

Memory function for dielectric relaxation

R. Díaz-Calleja, A. García-Bernabé, M. J. Sanchis, and L. F. del Castillo

Citation: *J. Chem. Phys.* **113**, 11258 (2000); doi: 10.1063/1.1326913

View online: <https://doi.org/10.1063/1.1326913>

View Table of Contents: <http://aip.scitation.org/toc/jcp/113/24>

Published by the [American Institute of Physics](#)

PHYSICS TODAY

WHITEPAPERS

ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these environmentally friendly adhesive systems can do

READ NOW

PRESENTED BY
 **MASTERBOND**
ADHESIVES | SEALANTS | COATINGS

Memory function for dielectric relaxation

R. Díaz-Calleja, A. García-Bernabé, and M. J. Sanchis

Departamento de Termodinámica Aplicada, Universidad Politécnica de Valencia, Valencia E-46071, Spain

L. F. del Castillo

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

(Received 29 November 1999; accepted 28 September 2000)

The second-order memory function (SOMF) for the dicyclohexylmethyl-2methyl succinate is obtained by using simple numerical manipulation of the experimental dielectric data. According to the prescription given in a previous paper [J. Chem. Phys. **109**, 9057 (1998)], the frequency behavior of the real and imaginary parts of the SOMF is discussed in terms of the Havriliak-Negami equation of the dielectric function, and together with the three-variable model describing the evolution of the torque-autocorrelation function. Furthermore, in this paper we present the temperature dependence of the parameters, which characterize the SOMF behavior for two ester substances. © 2000 American Institute of Physics. [S0021-9606(00)51048-4]

I. INTRODUCTION

To describe the time evolution of the correlation function of a molecular dynamic variable, the concept of the memory function was given in the projection operator formalism of Zwanzig¹ and the linear response theory of Kubo.² Similarly, the second-order memory function (SOMF) was introduced by Mori in the continued fraction scheme for the correlation function.³ The application of this formalism to dielectric relaxation has been discussed in several papers.⁴⁻⁶ Particularly, the central point of the application of the correlation function formalism to understand dielectric friction^{7,8} and the libration mechanism was the average of the fluctuations of the interacting torque acting on the dipolar particles.^{9,10}

On the other hand, molecular theories have been proposed in order to have explicit expressions for the friction coefficient of dielectric relaxation.¹¹⁻¹³ From that mentioned physical basis, the memory processes have been worked out by several authors.¹⁴ It is of particular interest for the present goal to mention the three-variable model, in which the dielectric response can be described using the SOMF, and gives in an exponential form the evolution of the torque-autocorrelation function.^{15,16}

Recently, the physical role played by the SOMF, obtained from experimental data and neglecting the inertial contribution, was reported elsewhere.¹⁷ Nevertheless, several points were not yet discussed, like the role played by the dynamic heterogeneity and the thermal behavior of the SOMF. In the present paper, we deal with these questions for two ester substances. In Sec. II, we present the definition of the SOMF and its interpretation based in the three-variable model. The comparison between the SOMF obtained from experimental data and from the Havriliak-Negami (HN) equation is also discussed. In Sec. III the explicit temperature dependence of the parameters of the three-variable model are presented and the root mean square (rms) value of the torque fluctuations is addressed.

We emphasize that the purpose of this paper is not to

present a data processing algorithm as an alternative or competitive way to those of the HN representation. On the contrary, our main objective is to show that the SOMF can give us valuable information about the molecular motions responsible for the dielectric relaxation.

II. THE SOMF AND THE COMPLEX RESPONSE FUNCTION

A. Physical background

The complex response function of a dielectric material to a harmonic electric field is usually expressed in terms of the microscopic decay function as

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

where function $f(\omega)$ is the field factor and $\phi(t)$ is the normalized autocorrelation function for a system of dipolar molecules. We identify this autocorrelation function with the single molecule function by assuming that the collective effects are of minor relevance. In this way $\phi(t)$ is given by

$$\phi(t) = \langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0) \rangle \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(0) \rangle^{-1}, \quad (2)$$

where $\boldsymbol{\mu}(t)$ is the dipole moment of the molecule and we take $\phi(0) = 1$.

Equation (1) is known as the Kubo relation² which relates the dynamic behavior of a collection of dipoles with the statistical equilibrium properties of this system. The Kubo relation is an alternative way to the fluctuation-dissipation theorem¹ as a starting point in an attempt to calculate the dynamic response of the macroscopic system from the molecular ensemble of dipoles. In other words, dipole moment fluctuations decay, on the average, to the same law as an external electric field produced macroscopic polarization. This is the essence of the fluctuation-dissipation theorem in our particular case.

Now, according to the generalized linear theory, Mori³ and Zwanzig¹ have shown that time-correlation function may

be projected in a memory-function formalism giving a continued fraction in such a way that the complex response function can be cast in the form of a convolution integral equation. This equation may be transformed into the Fourier–Laplace space to give the relationship between the complex response function and the first-order memory function $K_1^*(\omega)$ (FOMF). It was discussed in Ref. 14 that the FOMF can be interpreted in molecular terms considering the angular velocity correlation function.

The starting equation is

$$\frac{d\phi(t)}{dt} = - \int_0^t K_1(t-\tau)\phi(\tau)d\tau, \quad (3)$$

which is a generalized Langevin equation.

After taking the Laplace transformation in Eq. (3), the following expression is obtained:

$$\phi^*(\omega) = \frac{1}{i\omega + K_1^*(\omega)}. \quad (4)$$

Then from Eq. (1),

$$R^*(\omega) = \frac{K_1^*(\omega)}{i\omega + K_1^*(\omega)}, \quad (5)$$

where the field factor $f(\omega)$ introduced in Eq. (1) is taken equal to one for the sake of simplicity. As a consequence, Eq. (5) can be written as

$$R^* = \left[1 + \frac{i\omega}{K_1^*(\omega)} \right]^{-1}. \quad (6)$$

Now, following the formalism of Mori,³ the first-order memory function is expressed in terms of the SOMF $K_2^*(\omega)$ by means of the following relationship:

$$K_1^*(\omega) = K_1(0)[i\omega + K_2^*(\omega)]^{-1}, \quad (7)$$

where $K_1(0)$ is the first-order memory function at $t=0$.

We also note that this second-order memory function can be interpreted in molecular terms considering the torque-torque correlation function.

Now, by combining Eqs. (1) and (7), the relation between the SOMF and the complex response coefficient takes the following form:

$$\begin{aligned} R^*(\omega) &= \left[1 + i\omega \frac{i\omega + K_2^*(\omega)}{K_1(0)} \right]^{-1} \\ &= \frac{K_1(0)}{K_1(0) + i\omega K_2^*(\omega) + (i\omega)^2}, \end{aligned} \quad (8)$$

and the value of the SOMF is given by

$$K_2^*(\omega) = K_2'(\omega) - iK_2''(\omega) = \frac{K_1(0)(1 - R^*(\omega))}{i\omega R^*(\omega)} - i\omega. \quad (9)$$

The corresponding real and imaginary parts of the SOMF are

$$K_2'(\omega) = \frac{K_1(0)}{\omega} \left[\frac{R''}{(R')^2 + (R'')^2} \right], \quad (10a)$$

$$K_2''(\omega) = - \frac{K_1(0)}{\omega} \left[\frac{(R')^2 + (R'')^2 - R'}{(R')^2 + (R'')^2} \right] + \omega. \quad (10b)$$

These are the *exact* relationships between the SOMF and the complex response coefficient. However, as it has been shown, (see Ref. 14), we can interpret $K_1(0)$ as the square of the rotation frequency of a free rotator, that is

$$K_1(0) = \frac{2k_B T}{I}, \quad (11)$$

where k_B is the Boltzmann constant, T the absolute temperature and I the inertia moment of the molecule. In our case at the sight of the values appearing in the literature for the inertia moment of the small molecules (see, for example, Ref. 14) it is clear that the following condition is fulfilled:

$$\omega^2 \ll K_1(0). \quad (12)$$

This is consistent with the fact that in the frequency domain of the α relaxation there is not contribution of any resonance processes. In other words we can drop the second term of the right-hand side of Eq. (9) and then the second term of the right-hand side of Eq. (10b).

The interpretation of the SOMF can be given considering the generalized diffusion coefficient

$$\frac{K_2^*(\omega)}{K_1(0)} = \frac{1}{2D^*(\omega)}. \quad (13)$$

An alternative expression for the generalized diffusion coefficient was given by Nee-Zwanzig⁷ in terms of the dipolar torque-autocorrelation function

$$\psi(t) = \langle \mathbf{N}(t) \cdot \mathbf{N}(0) \rangle, \quad (14)$$

namely,

$$D^*(\omega) = k_B T [\mathcal{L}(\psi)]^{-1}, \quad (15)$$

where $\mathcal{L}(\psi)$ is the Laplace transformation $\psi(t)$. To accomplish Eq. (15), the three-variable model assumes that ψ decays exponentially with a relaxation time (δ). Therefore, the normalized torque-autocorrelation function, in the transformed space, is given by

$$\frac{\mathcal{L}(\psi(t))}{\psi(0)} = \frac{\delta}{1 + i\omega\delta}, \quad (16)$$

where the torque normalization factor $\psi(0)$ is equal to

$$\psi(0) = \langle \mathbf{N}(0) \cdot \mathbf{N}(0) \rangle. \quad (17)$$

Therefore, in the three-variable model the SOMF takes the following form,

$$\frac{K_2^*(\omega)}{K_1(0)} = \frac{\tau_0}{1 + i\omega\delta}, \quad (18)$$

where τ_0 is the ‘‘microscopic’’ relaxation time expressed in terms of some macroscopic parameters

$$\tau_0 = \frac{\varepsilon_0 + 2\varepsilon_\infty}{2\varepsilon_0 + \varepsilon_\infty} \tau_D. \quad (19)$$

On the other hand, according to the three-variable model, τ_0 is also expressed in terms of the torque normalization factor, namely

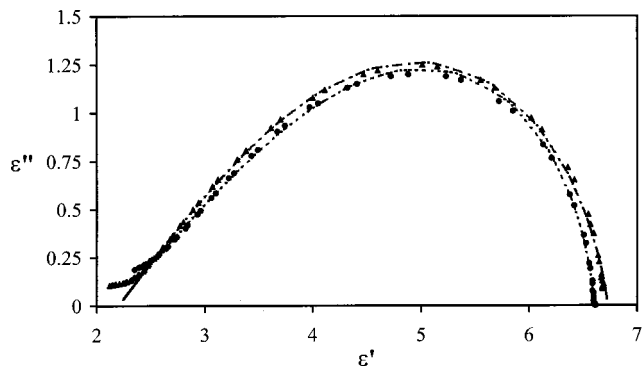


FIG. 1. The Cole–Cole plot of the relaxation data obtained for the DCMMS for two temperatures: $T=230$ K (black points) and $T=224$ K (black triangles). The solid line is the HN equation of the same data. The characteristic parameters for this representation are given in Table I.

$$\tau_0 = \frac{\psi(0)\delta}{2(k_B T)^2}. \quad (20)$$

Now, we consider that the description given by the three-variable model in Eq. (18) is the proper behavior for the description of the interaction torque relaxation dynamics in liquids in an equilibrium state, while the substances studied here are glass-forming esters in the undercooled liquid regime.

B. The general characteristic of the SOMF from experimental data and the HN equation

In Fig. 1, the Cole–Cole plot of the dicyclohexylmethyl-2-methyl succinate (DCMMS) is shown for two temperatures. The complex response of a dielectric material is usually expressed by the Havriliak-Negami equation,

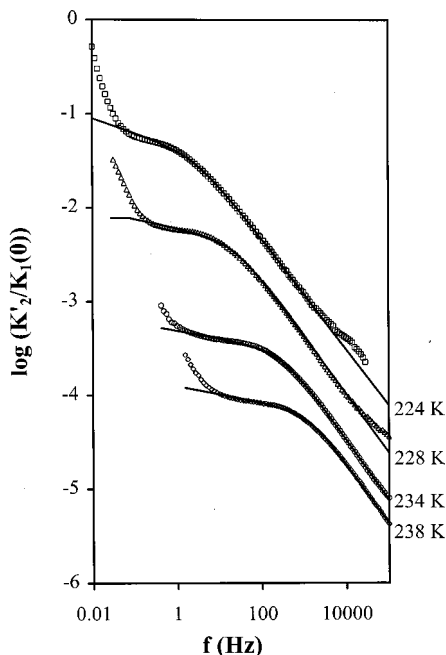


FIG. 2. Variation of the real part of the SOMF obtained from the HN equation (solid lines) and the experimental data (symbols) plotted logarithmically vs the frequency.

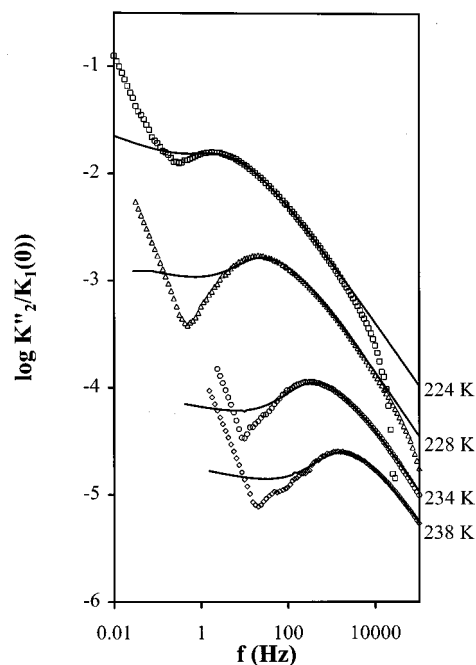


FIG. 3. Variation of the imaginary part of the SOMF obtained from the HN equation (solid lines) and the experimental data (symbols) plotted logarithmically vs the frequency.

$$R^*(\omega) = \frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} f(\omega) = \frac{1}{[1 + (i\omega\tau_D)^{1-\alpha}]^\beta}, \quad (21)$$

where the parameters α, β and τ_D which are temperature dependent have been determined by using a fitting procedure of the experimental data.¹⁸ As before, the field factor will be taken equal to one.

In Fig. 1, it should be noted that in the high frequency limit there is a discrepancy between the HN equation and experimental data. The last does not go to zero in this limit as predicted by the HN equation.

The frequency dependence of the real and imaginary parts of the SOMF for DCMMS is shown in Figs. 2 and 3. In

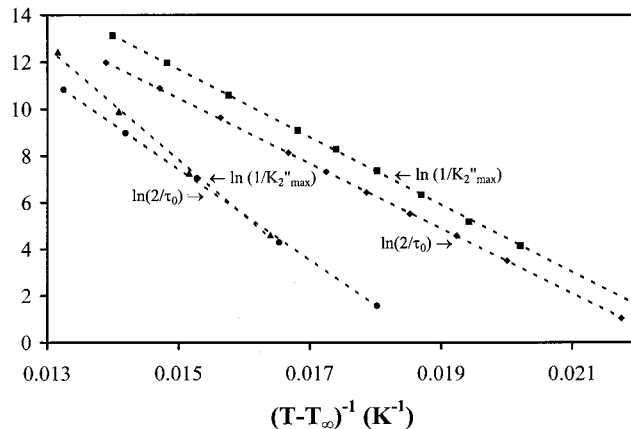


FIG. 4. Temperature dependence of the maximum of the imaginary part of the SOMF and the half of τ_0 for two substances: The DCMMS (squares) and the IB2G (triangles and points). Dashed lines give the VFT representations. The characteristic parameters of these representations are given in Table II.

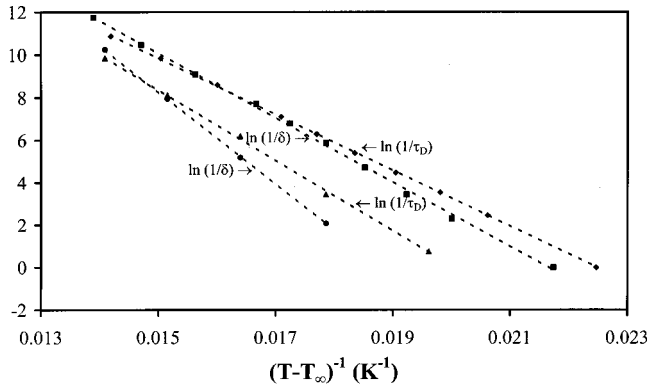


FIG. 5. Temperature dependence of the characteristic relaxation time (τ_D) and the torque correlation time (δ) for two substances. The DCMMS (squares) and the IB2G (triangles and points). Dashed lines give the VFT representation. The characteristic parameters of these representations are given in Table II.

these figures, the symbols lines correspond to the SOMF obtained directly from the experimental data. The solid lines correspond to the SOMF obtained from fitting the same experimental data with the HN equation (this procedure was reported elsewhere¹⁸). The most relevant feature of these figures is the relative maximum of the imaginary part of the SOMF, which coincides with the end of a relative plateau in the real part. The position of this relative maximum is identified with the torque correlation time (δ).

Furthermore, it should be noted that in Figs. 2 and 3 there are some discrepancies between the SOMFs obtained directly from the experimental data and from the HN equation:

- (1) For low frequencies, the imaginary part of the SOMF describes a decreasing function, while the HN equation shows a smooth region.
- (2) For the high frequencies region the discrepancies are also notorious, but the HN equation fails into this frequency region, as it was previously mentioned concerning Fig. 1.

C. Comparison between the three-variable model and the SOMF obtained from experimental data

From the comparison between Eq. (18) and results obtained from experimental data, we seek the behavior of the SOMF. The presence of the relative maximum on the imaginary part is consistent with the description of this model.

Another prediction of the three-variable model is that the maximum value of the imaginary part of the SOMF is equal to the half of τ_0 . These two values are plotted against temperature in Fig. 4 for two substances; one is DCMMS and the other is 2-biphenylisobutyrate acetate of *cis/trans* (IB2G), whose SOMF was reported elsewhere.¹⁷ For the former material, the difference of the maximum value of the imaginary part of the SOMF and the half of τ_0 is almost constant (a factor of about 2.4) and for the last material there is a good agreement for several temperatures.

Now, looking at the high-frequency region, the imaginary and the real parts of the SOMF describe a decaying memory function with a power-law exponent of 0.55

TABLE I. Dielectric measurement parameters used to represent the experimental data in terms of the HN equation and to analyze the characteristic of the SOMF for the DCMMS.

T(K)	ϵ_∞	$\Delta\epsilon$	$1-\alpha$	β	τ_D (s)	δ (s)
220	2.140	4.650	0.85	0.48	1.01	1.0
224	2.200	4.530	0.85	0.48	8.57×10^{-2}	1.0×10^{-1}
226	2.210	4.520	0.84	0.48	2.91×10^{-2}	3.2×10^{-2}
228	2.179	4.456	0.90	0.41	1.14×10^{-2}	8.9×10^{-3}
230	2.162	4.441	0.92	0.40	4.54×10^{-3}	2.8×10^{-3}
232	2.168	4.410	0.91	0.39	1.86×10^{-3}	1.1×10^{-3}
234	2.147	4.403	0.92	0.38	8.26×10^{-4}	4.5×10^{-4}
238	2.114	4.380	0.91	0.38	1.85×10^{-4}	1.1×10^{-4}
242	1.942	4.496	0.93	0.34	5.35×10^{-5}	2.8×10^{-5}
246	1.485	4.895	0.94	0.29	1.91×10^{-5}	8.0×10^{-6}

± 0.02 . The actual decaying function follows to a power law at high frequencies instead of a simple Lorentzian function as predicted by Eq. (18). This is due to the effect of dynamic heterogeneity,^{19,20} which relates to a continuous distribution of Lorentzian functions²¹ in order to generate the power-law behavior.

The decaying behavior of the real and imaginary parts of the SOMF at the low-frequency region is produced by the factor $1/\omega$ at the front of Eqs. (10a) and (10b). This factor modifies the actual shape of the real and imaginary parts of the SOMF in the representation of Fig. 3. However, considering that the form of the libration band should be complete, the power-law exponent of the imaginary part of the SOMF at the low frequency region is of 0.46 ± 0.02 .

III. TEMPERATURE DEPENDENCE OF THE MODEL PARAMETERS OF THE SOMF

We use the Vogel-Tammann-Fulcher (VTF) law²² to give the temperature dependence of the relaxation times. In this representation, the characteristic time has the following expression:

$$\tau_D(T) = \tau_{D0} \exp\left(\frac{E_D}{k_B(T - T_\infty)}\right), \tag{22}$$

where τ_{D0} is a reference characteristic time, T_∞ is the Vogel temperature at the end of the configuration transitions in undercooled liquids²¹ and E_D is the activation energy. The parameters for several relaxation times of the theory are reported in Table II. Note that τ_0 is obtained using Eq. (19).

TABLE II. VTF parameters for two ester substances. The reference parameters are the logarithm of the corresponding relaxation time reference. The value for K_2'' corresponds to the maximum of the imaginary part of the SOMF, whose temperature dependence is shown in Fig. 4.

Relaxation time	DCMMS ($T_g=220$ K)			IB2G ($T_g=213$ K)		
	E (J/mol)	T_∞ (K)	Reference parameter	E (J/mol)	T_∞ (K)	Reference parameter
τ_d	10 967	176	29.64	13 826	162	33.30
τ_0	11 622	174	31.43	22 322	155	44.68
δ	12 627	174	32.86	18 057	162	40.83
K_2''	12 045	175	33.42	16 247	158	36.73

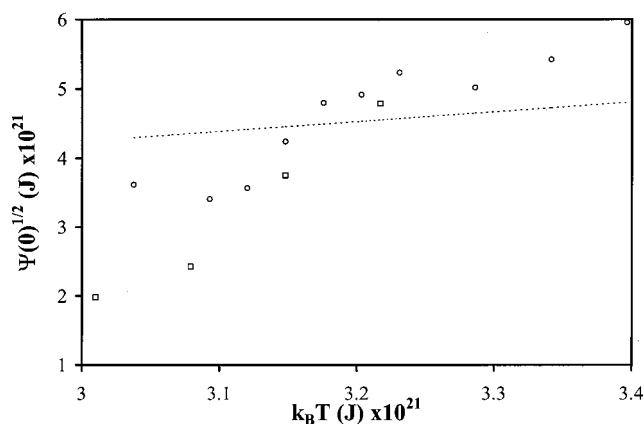


FIG. 6. The rms value of the torque-autocorrelation function against $k_B T$ is shown by the point marks for DCMMS and the square marks for IB2G. The dashed lines represent the linear behavior with $\tau_0 = \delta$.

The temperature dependency of the characteristic time and the torque relaxation time is shown in Fig. 5 for two substances, DCMMS and IB2G. It is interesting to note that the activation energy of the memory process is about 20% more than that required in the rotational polarization effect. The meaning of this difference lies in the fact that the memory process involves several molecules and so does higher activation barrier.

In order to make contact with molecular dynamic calculation, the torque normalization factor can be obtained using Eqs. (19) and (20), namely,

$$\psi = \frac{2\tau_0}{\delta} (k_B T)^2. \quad (23)$$

From here, the root mean square (rms) value of the torque fluctuations is obtained as $\psi^{1/2}$. This quantity expresses the value of the torque acting on the molecular dipoles involved in a random process of the fluctuations of dipole-dipole interactions. The temperature dependence of the rms value is shown in Fig. 6 for two substances, the DCMMS and IB2G. In this figure, the dashed line shows the linear dependence with $k_B T$ for which $\tau_0 = \delta$. It can be observed that some points deviate from this line, caused by the differences on temperature behavior of the τ_0 and δ . Notice should be made that the rms value of the torque fluctuations is proportional to the factor $k_B T$ and then to the kinetic energy of the material. According to the equipartition principle of the energy, the dipole-interaction fluctuations make an important contribution to the memory process if the ratio of τ_0 and δ is of the order of one. Therefore, the experimental observation of the SOMF has the limit condition given by $\tau_0 > \delta$. Libration oscillations were reported^{14,15} for condensed systems of molecules with permanent dipoles with $\tau_0 = \delta$.

IV. DISCUSSION AND CONCLUSIONS

The SOMF obtained directly from the experimental data was compared with that obtained using the HN equation and the three-variable model. This comparison shows that the HN equation does not describe some important features of

the real and imaginary parts of the SOMF in the used frequency domain (10^{-2} – 10^5 Hz). The study of these features is the main goal of this paper.

The comparison between the SOMF obtained from experimental data and the three-variable model leads to some interesting observations.

- (1) The presence of the relative maximum in the imaginary part of the SOMF is related to the maximum of the libration peak described by the model. From the knowledge of the position of this peak, the relaxation time of the torque correlation is obtained.
- (2) The value of this relative maximum is proportional to the half of the microscopic time (τ_0), while the equality is predicted by the model.
- (3) In the low-frequency limit, the behavior of the SOMF is not well defined.
- (4) In the region of the high frequencies, the actual behavior of the imaginary part of the SOMF does not follow a Lorentzian form as the three-variable model predicts. The decaying is of the power-law form with a fractional exponent, and this is explained by considering the dynamic heterogeneity effect. In this way, the memory and the dynamic heterogeneity can be separated in the representation of the SOMF using experimental data, as it was prescribed in this paper.
- (5) Finally, the relaxation time of the torque-autocorrelation function and the Debye-characteristic time are temperature dependent, having the form of the VTF law. The two main parameters of this law are E_D and T_∞ . Particularly, the activation energy associated with the memory process is about 20% more than that of the rotational diffusion process, whereas T_∞ is almost the same. This conclusion remains valid for the two substances considered here.
- (6) The rms value of the torque fluctuations is the other quantity we have reported in this paper, the results of which are proportional to the kinetic energy of the sample if τ_0 is of the same order of magnitude as δ .

ACKNOWLEDGMENTS

This work was supported in part by the UPV. One of the authors (L. F del C.) wishes to thank DGAPA-UNAM for support from Grant No. IN119200. Authors of the UPV also thank the Science and Technology Office of Spain for Grant No. MAT 1999-1127-C04-03.

¹J. P. Boon and S. Yip, *Molecular hydrodynamics* (McGraw-Hill, New York, 1960).

²R. Kubo, *J. Phys. Soc. Jpn.* **12**, 570 (1957).

³H. Mori, *Prog. Theor. Phys.* **33**, 423 (1965); **34**, 399 (1965).

⁴L. C. Sparling and L. E. Reichl, *Phys. Rev. A* **29**, 2194 (1984).

⁵J. B. Hubbard and P. G. J. Wolynes, *J. Chem. Phys.* **69**, 998 (1978).

⁶L. C. Sparling, L. E. Reichl, and J. E. Sedlak, *Phys. Rev. A* **33**, 699 (1986).

⁷T. W. Nee and R. Zwanzig, *J. Chem. Phys.* **52**, 6353 (1970).

⁸E. Fatuzzo and P. R. Mason, *Proc. Phys. Soc., London* **90**, 741 (1967).

⁹R. Kubo, *Rep. Prog. Phys.* **29**, 255 (1966).

¹⁰D. Kivelson and P. A. Madden, *Mol. Phys.* **30**, 1749 (1975).

- ¹¹R. L. Fulton, *Mol. Phys.* **29**, 405 (1975).
- ¹²W. Götze, in *Liquids Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1989).
- ¹³A. Rahman and F. H. Stillinger, *J. Chem. Phys.* **55**, 3336 (1971).
- ¹⁴P. A. Madden and D. Kivelson, *Adv. Chem. Phys.* **56**, 467 (1984).
- ¹⁵R. Lobo, J. E. Robinson, and S. Rodriguez, *J. Chem. Phys.* **59**, 5992 (1973).
- ¹⁶W. A. Steele, *Adv. Chem. Phys.* **34**, 1 (1964).
- ¹⁷R. Díaz-Calleja, M. J. Sanchis, and L. F. del Castillo, *J. Chem. Phys.* **109**, 9057 (1998).
- ¹⁸J. R. McDonald, "Complex Non-Linear Least Squares Inittance Fitting Program," LEVM6, 1993.
- ¹⁹K. Schmidt-Rohr and H. W. Spiess, *Phys. Rev. Lett.* **66**, 3020 (1991).
- ²⁰M. T. Cicerone, R. F. Blackburn, and M. D. Ediger, *J. Chem. Phys.* **102**, 471 (1995).
- ²¹C. T. Moynihan, *Phys. Chem. Glasses* **14**, 122 (1973).
- ²²C. A. Angell, *J. Non-Cryst. Solids* **3**, 131 (1991).