>

Recently, Williams and Fournier<sup>17</sup> have described the first memory function in terms of the so-called apparent memory. They found the corresponding first-order memory function for the Cole–Cole and the Kohlrausch representation of the dielectric constant expression for polymers and glass-forming liquids considering relaxation data. They also emphasize that if the dynamic heterogeneity of Schmith-Rohr and Spiess<sup>18</sup> and Cicerone *et al.*<sup>19</sup> is considered for the  $\alpha$  relaxation in glass-forming materials, the physical meaning of the memory may change. The dynamic heterogeneity point of view explains the relaxation function as an average of a series of parallel and independent decaying elementary processes with a broad distribution of relaxation times. From the interpretation of this point of view, the presence of the first- and second-order memory function is only apparent.

Following the lines of the validity of the fluctuating-dissipation theorem for the polarization correlation function for the  $\alpha$  relaxation, we now propose as a further advance, the use of a semiempirical SOMF for general applications in order to describe dielectric relaxation data for amorphous polymers and glass-forming liquids. The method we use to determine the SOMF is a variation of that described recently by Williams and Fournier,<sup>17</sup> which queried the values of the first-order memory function.

The structure of this paper is as follows. In Sec. II we present the definition of the SOMF and its interpretation considering the absence of any contribution from inertial effects.

<sup>a)</sup>To whom correspondence should be addressed.

In Sec. III the explicit form of the SOMF for several models is presented. We give, in Sec. IV, the procedure to evaluate the SOMF from experimental data and from the Havriliak–Negami expression. Finally, we include a short discussion on the aspects of the imaginary and real parts of this memory function for the experimental data of three ester substances.

## II. SECOND-ORDER MEMORY FUNCTION AND THE DYNAMIC FRICTION COEFFICIENT

The normalized autocorrelation function for a system formed by a collection of molecular dipoles is given by

$$\Phi(t) = \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(0) \rangle^{-1}, \quad (2.1)$$

where  $\boldsymbol{\mu}(t)$  is the time-dependent dipole moment. The equation that governs the time evolution of  $\Phi(t)$  is given by the master equation,<sup>1</sup>

$$\dot{\Phi} = - \int_0^t dt' K_1(t-t') \Phi(t'). \quad (2.2)$$

$K_1(t)$  is the memory kernel of the relaxation process and it contains the full dynamics of the  $N$  bodies as it is prescribed by the Liouville equation without any additional assumption. According to Mori,<sup>20</sup> it is possible to represent the time evolution of  $K_1(t)$  in terms of the SOMF  $K_2(t)$  by means of the following relationship:

$$\dot{K}_1 = - \int_0^t dt' K_2(t-t') K_1(t'). \quad (2.3)$$

In Eq. (2.3), the kernel  $K_2(t)$  accounts for the time lag effects produced by the internal mechanism, which ultimately represents the ensemble-average dynamics of the system.

To relate the SOMF with the correlation function, we take the Laplace transform of Eqs. (2.2) and (2.3)

$$\Phi(\omega) = \Phi(0) [K_1^*(\omega) + i\omega]^{-1}, \quad (2.4)$$

$$K_1^*(\omega) = K_1(0) [i\omega + K_2^*(\omega)]^{-1}, \quad (2.5)$$

where  $\Phi(0)$  and  $K_1(0)$  are the autocorrelation function and the first-order memory function at  $t=0$ , respectively. By the normalization condition  $\Phi(0) = 1$ .

The relation between the SOMF and the response coefficient is given through the correlation function, namely,

$$R^*(\omega) = \frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} f(\omega) = 1 - i\omega\Phi(\omega), \quad (2.6)$$

where  $f(\omega)$  is the field correction factor.<sup>6</sup> Using Eqs. (2.4) and (2.6) the response coefficient takes the following form:

$$R^*(\omega) = R'(\omega) - iR''(\omega) = \left[ 1 + i\omega \frac{i\omega + K_2^*(\omega)}{K_1(0)} \right]^{-1}. \quad (2.7)$$

If we compare Eq. (2.7) with the expression for the complex dielectric function, including the inertial and the generalized friction terms,<sup>8,11</sup>

$$R^*(\omega) = \left[ 1 - \frac{I\omega^2}{2k_B T} + \frac{i\omega I}{2k_B T} \xi^*(\omega) \right]^{-1}, \quad (2.8)$$

we note that  $K_1(0) = 2k_B T/I$ , which represents the resonance frequency squared, and the SOMF may be identified directly by means of the generalized friction coefficient;

$$K_2^*(\omega) = \xi^*(\omega). \quad (2.9)$$

In Eq. (2.8)  $k_B T$  is Boltzmann's constant times temperature and  $I$  is the relevant moment of inertia.

Now we consider that in the frequency domain of the  $\alpha$  relaxation there is no contribution of any resonance processes. In fact, in the diffusive regime,<sup>11</sup> the following condition is fulfilled:

$$\frac{I\omega^2}{2} \ll k_B T \quad \text{and from here, it has} \quad \frac{\omega^2}{K_1(0)} \ll 1.$$

In other words, it is essential to drop out the inertial term from Eq. (2.8), since we are interested in  $\epsilon^*(\omega)$  at frequencies smaller than  $(2k_B T/I)^{1/2}$  to take in consideration only the diffusive regime. Therefore, the following equation:

$$R^*(\omega) = \left[ 1 + \frac{i\omega}{K_1(0)} \xi^*(\omega) \right]^{-1} \quad (2.10)$$

and Eq. (2.9) allow us to evaluate the SOMF without taking into consideration the first-order memory function. Furthermore, Eq. (2.9) allows us a direct interpretation of this memory in terms of the internal frictional mechanism.

An alternative interpretation of the SOMF is obtained analyzing the frequency dependent diffusion coefficient, namely,

$$\frac{I\xi^*(\omega)}{2k_B T} = \tau^*(\omega) = \frac{1}{2D^*(\omega)}. \quad (2.11)$$

Furthermore, another consideration for the interpretation of this memory is considering the relationship between the dynamic friction coefficient and the complex shear viscosity, as it was prescribed by Di Marzio and Bishop<sup>21</sup>

$$\frac{K_2^*(\omega)}{K_1(0)} = \tau^*(\omega) = A\eta^*(\omega), \quad (2.12)$$

$A$  is a parameter of the order of  $10^{-9}$ . From Eq. (2.12) the SOMF also can be related with the shear modulus by using

$$G^*(\omega) = G'(\omega) + iG''(\omega) = i\omega\eta^*(\omega). \quad (2.13)$$

In terms of the real and imaginary parts of  $K_2^*(\omega) = K_2'(\omega) - iK_2''(\omega)$ , the storage and loss parts of shear modulus are given by

$$G'(\omega) = \frac{\omega K_2''(\omega)}{K_1(0)A}, \quad (2.14)$$

$$G''(\omega) = \frac{\omega K_2'(\omega)}{K_1(0)A}. \quad (2.15)$$

Therefore, Eqs. (2.9), (2.11), and (2.12) show that the results of any experimental-dielectric relaxation observation can be explained by any of three ways. One is the frictional interpretation in which the energy is going to be dissipated by the internal mechanisms. A second view is the diffusion one in which the molecular-dipoles undergo diffusion processes by means of rotational Brownian molecular motion. The third

view is the interpretation by considering generalized hydrodynamics to describe the evolution of the shear viscosity. Eqs. (2.14) and (2.15) correspond to this last treatment.

### III. SECOND-ORDER MEMORY FUNCTION FROM THEORETICAL AND EMPIRICAL MODELS

We now analyze several models which give formal results for the SOMF.

#### A. The Havriliak–Negami and Cole–Cole models

Considering the Havriliak–Negami (HN) empirical expression,<sup>22</sup>

$$R^*(\omega) = [1 + (i\omega\tau_D)^{1-\alpha}]^{-\beta}, \quad (3.1)$$

where the parameters  $\alpha$ ,  $\beta$ , and  $\tau_D$  are constants, the SOMF is

$$K_2^*(\omega) = \xi^*(\omega) = K_1(0) \left\{ \frac{r^\beta}{\omega} \sin(\beta\theta) - \frac{i}{\omega} [r^\beta \cos(\beta\theta) - 1] \right\} \quad (3.2)$$

with

$$r^2 = \left[ 1 + (\omega\tau_D)^{1-\alpha} \sin\left(\alpha \frac{\pi}{2}\right) \right]^2 + \left[ (\omega\tau_D)^{1-\alpha} \cos\left(\alpha \frac{\pi}{2}\right) \right]^2 \quad (3.3)$$

and

$$\tan \theta = \frac{(\omega\tau_D)^{1-\alpha} \cos\left(\alpha \frac{\pi}{2}\right)}{1 + (\omega\tau_D)^{1-\alpha} \sin\left(\alpha \frac{\pi}{2}\right)}. \quad (3.4)$$

From this results, we can obtain two other empirical representations: The Cole–Cole when  $\beta=1$  and the Davidson–Cole when  $\alpha=0$ .

The Cole–Cole expression for the dielectric permittivity is given by

$$K_2^*(\omega) = K_1(0) \omega^{-\alpha} \tau^{1-\alpha} \left( \cos \frac{\alpha\pi}{2} - i \sin \frac{\alpha\pi}{2} \right). \quad (3.5)$$

Real and imaginary parts of  $K_2^*(\omega)$  go to zero when  $\omega$  increases. Similar conclusion can be obtained for the Davidson–Cole case.

#### B. The bipolarabolic model

The bipolarabolic model<sup>23</sup> was proposed as a generalization of the Cole–Cole expression. The corresponding  $\tau^*(\omega)$  is given by

$$\tau^*(\omega) = \frac{K_2^*(\omega)}{K_1(0)} = \delta(i\omega\tau_0)^{-1-n} + (i\omega\tau_0)^{-1-h}, \quad (3.6)$$

where  $\delta = \tau_0^\beta$ ,  $\beta = 1 - n$ , and  $0 < n, h < 1$ .

In Eq. (3.6) the real and imaginary parts of secondary-order memory function go to zero when the frequency increases.

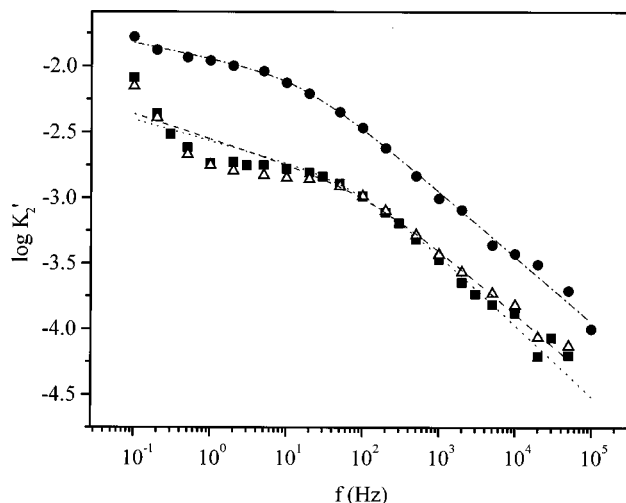


FIG. 1. Variation of the real part of the SOMF obtained from HN expression (dashed lines) and the experimental data for ib2g ( $\Delta$ ), d2gf ( $\blacksquare$ ), and afedio ( $\bullet$ ), plotted logarithmically vs frequency.

#### C. The BEL model

Considering that in amorphous materials and glass-forming materials, the molecular behavior of mechanical relaxation is the same as that involved in the memory of the dielectric relaxation, we take into account the expression for the complex relaxation time, presented by Barlow *et al.*<sup>24</sup> (BEL),

$$\tau^*(\omega) = \frac{K_2^*(\omega)}{K_1(0)} = \tau_0 (1 + 2A \sqrt{i\omega\tau_0} + i\omega\tau_0)^{-1}. \quad (3.7)$$

The parameter  $A$  was estimated by computer simulation experiments<sup>25</sup> to be of the order 0.1, and  $\tau_0$  is the Maxwell relaxation time. Equation (3.7) was first proposed as an empirical one and afterwards, it was obtained within the theoretical frame of defect diffusion model.<sup>25</sup>

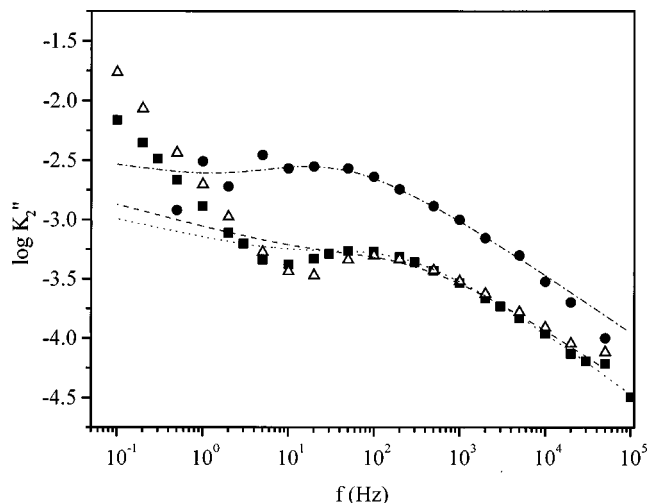


FIG. 2. Variation of the imaginary part of the SOMF obtained from HN expression (dashed lines) and the experimental data for ib2g ( $\Delta$ ), d2gf ( $\blacksquare$ ), and afedio ( $\bullet$ ), plotted logarithmically vs frequency.

TABLE I. Dielectric measurements parameters used to analyze the characteristics of the second-order memory function for the three substances.  $T$  is the temperature ( $^{\circ}\text{C}$ ),  $\alpha$ ,  $\beta$ , and  $\tau_D$  are the parameters to represent the experimental data with the HN expression,  $\delta$  is considered the correlation time of the torques interaction between dipoles.

Sample	Ester	$T$ ( $^{\circ}\text{C}$ )	$\alpha$	$\beta$	$\tau_D$ ( $\text{s}^{-1}$ )	$\delta$ ( $\text{s}^{-1}$ )	$\epsilon_{\infty}$	$\Delta\epsilon$
d2gf	bis(2'-biphenyl) 2, 4-dimethylglutarate	5	0.84	0.54	$2.71 \times 10^{-3}$	$2.5 \times 10^{-3}$	2.511	1.183
ib2g	2-biphenyl isobutyrate acetate of cis/trans	-50	0.81	0.62	$2.08 \times 10^{-3}$	$1.5 \times 10^{-3}$	2.661	1.706
afedio	2-phenyl 5 ethyl 5-hydroxymethyl 1-3-dioxane	-40	0.88	0.57	$1.54 \times 10^{-2}$	$6.3 \times 10^{-2}$	2.929	6.125

#### D. The three-variable theory

The second-order memory function is related in the three-variable theory with the correlation function for intermolecular torques which decays exponentially.<sup>10,26,27</sup> The corresponding expression is given by

$$\frac{K_2^*(\omega)}{K_1(0)} = \tau^*(\omega) = \frac{\tau_0}{1 + i\omega\delta}, \quad (3.8)$$

where  $\delta$  is the relaxation time of the decaying of the torques acting on the molecular dipoles. According to the evaluation in the model of Maddem and Kivelson,<sup>9</sup>  $\delta$  is a parameter of the order of picoseconds for polar liquids.

Thanks to this model it is possible to get a microscopic interpretation of the second-order memory function. In fact, considering Mori's theory of the continued fraction representation of the correlation function, the first-order memory function is directly related with the autocorrelation function of the angular velocity of the dipole particles.<sup>9</sup> On the other hand, the second-order memory function is directly related to the evolution of the interacting dipole-dipole torques. According to this molecular interpretation, the dielectric relaxation is then governed by the decay of the libration of dipoles into the field produced by the neighbors. Additionally, the molecules which the dipoles are attached produce viscoelas-

tic relaxation. Thus, the relaxation of dipole-dipole interactions might be coupled to the collective behavior of the substances. For example, for supercooled liquids or as a material becomes extremely viscous, the time scale separation between the decay of the torques and of the angular position of the dipoles becomes too small to be distinguished, and in Eq. (3.8) the parameter  $\delta$  should be of the same order of magnitude of  $\tau_0$ .

On the other hand, it should be stressed, according to Eqs. (3.4) and (3.5), that the behavior of the SOMF is not necessarily a monotonically decreasing function of the frequency. In fact, the imaginary part of Eq. (3.8) has a maximum at  $\omega_0 = 1/\delta$ . This particular feature will be discussed later in relation to the appearance of a relative maximum in the plot of the imaginary part of three substances analyzed in the next section.

#### IV. SECOND-ORDER MEMORY FUNCTION DETERMINED FROM EXPERIMENTAL DATA

We consider that the values of  $R'(\omega)$  and  $R''(\omega)$  are known from experimental measurements. Then, we are able to obtain the complex friction coefficient by means of Eq. (2.10). In fact, the real and imaginary parts for the complex friction coefficient are given by

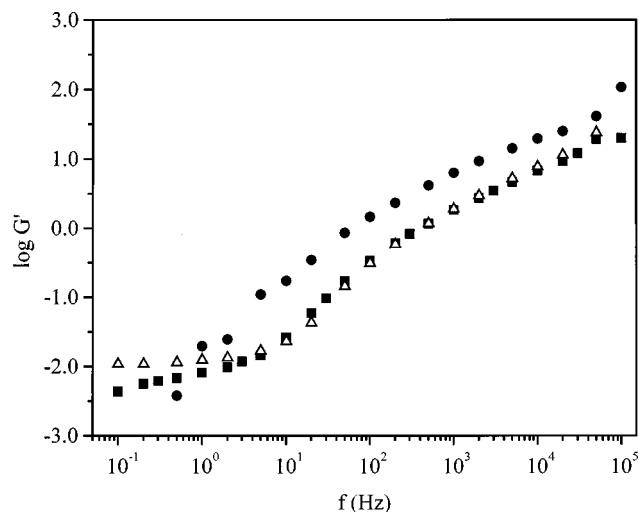


FIG. 3. Variation of the real part of the complex modulus for ib2g ( $\Delta$ ), d2gf ( $\blacksquare$ ), and afedio ( $\bullet$ ), plotted logarithmically vs frequency.

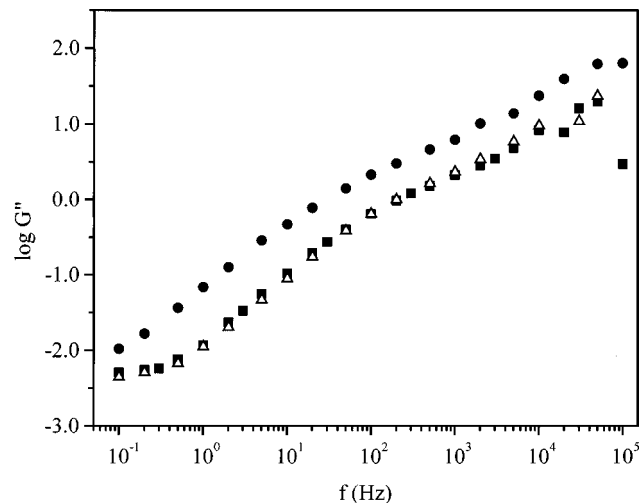


FIG. 4. Variation of the imaginary part of the complex modulus for ib2g ( $\Delta$ ), d2gf ( $\blacksquare$ ), and afedio ( $\bullet$ ), plotted logarithmically vs frequency.

$$K_2'(\omega) = \xi'(\omega) = \frac{K_1(0)}{\omega} \left[ \frac{R''}{(R')^2 + (R'')^2} \right], \quad (4.1)$$

$$K_2''(\omega) = \xi''(\omega) = -\frac{K_1(0)}{\omega} \left[ \frac{(R')^2 + (R'')^2 - R'}{(R')^2 + (R'')^2} \right]. \quad (4.2)$$

The frequency dependence of the real and imaginary parts of the SOMF for three ester samples are shown in Figs. 1 and 2 considering for the sake of simplicity  $K_1(0) = 1$ .

In these figures, the points marks correspond to the SOMF obtained from the experimental data using Eqs. (4.1) and (4.2). The dashed lines correspond to memories obtained from the HN representation of the same experimental data using Eqs. (3.2), (3.3), and (3.4). In Table I, the values of the parameters of Eq. (3.2) for the three esters are listed. It should be noted that the HN representation does not apply over the whole range, the accuracy for the determination of the real and imaginary parts of  $K_2^*(\omega)$  is not good for low and medium frequencies.

In Figs. 1 and 2, the real part of  $K_2^*(\omega)$  decreases as the frequency increases, representing that the rotational friction also decreases and the characteristic time of the angular movement of the dipoles diminishes when the frequency increases. On the other hand, the imaginary part of  $K_2^*(\omega)$  decreases when the frequencies increase, indicating that the storage energy in the intermolecular torque-torque interaction decreases with the frequency. On the other hand, it is notorious that in Fig. 1 there is a plateau in the first half of the plot. It corresponds, in Fig. 2, to the relative maximum of the imaginary part of SOMF. The position of this peak can be determined by inspection, and this value related to the parameter  $\delta$ , following the model representation of this function according to Eq. (3.8). In Table I, the obtained values of this parameter and the corresponding parameters of the experimental data of three substances are listed. Note that the relaxation time  $\tau_D$  and  $\delta$  are of the same order of magnitude as it was discussed at the end of Sec. III. Therefore, if we consider the interpretation of these features of the SOMF according to the three variable model, it suggests that the presence of the relative maximum in the imaginary part of this memory may be related to the relaxation of the autocorrelation function of the torques arising from the dipoles interaction. The corresponding correlation time is given by the parameter  $\delta$ . On the other hand, the frequency dependence of  $G'(\omega)$  and  $G''(\omega)$  obtained using Eqs. (2.14) and (2.15) for the same three ester samples is shown in Figs. 3 and 4. We again consider the factor  $K_1(0)A$  equal to one, for the sake of simplicity. Both functions,  $G'(\omega)$  and  $G''(\omega)$  increase with the frequency and do not show any particular detail related with these features of the SOMF discussed before. This point takes into consideration that the frequency factor in Eqs. (2.14) and (2.15) is enough to modify the behavior as it is presented in Figs. 1 and 2.

## V. DISCUSSION

The second-order memory function (SOMF) has been considered to describe the dielectric relaxation data for amorphous and glass forming materials, whereas the use of the first memory was already discussed in referenced papers.

Regarding to the interpretation of the SOMF, three different points of view might be adopted in terms of the generalized frictional coefficient, the complex diffusion coefficient, and the shear modulus of relaxation. The physical meaning of these coefficients gives us an insight on the possible internal mechanism responsible of the deviation of the real and imaginary parts of the complex dielectric constant from ideal Debye's model, both at low and high frequencies.

We have considered how the SOMF can be evaluated from the knowledge of the complex permittivity data or from their equivalent representation of the Havriliak-Negami expression. This method was used to determine the real and imaginary parts of the SOMF for three different polymeric substances. The behavior of these functions were given in terms of frequencies, which are in qualitative agreement with the prediction of some previous proposed models, as it was discussed in Sec. III. Particularly, the imaginary part of the second-order memory for experimental data of the three ester substances analyzed here, shows a relative maximum, and it suggests that the presence of this peak might be related with the relaxation of the autocorrelation function of the torques arising from dipole-dipole interaction.

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