

Dielectric and shear mechanical relaxations in glass-forming liquids: A test of the Gemant-DiMarzio-Bishop model

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The Gemant-DiMarzio-Bishop model, which connects the frequency-dependent shear modulus to the frequency-dependent dielectric constant, is reviewed and a new consistent macroscopic formulation is derived. It is moreover shown that this version of the model can be tested without fitting parameters. The reformulated version of the model is analyzed and experimentally tested. It is demonstrated that the model has several nontrivial qualitative predictions: the existence of an elastic contribution to the high-frequency limit of the dielectric constant, a shift of the shear modulus loss peak frequency to higher frequencies compared with the loss peak frequency of the dielectric constant, a broader alpha peak, and a more pronounced beta peak in the shear modulus when compared with the dielectric constant. It is shown that these predictions generally agree with experimental findings and it is therefore suggested that the Gemant-DiMarzio-Bishop model is correct on a qualitative level. The quantitative agreement between the model and the data is on the other hand moderate to poor. It is discussed if a model-free comparison between the dielectric and shear mechanical relaxations is relevant, and it is concluded that the shear modulus should be compared with the rotational dielectric modulus, $1/(\epsilon(\omega)-n^2)$, which is extracted from the Gemant-DiMarzio-Bishop model, rather than to the dielectric susceptibility or the conventional dielectric modulus $M=1/\epsilon(\omega)$. © 2005 American Institute of Physics. [DOI: 10.1063/1.2136886]

I. INTRODUCTION

The understanding of the dynamics in liquids close to the glass transition is one of the main fundamental questions in condensed-matter physics. The phenomenology is rich and a full understanding calls for measurements over a large range of temperatures and frequencies.^{1,2} Dielectric spectroscopy plays an important role in the field, because dielectric measurements are comparably easy to perform with high accuracy over a large frequency span.^{3,4} It is, however, rare that theories and models refer directly to the dielectric properties of the liquid. It is therefore important to understand how the dielectric response is related to microscopic dynamics and more fundamental macroscopic properties, such as the shear viscosity.

It is a general understanding that shear mechanical and dielectric relaxations are somehow connected. The results of dielectric measurements are therefore often compared with the shear mechanical behavior of the liquid either via the Debye-Stoke-Einstein (DSE) time,⁵⁻⁹ or by direct comparisons of the shear relaxation and the dielectric relaxation.⁶⁻¹³

The idea of connecting dielectric relaxation to shear properties goes back to the classical Debye model which attributes the frequency dependency of the dielectric spectrum to the interaction of the dipoles with a viscous liquid.¹⁴ The Debye model predicts exponential relaxation, commonly referred to as Debye relaxation, while the spectrum found in glass forming liquids is considerably broader. Cole¹⁵ and Fatuzzo and Mason¹⁶ attempted to improve the Debye model by using, respectively, the Onsager field and a frequency-dependent Onsager-type field in place of the Lorentz field which was used by Debye. A different approach to improve the Debye model is to take the liquid's viscoelasticity, i.e., the frequency dependence of the viscosity itself, into account. This type of generalization of the Debye model was first proposed by Gemant¹⁷ and later derived by DiMarzio and Bishop.¹⁸ We therefore refer to the model as the Gemant-DiMarzio-Bishop model (the GDB model, for convenience).

The purpose of the present work is to test the GDB model against the set of shear mechanical and dielectric data, taken on seven different liquids, which we present in Ref. 19. However, the macroscopic version of the GDB model which was tested in the original paper, and which has been quoted and tested by other groups, is inconsistent with the physics that it aims to describe. In order to test the model, we therefore recast the macroscopic model in a physically consistent form and analyze which qualitative and quantitative predictions the model can be brought to give.

We start by briefly reviewing the Debye and GDB models and proceed by formulating the new consistent macroscopic formulation in Sec. III. In Secs. IV and V we discuss

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and test the qualitative and the quantitative predictions which can be extracted from the GDB model and compare these predictions to the data. In Sec. VI we consider the question of whether dielectric susceptibility or modulus can be compared with shear modulus and show that the GDB model offers a third, physically meaningful alternative. The overall status of the GDB model is finally discussed in Sec. VII.

II. REVIEW OF THE DEBYE AND THE GDB MODELS

The GDB model and the Debye model are microscopic models, describing the average linear rotational response of a single dipole, when subjected to an average local field, \mathbf{E}_d . Such a description relies on the assumption that the average of the permanent dipole moment $\langle \boldsymbol{\mu} \rangle$ can be written as

$$\langle \boldsymbol{\mu} \rangle = \alpha_r \mathbf{E}_d, \quad (1)$$

and hence the scope of the model is to give an expression for the rotational polarization coefficient (α_r).

It is hard to test the microscopic model directly, hence (as we will discuss later in detail) the microscopic model is normally converted to a macroscopic model using some assumptions. This macroscopic formulation is commonly what is meant when the GDB model is discussed, and we will also frequently use the term “model” when referring to the macroscopic model, but it is important to realize that different macroscopic formulations can be derived from the same microscopic model.

The original Debye model,¹⁴ which is based on Einstein’s work on translational diffusion,²⁰ can be summarized in the following five points.

- The liquid is assumed to have a frequency-independent viscosity η_0 .
- The relaxing entity is an ideal dipole (with a dipole moment of norm μ) in the center of a sphere with radius r .
- The dipoles are noninteracting (giving a random orientation of the dipoles in the equilibrium situation without an external electric field).
- The dipole’s interaction with its surroundings is modeled as a macroscopic entity in a continuous liquid (using Stokes law and a no slip boundary condition).
- The Lorentz field is used as local field.

To our knowledge the first to consider the effect of viscoelasticity was Gemant.¹⁷ Gemant arrives at his model by a generalization of an electrical circuit model of the Debye model. Havriliak and Havriliak²¹ suggest that the Gemant model should be erroneous or unphysical as they are not able to reproduce the results of Gemant. We are able to reproduce the results of Gemant and disagree that there should be anything erroneous in the model of Gemant. The Gemant model is in fact just a less general form of the model suggested by DiMarzio and Bishop. The only difference is that Gemant restricts the analysis to a specific model for the shear response.

DiMarzio and Bishop¹⁸ derive the model in a general form using the same approach and assumptions as Debye, but generalizing the equations to describe a viscoelastic liquid. This means that DiMarzio and Bishop maintain all but the first of the five points listed above.

The model leads to a differential equation describing how the average orientation of the dipole changes as a function of time when a field is applied. It is given by²²

$$\frac{\partial f}{\partial t} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \left(\int_{-\infty}^t D(t-t') \frac{\partial f}{\partial \theta} \Big|_{t=t'} dt' - f \int_{-\infty}^t V(t-t') M(t') dt' \right) \right], \quad (2)$$

where f is the probability density function describing the distribution of orientations of dipoles, θ is the angle between the field and the dipole, D is the angular diffusion memory function, V is the angular mobility memory function, and M is the torque due to the directing field ($M = -\mu E_d \sin \theta$). The two memory functions are related by $D(t) = k_B T V(t)$.

Solving the above differential equation, for a harmonic input, to first order, using a frequency-dependent Stokes friction term [$1/V(\omega) = 8\pi\eta(\omega)r^3$], where r is the molecular radius, and averaging over the directions of the dipoles, leads to the following model for the rotational polarization coefficient:

$$\begin{aligned} \alpha_r(\omega) &= \frac{\mu^2}{3k_B T (1 + (4\pi r^3/k_B T) i\omega \eta(\omega))} \\ &= \frac{\mu^2}{3k_B T (1 + (4\pi r^3/k_B T) G(\omega))}, \end{aligned} \quad (3)$$

where the second equality is obtained by using the relation $G(\omega) = i\omega \eta(\omega)$. This result is identical to the Debye model, except for the fact that the η_0 which appears in the Debye model has been replaced by $\eta(\omega)$. This difference between the GDB model and the Debye model can also be expressed in terms of the memory functions in Eq. (2), since the assumption of a frequency-independent viscosity results in memory functions of the form $V(t) = V_0 \delta(t)$ with $(1/V_0 = 8\pi\eta_0 r^3)$, which reduces the integrals to products. As no assumptions about the frequency dependency of $\eta(\omega)$ enters the derivation of the microscopic model, it can equally well be used at all frequencies and hence it should in principle describe both the alpha and the beta relaxations.

Equation (3) is in principle the model prediction we aim to discuss and test. However, it deals with microscopic quantities which are not directly accessed by dielectric spectroscopy. The measured quantity is the total polarization which contains a contribution from molecular induced polarization (changed electron distribution) in addition to the rotational contribution which has our interest. An additional problem arises because the average field which in effect contributes to the rotation of the molecules, \mathbf{E}_d , and that which contributes to the induced polarization, \mathbf{E}_i , are different and in both cases different from the macroscopic average field which is applied \mathbf{E}_m , (see Refs. 23 and 24).

The relation between the total polarization (\mathbf{P}) and the macroscopic and microscopic quantities, respectively, is given by

$$\begin{aligned}\mathbf{P} &= N(\alpha_i \mathbf{E}_i + \langle \boldsymbol{\mu} \rangle) \\ &= N(\alpha_i \mathbf{E}_i + \alpha_r(\omega) \mathbf{E}_d) \\ &= (\epsilon(\omega) - 1) \epsilon_0 \mathbf{E}_m,\end{aligned}\quad (4)$$

where N is the number of dipoles per volume, α_i is the molecular induced polarization coefficient, and $\epsilon(\omega)$ is the frequency-dependent dielectric constant. It is hence necessary to have a relation between the macroscopic field and the local fields, and to eliminate the contribution from induced polarization, when testing the model for α_r by measuring the dielectric constant.

DiMarzio and Bishop assume that $G(\omega) \rightarrow \infty$ for $\omega \rightarrow \infty$ and $G(0)=0$ and they use the Lorentz field for both local fields in order to arrive at a macroscopic formulation. The macroscopic formulation they test and the equation which is considered in all the references that cite them [Eq. (I.1) of Ref. 18] reads

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_e - \epsilon_\infty} = \frac{1}{1 + (4\pi r^3/k_B T)((\epsilon_e + 2)/(\epsilon_\infty + 2))G(\omega)}, \quad (5)$$

where ϵ_∞ is the high-frequency limit of the dielectric constant, and ϵ_e is the low-frequency equilibrium value.

The limit $\omega \rightarrow \infty$ value is interpreted by DiMarzio and Bishop as the plateau value which is reached in dielectric spectroscopy (≈ 1 MHz). It is noted by DiMarzio and Bishop that the assumption $G(\omega) \rightarrow \infty$ for $\omega \rightarrow \infty$ is wrong if a Maxwell model is used for the frequency-dependent shear modulus. However, a more serious problem, which DiMarzio and Bishop do not consider, is that the assumption is wrong in general since it is an experimental fact that G reaches a plateau in the considered frequency region meaning that G_∞ is finite. The consequence is that the high-frequency limit of Eq. (5) is wrong. This can be seen by considering the high-frequency limiting behavior: the left side of the equation will approach zero while the right side approaches a finite value.²⁵ DiMarzio and Bishop give a consistent formulation in the Appendix of Ref. 18. However, this formulation is rather inconvenient because it requires that G_∞ , ϵ_∞ , and ϵ_e must all be known, which is rarely the case, and experimental tests of this version of the model have never been reported. A different macroscopic version of the GDB model is therefore needed in order to make an adequate test of the model.

III. REFORMULATION OF THE MACROSCOPIC GDB MODEL

In the following we propose a new consistent and simple macroscopic formulation of the GDB model which we use as starting point for testing the model [Eq. (3)] in the following sections.

The Lorentz field is used as the local fields (the directing and inducing fields) as it is also done in the Debye and DiMarzio-Bishop formulations. We will return to a brief discussion of the consequence of this choice at the end of Sec.

V. The use of the Lorentz field leads to the Clausius-Mossotti approximation,²³ which connects the macroscopic accessible dielectric constant to the microscopic properties,

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{N}{3\epsilon_0}(\alpha_r(\omega) + \alpha_i). \quad (6)$$

The induced polarizability can be related to the refraction index through the Clausius-Mossotti approximation as²⁶

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N}{3\epsilon_0} \alpha_i. \quad (7)$$

Combining Eqs. (3), (6), and (7) with the fact that $G(0)=0$ yields the below result after some algebraic manipulation²⁷

$$\frac{\epsilon(\omega) - n^2}{\epsilon_e - n^2} = \frac{1}{1 + (4\pi r^3/k_B T)((\epsilon_e + 2)/(n^2 + 2))G(\omega)}. \quad (8)$$

The result appears similar to the original macroscopic formulation (5), however, it has a different high-frequency behavior, because ϵ_∞ may differ from n^2 . The consequence is that both right and left sides of the equation have finite high-frequency limiting values. The physical meaning of this is that the rotation of the dipoles contributes to the polarization even at high frequencies, due to an instantaneous elastic rotation. Note that we have adapted the convention of referring to the plateaus found in $\epsilon(\omega)$ and $G(\omega)$ around 1 MHz as high-frequency limits. This is a regime where the inertia of the molecule plays no significant role.

IV. QUALITATIVE PREDICTIONS OF THE REFORMULATED MODEL

The GDB model is a simple model and it is therefore not expected to capture all details of the relation between the dielectric and the shear mechanical relaxations. We have therefore investigated which qualitative predictions the model offers and include these in our overall test and discussion of the GDB model.

A. Comparison of the dielectric and shear mechanical losses

A detailed analysis of the model, where we have taken a characteristic shear spectra and calculated the corresponding dielectric signal from the GDB model while varying the controlling parameter in a complete manner,²⁸ reveals the following qualitative predictions regarding the shear modulus and dielectric constant.

- The alpha loss peak of the shear modulus is found at a higher frequency than the alpha loss peak in the dielectric constant measured at the same temperature.
- The shear alpha loss peak is broader than the dielectric alpha loss peak.
- The relative beta relaxation strength, measured as beta relaxation strength over alpha relaxation strength, is larger in the shear modulus than in the dielectric constant.

The position of the loss peaks has been analyzed multiple times in the literature (see, e.g., Refs. 6–8, 10, and 29–31), and it is always found that the shear moduli loss peak is positioned at a higher frequency than the loss peak of the dielectric constant in agreement with the GDB model. In Ref. 19 we present a comparison covering all the three predictions above (see also Ref. 9 for comparison of the shape of the loss peaks), and the general behaviors found are in agreement with the GDB model prediction. Hence the model appears to capture some of the general tendencies of the relationship between the two relaxation processes. Especially the shift in loss peak is a robust result which has been reported several times, while to our knowledge it has not been pointed out that this is in fact a general prediction of the GDB model.

B. High-frequency limit of dielectric constant

The main difference between the original macroscopic version of the GDB model [Eq. (5)] and the reformulation which we present here [Eq. (8)] lies, as earlier pointed out, in the high-frequency limit. From Eq. (8) it is seen that $\lim_{\omega \rightarrow \infty} \epsilon(\omega) > n^2$ because $\lim_{\omega \rightarrow \infty} G(\omega) < \infty$. Thus we find that the GDB model predicts a contribution from elastic rotation to the dielectric constant. This is an important qualitative difference from the original Debye model, and this prediction cannot be extracted from the macroscopic formulation in Eq. (5) and it has not been considered in the treatment of DiMarzio and Bishop nor by those who cite them.

It is not as simple as it might seem to test directly whether $\epsilon_\infty > n^2$, and hence difficult to verify the existence of the predicted elastic contribution to the dielectric constant. The first obstacle is that it is rare to find refraction index data at low temperatures. This problem could be overcome if expansivity data were available in the relevant temperature range.

The second problem is to perform dielectric measurements with high absolute precision. This is difficult because the degree to which the measuring capacitor is filled with sample, $f(T)$, and the distance between the capacitor plates $d(T)$ need to be known very exactly. These quantities are both temperature dependent and not trivial to control or monitor during the experiment, due to the thermal expansion/contraction of the sample. The consequence is that the measured capacitance will be given by

$$C(\omega, T) = f(T) \frac{A \epsilon(\omega, T) \epsilon_0}{d(T)} + (1 - f(T)) \frac{A \epsilon_0}{d(T)}, \quad (9)$$

this is divided by a temperature-independent capacitance of the empty cell, $C_0 = A \epsilon_0 / d_0$, to obtain the measured dielectric constant,

$$\begin{aligned} \epsilon_m(\omega, T) &= \frac{C(\omega, T)}{C_0} \\ &= \frac{d_0}{d(T)} f(T) \epsilon(\omega, T) + \frac{d_0}{d(T)} (1 - f(T)). \end{aligned} \quad (10)$$

Hence $\epsilon_m(\omega, T) = \epsilon(\omega, T)$ will only be true in the ideal situation where $d(T) = d_0$ and $f(T) = 1$.

An alternative to direct verification of $n^2 < \epsilon_\infty$ is to study the temperature dependence of the high-frequency value of the dielectric constant. In doing so we include considerations on how the change of sample geometry due to thermal effects influences the absolute value of the dielectric constant which is actually measured.

The high-frequency limit of the GDB model is in the Maxwell approximation³² given by

$$\epsilon_\infty - 1 = \frac{N}{\epsilon_0} \left(\alpha_i + \frac{\mu^2}{3k_B T (1 + (4\pi r^3 / k_B T) G_\infty)} \right). \quad (11)$$

Combining this expression with Eq. (10), and assuming that α_i is temperature independent, gives the following changes in the measured high-frequency limit of the dielectric constant as the temperature increases.

- (1) Model predictions
 - (a) Effect giving increasing ϵ_∞
 - (i) G_∞ decreases
 - (b) Effects giving decreasing ϵ_∞
 - (i) N decreases due to thermal expansion
 - (ii) T increases
- (2) Experimental problems
 - (a) Effect giving increasing $\epsilon_{\infty, m}$
 - (i) Liquid expands in the direction parallel to the plates, leading to an increase in the degree of filling of the capacitor $f(T)$.
 - (b) Effects giving decreasing $\epsilon_{\infty, m}$
 - (i) Liquid expands in the direction perpendicular to the plates, leading to an increase in the spacing of the capacitor $d(T)$.

There are two effects giving an increase in the measured high-frequency dielectric constant, an expansion which leads to increased filling of the capacitor and an increasing elastic contribution. It is easily shown that the effect of the increased filling of the capacitor is counterbalanced by the effect from the decreased dipole density in the extreme case where the expansion only leads to a change in $f(T)$ while $d(T)$ is constant (exploiting that the total number of dipoles is constant). This means that an increase in the measured $\epsilon_{\infty, m}$ cannot be due to geometrical effects but has to be due to an increase in the microscopic high-frequency polarizability corresponding to the increase in the elastic contribution.

In Fig. 1 the measured high-frequency dielectric constant, $\epsilon_{\infty, m}$, is shown for three liquids with increasing dielectric relaxation strength (data from Ref. 19). We see a decrease in $\epsilon_{\infty, m}$ with rising temperature in the case of triphenylethylene (TPE) and tetramethyltetraphenyltrisiloxane (DC704), which are both liquids with small dielectric strength. Our interpretation of the results is that the primary expansion is an isoarea expansion giving an increasing

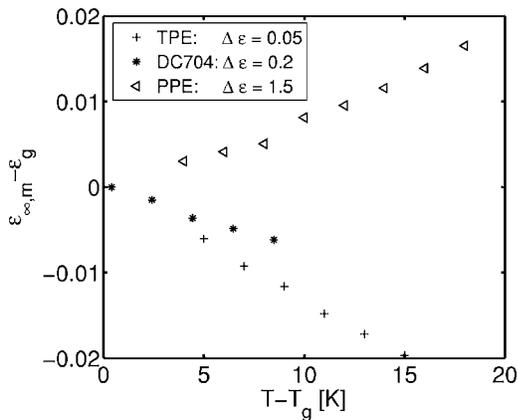


FIG. 1. High-frequency limit of the measured dielectric constant [see Eq. (10)] from three liquids; triphenylethylene (TPE), tetramethyltetraphenyltrisiloxane (DC704), and polyphenyl ether (PPE). $\Delta\epsilon$ is the dielectric relaxation strength (difference between zero-frequency limit and high-frequency plateau), T_g is the glass temperature, and ϵ_g is the high-frequency limit of the dielectric constant at the glass temperature. These results are based on the data presented in Ref. 19, where full information on experimental techniques can be found.

distance between the capacitor plates, $d(T)$, while $f(T)$ is constant. This thermal expansion will give a decrease in the measured high-frequency value, $\epsilon_{\infty,m}$. It is reasonable to assume $\epsilon_{\infty}(T) \approx n^2(T)$ in the case of TPE where the dielectric strength is very small. Combining this with the assumption of an isoarea expansion leads to the result that $d\epsilon_{\infty,m}/dT = -\alpha$, where α is the thermal-expansion coefficient. The value found for TPE is $d\epsilon_{\infty,m}/dT = -1.4 \times 10^{-3} \text{ K}^{-1}$, which corresponds well to the α values normally found for viscous liquids close to T_g , thus supporting the interpretation of isoarea expansion.

The $\epsilon_{\infty,m}$ of polyphenyl ether (PPE) which has an order of magnitude larger dielectric strength than DC704 shows an increase with temperature. This means that the microscopic high-frequency polarizability increases with temperature. The effect dominates over the effect of expansion because PPE has a larger dielectric strength.

It is impossible to calculate if the actual ϵ_{∞} has a T dependence corresponding to that of G_{∞} because of the large uncertainties on n as well as $f(T)$ and $d(T)$. It is, however, clear that the increase in $\epsilon_{\infty,m}$ as a function of temperature which is seen in the PPE data must be due to a high-frequency rotational reorientation of the permanent dipoles, meaning that $\epsilon_{\infty} > n^2$ such as it is predicted from the GBD model.

V. QUANTITATIVE TEST

The GDB model has been tested and used a number of times (see, e.g., Refs. 10, 12, 13, and 31), but all these tests are performed in different ways, and it is hard to be conclusive about the quality of the microscopic model. We have therefore tested the quantitative predictions of the model on the systematic data sets presented in Ref. 19.

The GDB model is normally tested in a dielectric constant formulation [like Eq. (8)] making the molecular radius r the controlling parameter. r is inconvenient since it is an inaccessible microscopic parameter, and the interpretation

can be disputed as real molecules are not spheres. The interpretation of r is, in particular, ambiguous in the case of polymers where the size of the relaxing entity is not *a priori* known. In order to test the GDB model on the relaxation spectra it is therefore convenient to express it in terms of the moduli, rewriting Eq. (8) to

$$G(\omega) = \left(\frac{k_B T}{4\pi r^3} \right) \left(\frac{n^2 + 2}{\epsilon_e + 2} \right) \left(\frac{\epsilon_e - n^2}{\epsilon(\omega) - n^2} - 1 \right). \quad (12)$$

As n^2 and ϵ_e are real numbers this can be formulated as

$$\text{Im}(G(\omega)) = A \text{Im} \left(\frac{1}{\epsilon(\omega) - n^2} \right), \quad (13)$$

if only the imaginary part is considered. A is a real temperature-dependent constant given as $A = (k_B T / 4\pi r^3) \times (n^2 + 2)(\epsilon_e - n^2) / (\epsilon_e + 2)$.

Whereas Eqs. (5) and (8) differ because they are based on different physical assumptions, there is no difference in the physical content of Eqs. (8) and (13). It is just a matter of which quantity is isolated in the equation. This, however, does not mean that one equation can be used just as well as the other. Equation (13) is much better suited for experimental tests of the model, because the shape and position of the calculated shear mechanical loss peak depend only on the macroscopic physical quantity n^2 . This means that a *parameter-free* test of the GDB model is possible by comparing the loss peak shape and position of the left- and right-hand sides of Eq. (13), and that this is possible even if the high-frequency and low-frequency limiting values are not known from the experiment.

As discussed earlier, the absolute errors of $\epsilon(\omega)$ are large, and n^2 is not commonly available at the relevant temperatures. These uncertainties can be formulated in terms of the value of n which is to be used in testing the model, hence replacing n in Eq. (13) with a parameter \tilde{n} . Following the line of thought in Sec. IV B it can easily be shown that a lower bound on \tilde{n}^2 is the actual n^2 at room temperature, T_{room} , and that an upper bound is the measured high-frequency value of the dielectric constant; that is $n^2(T_{\text{room}}) < \tilde{n}^2(T) < \epsilon_{\infty}(T)$ for $T < T_{\text{room}}$. We have for each sample determined \tilde{n}^2 at a temperature where both high- and low-frequency ends of dielectric and shear responses were reached by the measurement by using the value of \tilde{n}^2 within these constraints, which gives the best fit between the measured and calculated shear moduli. The temperature dependence of \tilde{n}^2 was subsequently estimated assuming isoarea expansion, in order to test the model at all temperatures. The consequence is that the test of the model is not parameter free as it could ideally be according to Eq. (13). However, there is just one parameter, and the physical values of this parameter are firmly restricted because it is a parameter that refers directly to macroscopic properties of the liquid.

The absolute size of the interval which is permitted for \tilde{n}^2 by the procedure described above is of the same order of magnitude for all liquids (all having room temperature \tilde{n}^2 and high-frequency value in a rather narrow interval). This

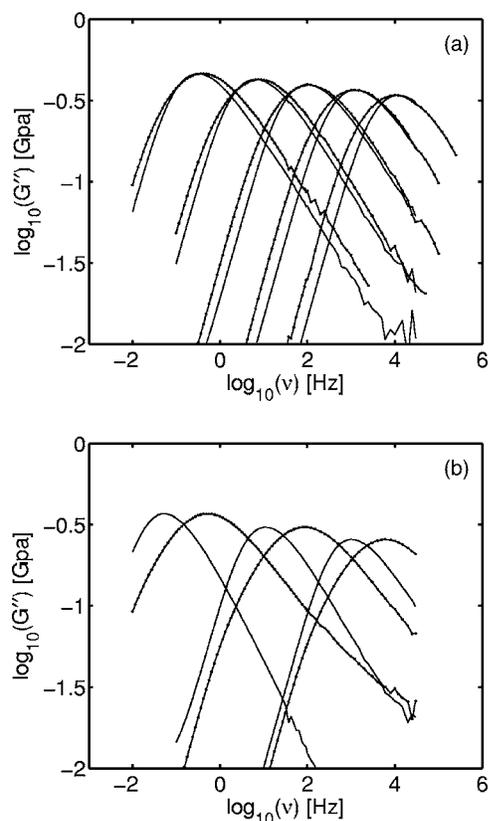


FIG. 2. Test of the GDB model on tetramethyltetraphenyltrisiloxane (DC704) (a) and polyphenyl ether (PPE) (b), data (solid line) are from the datasets presented in Ref. 19 where all experimental details also exists. Predicted shear modulus (solid dotted line) is calculated from the dielectric constant using Eq. (12), refraction index is chosen as described in the text, and the constant A in Eq. (13) is chosen to make the level of the loss peaks agree, thus focusing on the position and shape of the loss peak. DC704: Temperatures are 215.4, 219.5, 223.5, 227.6, and 231.6 K with \bar{n}^2 chosen as 2.5073, 2.5024, 2.4976, 2.4927, and 2.4879. PPE: Temperatures are 248.0, 256.0, and 264.0 K with \bar{n}^2 chosen as 2.71, 2.70, and 2.69.

leads to a larger relative uncertainty (compared with the dielectric strength) in the case of liquids with little dielectric strength.

In Fig. 2 tests on two liquids without a visible beta relaxation are shown. DC704 has a small dielectric relaxation strength, the difference between zero-frequency limit, and high-frequency plateau is approximately 0.2, PPE has a rather large dielectric relaxation strength of approximately 1.5. It can be seen that the model predictions agree fairly well for DC704, but that in the case of PPE the model predicts a loss peak frequency which is approximately one decade too high. The loss peak predicted by the model is moreover too wide as compared with the actual shear mechanical loss peak.

In Fig. 3 a test of the model on tripropylene glycol (TPG), which shows a pronounced beta relaxation, is shown. The model has the same flaws as in the case of PPE and it furthermore overestimates the beta relaxation strongly.

The same procedure of testing the GDB model was performed on TPE, squalane, polybutadiene, and decahydroisoquinoline.²⁸ The general picture is as illustrated above. The beta relaxation is never well described by the

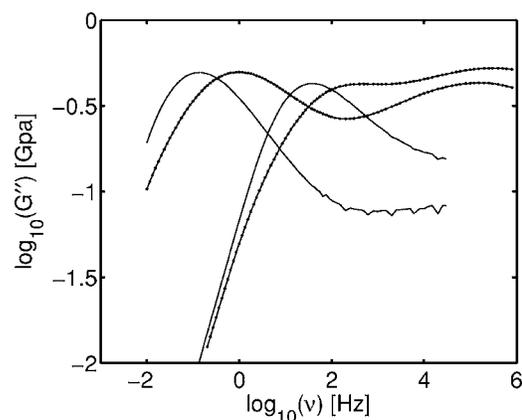


FIG. 3. Test of the GDB model on tripropylene glycol (TPG), details as in Fig. 2. Temperatures are 192.0 and 200.0 K, with $\bar{n}^2=2.1$.

model, while the alpha relaxation is reasonably well described when the dielectric relaxation strength is small but not when it is large.

The correlation between the size of the dielectric strength and the lack of the model predictions leads to the suspicion that the discrepancies could be due to the inadequateness of the Lorentz field used as the local fields. The consequence of using a different local field has been tested by Diaz-Calleja *et al.*³¹ and Diaz-Calleja and Riande³³ who compare the original version of the GDB model with a version modified by using the frequency-dependent Onsager-type field³⁴ of Fatuzzo and Mason¹⁶ and find that the effect is small. We have also studied the effect of using different fields²⁸ and find that the choice has virtually no effect in the case of liquids with small dielectric strength and small effect in the case of liquids with large dielectric strength. The result in the latter case depends on how the fitting parameters are chosen; the difference between the fields is only seen if the controlling fitting parameter is kept fixed while changing field, whereas no difference is found in the model's ability to fit the data if different, yet physically reasonable values are used for the parameter along with the Maxwell, the Lorentz, Onsager, or Fatuzzo-Mason fields, respectively.

Another consideration is that if field effects, referred to in Refs. 31 and 33 as dielectric friction, were of major importance then we should expect that the dielectric relaxation itself would have different shape depending on the dielectric strength. However, such a relation does not seem to be present.¹⁹

The conclusion drawn from the above is that it is the microscopic model itself that fails to describe the relaxation for the liquids with large dielectric strength.

VI. MODULUS VERSUS SUSCEPTIBILITY

The GDB model is rather coarse grained and it could be argued that a model-free comparison between the dielectric and the shear mechanical signals could be as useful. However, "model-free" is not as trivial as it might sound, since there are always choices to be made. It is often argued that moduli should be compared with moduli when comparing different types of relaxation processes,^{1,35,36} and the dielectric modulus $M(\omega)=1/\epsilon(\omega)$ is often compared with the

shear mechanical modulus. The major, and generally ignored, problem with this quantity is that the induced polarization interferes with the rotational polarization in a non-trivial manner.

We define the rotational contribution to the dielectric constant, $\chi_r(\omega)$, by the total dielectric constant minus the squared refraction index, meaning,

$$\epsilon(\omega) = n^2 + \chi_r(\omega). \quad (14)$$

Thus the loss of the modulus can be written as

$$M''(\omega) = - \frac{\chi_r''(\omega)}{(n^2 + \chi_r'(\omega))^2 + \chi_r''(\omega)^2}. \quad (15)$$

The fact that n^2 appears in the denominator makes it influence both the shape and the peak position of the $M''(\omega)$ spectra. In other words, two liquids which have the same $\chi_r(\omega)$ but different n^2 can have quite different dielectric modulus. The effect of the induced polarization on the dielectric modulus is dependent of the dielectric relaxation strength compared with n^2 . There is little difference between the shape and position in loss peak of ϵ and $1/\epsilon$, if the dielectric relaxation strength is small. This can be seen from the following approximation:

$$M''(\omega) \approx - \frac{1}{n^4} \chi_r''(\omega) \quad \text{given that } |\chi_r(\omega)| \ll n^2 \text{ for all } \omega. \quad (16)$$

In the case of a large dielectric relaxation strength the effect of the induced polarization will be highly frequency dependent because the high-frequency limit of $\epsilon(\omega)$ is close to n^2 whereas the low-frequency limit is much greater. Hence there is a trivial difference between the dielectric modulus for substances with a large and small dielectric relaxation strengths, due to an effect which hardly can be imagined to be related to the mechanical properties of the liquid. A model-free comparison of moduli is consequently difficult.

It is instructive seen in this context to observe that the GDB model predicts a linear (affine) relation between the shear modulus and the quantity $1/(\epsilon(\omega) - n^2)$ which according to Eq. (14) is equal to $1/\chi_r(\omega)$. This quantity can be regarded as a rotational dielectric modulus, as it holds only information on rotation of the molecules in the liquid while the changes in electron distributions described by n^2 have been disentangled. It seems intuitively clear that it is the rotational dielectric response and not the change in electron distribution which should be compared with the shear mechanical response. Viewed like this the GDB model reduces to being the simplest physically reasonable phenomenological relation between shear and dielectric responses. The derivation of the model moreover offers a simple interpretation of the relation between the two responses.

VII. DISCUSSION

In this paper we have pointed out two rather strong qualitative predictions from the GDB model. One is that the shear loss peak is at a higher frequency than the dielectric loss peak. The other is that the high-frequency dielectric constant has a rotational contribution, meaning that $\epsilon_\infty > n^2$. The

first prediction is experimentally verified by our results as well as in several previous papers. The latter prediction is also demonstrated to hold in the one case where it was possible to test.

Moreover, the GDB model predicts that the shear spectra are broader and that the beta relaxation, if present, is more pronounced in the shear spectra. These predictions are less investigated, however, the results we report in Ref. 19 are largely in agreement with these predictions.

The result of the detailed testing of the GDB model in the reformulated consistent formulation, does, however, show that the GDB model power as quantitatively predictive is very questionable. The overall discrepancies could be due to the inadequateness of the Lorentz field used as the local fields. The effect from changing the local field is, however, minor,^{28,31} and a change of field cannot correct the rather large differences that are seen between the model and experiments.

The difference between the predicted and measured beta relaxation is one of the very pronounced discrepancies (as shown in Fig. 3). It has been speculated that the model might not work for beta relaxation¹² but in the derivation of the model nothing suggests this. Thus the model has to be re-derived with some modification if such a separation between the two relaxation processes is stipulated.

It is observed that the GDB model gives better results in the case of liquids with small dielectric constant. It could be speculated that the larger relative uncertainties on the value used for \tilde{n}^2 in the case of the liquids with a small dielectric strength could be the reason for the model's reasonable predictions. However, it could also be argued that the model might work better for substances with a small dipole moment, as the assumption of noninteracting dipoles should be more appropriate in this case. It is an important issue to clarify if the model in fact gives reasonable quantitative results in the case of small dielectric strength, further dielectric measurement with little absolute uncertainties, and direct measurement of n^2 are therefore needed.

It is clear that the GDB model is an oversimplified model, three of the major simplifications being that (i) continuum hydrodynamics is used to describe the interaction between a molecule and its surroundings, (ii) the dipoles are assumed to be noninteracting, and (iii) the molecules are described by spheres even though we know that they often differ largely from being spherical. It is therefore not surprising that the model seems to be only qualitatively correct and it has also been suggested earlier that the GDB model could be considered as qualitatively correct while quantitatively inadequate.¹² It should, however, be stressed that this conclusion was drawn on a totally different background than the one presented here. The earlier assertion were made on the basis of tests of the model where the radius of the relaxing entity, r , was used to fit Eq. (5) to the dielectric data. In Zorn *et al.*¹² such fits were performed on a series of different polybutadienes, and the r 's found in the fits reflected the expected difference in the size of the segmental dipole, even though the fits were not excellent. This was interpreted as a qualitative but not quantitative agreement between the GDB model and data.

The result of Zorn *et al.*¹² has been used in Ref. 13 to anticipate that the GDB model could be used for predicting the size of the dipole responsible for the alpha relaxation, and a similar approach is applied in Ref. 33. In our test of the GDB model we use the macroscopic parameter \tilde{n} as fitting parameter, and restrict the fit to the imaginary part of Eq. (12). If the real parts are included in the fit or if a measured value of one of the parameters (e.g., ϵ_e) is used then it is possible to estimate the molecular radius (r) from the parameters A and n^2 . We find that with our fits the order of magnitude of r is 1 Å. This value is consistent with values found previously by using r as fitting parameter,^{13,33} but it is too small to be a physically reasonable size for the relaxing entities. In addition to the fact that the order of magnitude of r appears too small, our analysis suggests that it is probably unreasonable to make even semiquantitative assertions regarding the size of r based on the GDB model. Acceptable fits using Eq. (13) (not shown) can be obtained for PPE and for the alpha relaxation of TPG if all values of \tilde{n}^2 are permitted. This gives $\tilde{n}^2=1.95$ in the case of PPE where $n(T_{\text{room}})^2=2.66$ and $\tilde{n}^2=-1$ (!) in the case of TPG. A negative value of \tilde{n}^2 as the one found for TPG is without any physical meaning as the absolute lower limit corresponding to the vacuum is $\tilde{n}^2=1$, and the value found for PPE is also clearly outside the physical reasonable range. The fits could of course equally well be done in a susceptibility picture using r as the fitting parameter. It is clear that an r value which corresponds to an \tilde{n}^2 value which is highly unphysical, cannot be expected in itself to hold any physical information. It is therefore highly questionable that the GDB model should be useful for predicting radii of dipoles.

Instead of trying to derive quantitative results (such as the molecular radius) from the model, the GDB model should rather be seen as the simplest physical picture of how the shear mechanical and the dielectric relaxations are related. The GDB model moreover lends itself as being the closest possible to a phenomenological comparison between the shear relaxations and the dielectric relaxations as neither a direct comparison between G and ϵ nor a comparison between G and M can be physically justified.

VIII. CONCLUSION

The GDB model has been reformulated and tested on a unique set of shear and dielectric data and it is concluded that the quantitative agreement between the model and measurements are moderate to poor. It is moreover argued that it is unlikely that the GDB model can be used for predicting molecular radii as suggested in earlier papers.

The GDB model does, however, predict a number of qualitative relations between shear and dielectric relaxation spectra, suggesting that the physical picture suggested by the GDB model, though simplified, might not be completely erroneous.

Rewriting the GDB model in terms of moduli gives an affine linear relation between the rotational dielectric modulus and the shear modulus. This relation can be regarded as a phenomenological relation between dielectric and shear responses and could very well prove useful as neither a direct

comparison between dielectric constant and shear moduli nor a comparison between the conventional dielectric modulus and shear modulus seems physically justified.

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