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An Eshelby model for highly viscous flow

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Abstract

The shear flow and the dielectric α -process in molecular glass formers is modeled in terms of local structural rearrangements which reverse a strong local shear. Using Eshelby's solution of the corresponding elasticity theory problem (Eshelby 1957 *Proc. R. Soc. A* **241** 376), one can calculate the recoverable compliance and estimate the lifetime of the symmetric double-well potential characterizing such a structural rearrangement. A full modeling of the shear relaxation spectra requires an additional parametrization of the barrier density of these structural rearrangements. The dielectric relaxation spectrum can be described as a folding of these relaxations with the Debye process.

1. Introduction

From an experimental point of view, broadband dielectric spectroscopy [1] is the most versatile method to study the flow process in undercooled molecular liquids. However, the relation between dielectric relaxation and shear flow is not yet clear. The classical Debye picture and its extension to viscoelasticity [2, 3] considers the molecule as a small sphere immersed in the viscoelastic liquid. It predicts a slow dielectric decay, about a factor of ten slower than the one found in experiment [4, 5]. A thorough quantitative analysis of dielectric and shear data in seven glass formers [6] showed a general qualitative agreement with the extended Debye scheme, but a rather poor quantitative fit.

One cannot help feeling that the extended Debye scheme mistreats the structural rearrangements of the highly viscous fluid. The Debye relaxation time of the molecular orientation is usually longer than the Maxwell relaxation time of the shear stress, the more so the larger the molecular volume is. No such retardation is expected for a local structural rearrangement, which ought to be characterized by the same relaxation time for shear and dielectrics. Thus the modeling should rather separate the viscous effects from those of the structural rearrangements, both in shear and dielectrics. Also, in the present unsettled state of understanding of the highly viscous flow, with many different ideas and recipes [7–11], an attempt to understand the viscous flow itself in terms of a sequence of structural rearrangements in time seems legitimate. This is the purpose of the present paper.

In order to contribute effectively to the flow, the structural rearrangement should change the shape of the rearranged

region in the direction of the flow. This implies a strained state of the embedding matrix, against the flow direction before the jump and in the flow direction after. This mechanism will be explained in detail in the next section, section 2. It leads to a finite lifetime of the corresponding double-well potential, because the surrounding matrix is itself able to flow. This lifetime implies a specific cut-off function for the barrier density of the structural rearrangements. The comparison with experiment in section 3 requires a specification of the barrier density, which does not follow from the same picture. As we will see, this requires three parameters even if there is no Johari–Goldstein secondary relaxation peak, and three more if such a peak is present. Such a large number of parameters makes it difficult to check the validity of the model with a certainty from the rather broad and featureless relaxation spectra.

2. The Eshelby model

2.1. Shear strain defects

The central concept of this model is a structural rearrangement of a limited region in the sample which changes its shape to a sheared one. A simple example of such a rearrangement is the special case of four closely packed spherical atoms or molecules shown in figure 1.

Imagine that the flow occurs by expansion in the vertical direction and a contraction of the horizontal direction of the figure. After a while, the four molecules at the top of the figure will no longer experience an adapted matrix, but rather a matrix which tends to compress them in the horizontal direction and

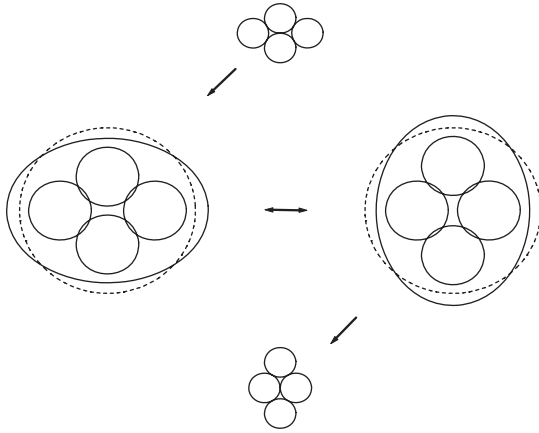


Figure 1. Elementary flow process (schematic), involving a rearrangement of four closely packed spherical atoms or molecules. The dashed lines show the shape of the hole containing the four molecules in the unstrained matrix, the continuous lines the shape of the hole in the strained matrix.

to tear them apart in the vertical one. Since the four molecules have the alternative of the equivalent close packing shown at the bottom of the figure, there is a moment in time at which one has a symmetric double-well potential for molecules and matrix, the situation at the center of the figure.

The Eshelby model described here supposes that the elementary flow process in molecular liquids is of this nature, not necessarily restricted to four molecules, but involving a structural rearrangement by a thermally activated jump between two stable locally ordered configurations with opposite shear strain with respect to the embedding matrix.

The physical problem of a small piece of matter able to transform to a sheared shape within an elastic matrix was treated fifty years ago by several authors, notably by Eshelby [12, 13].

Here, we translate Eshelby's result into the usual convention, in which the shear angle e and the shear stress σ are related by $\sigma = Ge$ (G infinite frequency shear modulus) at short times and by $\sigma = \eta \dot{e}$ (η viscosity) in the long time limit. Let v_i be the volume of the spherical inclusion and e_i the shear angle difference between its two stable configurations (in the example of figure 1, $e_i = \pi/3$). Then the energy of the two equally strained configurations of the center of figure 1 is

$$E_a = \frac{\gamma}{8} G v_i e_i^2. \quad (1)$$

The coefficient γ is given by

$$\gamma = \frac{7 - 5\sigma_P}{15(1 - \sigma_P)}, \quad (2)$$

where σ_P is Poisson's ratio. Since Poisson's ratio lies between 0.1 and 0.44 for the known glasses, γ lies between 0.48 and 0.57, close to 1/2.

Eshelby's solution divides the energy into two almost equal parts, one located in the inclusion and one outside. Their ratio is $\gamma/(1 - \gamma)$. The inclusion would have to distort by $e_i/2$ to fit exactly into the unstrained hole. In the four-atom case

of figure 1, this is the saddle point energy for the thermally activated jump between the two stable configurations. It is considerably less than twice the energy of the two stable Eshelby minima because the saddle point has a lower energy than the harmonic extrapolation. We will see later that this cannot be true for the defects which actually destabilize the amorphous solid.

The Eshelby treatment also supplies the interaction energy of the strain defect with the external stress component σ oriented along the shear strain e_i

$$E_{\text{int}} = -\frac{\sigma v_i e_i}{2}. \quad (3)$$

This implies that the asymmetry Δ between the two minima changes by $\sigma v_i e_i/2$ in the presence of an external stress σ , or by $e G v_i e_i/2$ in the presence of an applied external strain e .

2.2. Double-well potential lifetime and cut-off function

The lifetime τ_c of such a strain defect in the viscous liquid is estimated in a simple mean-field consideration. The shear stress outside the inclusion (see figure 1), where other and independent strain defects exist, can decay according to the Maxwell relaxation time

$$\tau_m = \frac{\eta}{G}. \quad (4)$$

We assume that the energy inside the inclusion can only decay by the yielding of the surrounding matrix. Then the energy which has to decay is about twice the outside energy, which implies that τ_c is about twice τ_m . More accurately, one has to take into account that the outside energy is not pure shear; about 10% of it is compressional energy, which cannot be expected to decay. Thus one should have

$$\tau_c = 2.2\tau_m. \quad (5)$$

The double-well potential lifetime τ_c determines the cut-off-barrier V_c of the strain defects participating in the flow process according to the Arrhenius equation

$$\tau_V = \tau_0 \exp(V/k_B T), \quad (6)$$

where T is the temperature and τ_0 is a microscopic lifetime of 10^{-13} s. At the critical energy barrier V_c , the potential decay begins to become faster than the jumps over the barrier. If the barrier is higher than V_c , the double-well potential begins to flow away before the population of the two minima can equilibrate. Therefore these higher barriers will not participate in the flow process.

Since one has two competing equilibration processes, the potential decay with the time constant τ_c and the thermally activated jumps over the barrier with the time constant τ_V , the contribution of the jump mechanism is given by the cut-off function $l_c(V)$

$$l_c(V) = \frac{\tau_c}{\tau_c + \tau_V} = \frac{1}{1 + \exp((V - V_c)/k_B T)}. \quad (7)$$

2.3. Stationary flow and recoverable compliance

In a stationary flow \dot{e} , the double-well potential asymmetry Δ changes continuously. If we ascribe \dot{e} to the continuous passage of inclusions from one stable configuration to the other, it must result from an integral over all these processes. The constant flow \dot{e} can be determined by counting all strain defects passing through the asymmetry zero. Let us denote by $n(V, \Delta)$ the number density of double-well potentials of barrier height V and asymmetry Δ in the sample. Since $\dot{\Delta} = \dot{e}Gve_i/2$ (see equation (3)), one would have a number of $\dot{e}Gve_i n(V, 0)\delta t/2$ of double-well potentials of height V per unit volume passing through the asymmetry zero in the time δt , if e and e_i had the same orientation. Since one has five independent shears, one has to add a factor $1/\sqrt{5}$ from the directional average.

The next question is: how much do these passing entities add to the shear flow? Each of these entities makes in the long run a contribution of ve_i to the flow, again with the factor $1/\sqrt{5}$ from the average orientation of the shear e_i of the defect to the flow direction. The total flow results from an integral over all these processes, so

$$\dot{e} = \dot{e} \int_0^\infty \frac{G(ve_i)^2}{2} \frac{n(V, 0)}{5} l_c(V) dV. \quad (8)$$

$l_c(V)$ is the cut-off at the barrier V_c from equation (7). Thus

$$\int_0^\infty \frac{(ve_i)^2 n(V, 0)}{10} l_c(V) dV = \frac{1}{G}. \quad (9)$$

Equation (9) can be used to calculate the contribution of the shear strain defects to the shear compliance. To do this, consider first the free energy $F = -k_B T \ln Z$ of a single strain defect with asymmetry Δ . The partition function Z is

$$Z = 2 \cosh \frac{\Delta}{2k_B T}. \quad (10)$$

Since the asymmetry Δ changes by $\sigma ve_i/2$ if one applies a stress σ in the direction of e_i , one has a contribution to the shear compliance determined by

$$\frac{\partial^2 F}{\partial \sigma^2} = - \frac{v^2 e_i^2}{16k_B T \cosh^2 \Delta / 2k_B T}. \quad (11)$$

In order to get the full recoverable compliance J_e^0 (the compliance after subtraction of the viscous flow contribution [14]), one has to integrate over the barrier heights V and the asymmetries Δ . Here, we assume that the dependence of $n(V, \Delta)$ on Δ is given by the Boltzmann factor $\exp(-F/k_B T)$

$$n(V, \Delta) = n(V, 0) \cosh \frac{\Delta}{2k_B T}. \quad (12)$$

The equation for the recoverable compliance is

$$J_e^0 = \frac{1}{G} + \int_0^\infty \int_{-\infty}^\infty \frac{v^2 e_i^2 n(V, 0)}{80k_B T \cosh \Delta / 2k_B T} dV d\Delta. \quad (13)$$

The asymmetry can be integrated out. With equation (9), one finds for the relaxational part of the recoverable compliance

$$GJ_e^0 - 1 \equiv f_0 = \frac{\pi}{4}. \quad (14)$$

3. Comparison to experiment

3.1. The parametrization of the barrier density

The comparison to experiment requires a knowledge of the barrier density $n(V, 0)$, which is difficult to model, particularly for glass-forming systems, which need to be complex to avoid crystallization. Therefore we describe $n(V, 0)$ or, more accurately, its product with the average square of the coupling constant, by the pragmatic form

$$l(V) = l_n l_c(V) \exp\left(\frac{\beta_K(V - V_c)}{k_B T}\right). \quad (15)$$

The normalization factor l_n is determined by the normalization condition

$$\int_0^\infty l(V) dV = 1. \quad (16)$$

The parameter β_K has a close correspondence to the Kohlrausch- β of approximately 0.5 of the Kohlrausch form $\exp(-t^\beta)$, the most popular fitting form for glassy relaxation. It supplies the slope $-\beta_K$ at frequencies slightly above the α -peak frequency. But the form is purely pragmatic, without any physical significance, with the exception of the cut-off. Note that this cut-off is not very sharp; therefore the β_K -values one obtains tend to be larger than those of a Kohlrausch fit, between 0.5 and 0.7. If the glass former exhibits a pronounced secondary peak (Johari-Goldstein peak) one needs to add a Gaussian with three parameters to the form of equation (15). In this case, one has to reckon with different peak amplitudes in shear and dielectrics.

The complex shear compliance, from which the complex modulus $G(\omega)$ can be easily calculated by inversion, is given by

$$GJ'(\omega) = 1 + f_0 \int_0^\infty l(V) \frac{1}{1 + \omega^2 \tau_V^2} dV \quad (17)$$

and

$$GJ''(\omega) = f_0 \int_0^\infty l(V) \frac{\omega \tau_V}{1 + \omega^2 \tau_V^2} dV + \frac{1}{\omega \tau_m}. \quad (18)$$

Note that the factor $f_0 = GJ_e^0 - 1$ appears here, which according to equation (14) should be $\pi/4$. τ_m is the Maxwell time η/G .

3.2. Dielectric susceptibility

If one deals with a single type of double-well potentials, they should show up with the same $l(V)$ in the shear compliance and in the dielectric susceptibility. The only difference lies in the viscous effects, which in the dielectric case should lead to a relaxation with the Debye relaxation time τ_D

$$\tau_D = \frac{4\pi \eta r_H^3}{k_B T}, \quad (19)$$

where r_H is the hydrodynamic radius of the molecule.

Since structural rearrangements and Debye relaxation must be considered as independent processes influencing the

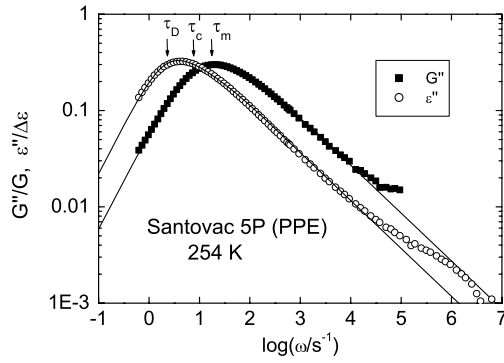


Figure 2. Model fits (continuous lines) for $G''(\omega)$ and $\epsilon''(\omega)$ of a diffusion pump oil.

same molecule, one has to fold the two processes in frequency or to multiply them in time. Thus one can use the same $l(V)$ as in the shear case, replacing the τ_v of the Arrhenius equation, equation (6), by the shorter relaxation time τ_v

$$\tau_v = \frac{\tau_v \tau_D}{\tau_v + \tau_D}. \quad (20)$$

With this definition, the dielectric susceptibility (after subtraction of the conductivity contribution) reads

$$\frac{\epsilon'(\omega) - \epsilon_\infty}{\epsilon(0) - \epsilon_\infty} = \int_0^\infty l(V) \frac{1}{1 + \omega^2 \tau_v^2} dV \quad (21)$$

and

$$\frac{\epsilon''(\omega)}{\epsilon(0) - \epsilon_\infty} = \int_0^\infty l(V) \frac{\omega \tau_v}{1 + \omega^2 \tau_v^2} dV. \quad (22)$$

Here $\epsilon(0)$ is the static dielectric susceptibility and ϵ_∞ is the real part of $\epsilon(\omega)$ in the GHz range (larger than n^2 , the square of the refractive index, because of vibrational contributions [15]).

3.3. An example: polyphenylene

Santovac 5P or PPE (polyphenylene) is a diffusion pump oil, consisting of a short chain of five phenyl rings connected by oxygens. The measurements were done by the Roskilde group [6].

If one adjusts the five parameters G , η , J_e^0 , β_K and τ_c to the shear data, they exhibit a strong scatter; the data are too featureless to be able to fix five parameters to the desired accuracy of about 10%. One way to overcome this difficulty is to fit both the shear and the dielectric data with the same τ_c (as one should do). This way was employed in our example PPE. Then one obtains the other four parameters with reasonable accuracy from the shear data and ϵ_0 , ϵ_∞ and τ_D from the dielectric data. One gets a good fit, as one can see in figure 2. The shear modulus parameters are $G = 1.067$ GPa and $\eta = 0.0634$ GPa s. f_0 was 2.4 ± 1 , clearly larger than the prediction of $\pi/4$ of equation (14), but close to other values reported in the literature [16]. β_K was 0.5 both for shear and dielectrics, the lifetime τ_c/τ_m was 2.37, close to the predicted value of equation (5), and τ_D/τ_m was 8.1.

4. Discussion and summary

The Eshelby model presented here has one distinct advantage, namely a direct connection to the elementary flow process. Thus its parameters can be linked to the details of the structure.

To illustrate this, let us consider the example of Santovac 5P or polyphenylene of figure 2. The molecule consists of five phenyl rings bonded by oxygen atoms. Such an oxygen bond is rather flexible. Therefore one should assess the typical molecular volume to one of these phenyl rings, as far as packing considerations are concerned. The density is about 1250 kg m^{-3} , so the volume of one phenyl ring is 0.12 nm^3 .

With this volume and the modulus of 1.06 GPa, the formation energy E_a of the four-molecule strain defect of figure 1 according to equation (1) is 0.173 eV, corresponding to a temperature of 2004 K. The barrier height should be of the same order, probably even quite substantially lower because of the anharmonicity of the potential. This barrier height is too low; the barriers which cause the flow are centered around $k_B T_g \ln \tau_m/\tau_0$, where τ_0 is the microscopic time of about 10^{-13} s. At 254 K, this means a barrier height of 0.7 eV, much higher than the one of the four-atom defect. Though we cannot answer the question about what kind of defect might have such a high barrier, the example shows that our Eshelby consideration allows us to check ideas on a quantitative level.

The measured recoverable relaxational compliance J_e^0 is clearly larger than the prediction of equation (13), in agreement with other findings [16] on molecular undercooled liquids in the literature. This indicates components of the relaxational jump which reverse after a while in following rearrangements, making the contribution of the shear defect to the flow smaller than expected from its coupling to the stress. Imagine, for example, that an ellipsoidal molecule orients itself in the direction of the external stress in the relaxational jump. Such a motion would enhance the relaxational compliance, but it would not contribute to the flow, because the molecule would reorient.

An unsolved riddle (an old riddle [4]) is the short Debye relaxation time. The ratio of τ_D and τ_m according to equation (19) is

$$\frac{\tau_D}{\tau_m} = \frac{4\pi G r_H^3}{k_B T}. \quad (23)$$

If we take r_H from the molecular volume by $4\pi r_H^3/3 = v_{\text{mol}}$, this ratio for the phenyl ring in Santovac 5P at 254 K should be 110, a factor of 14 higher than the one of 8.1 found in experiment. In terms of the radius r_H , this means that the radius must be only 40% of the one calculated from the molecular volume. One knows from NMR gradient measurements of the molecular diffusion [5, 17] that the hydrodynamic radius is a bit smaller than the one calculated from the molecular volume, but not that much.

Maybe the process which we characterize by τ_D has another and faster mechanism than the one considered by Debye, which might account for the fact that it is accompanied by the relaxation of the energy and by the relaxation of the structure [15, 18].

Another open question is whether the structural rearrangements fully relax the molecular orientation, as assumed for

simplicity in the derivation of equations (21) and (22). Their number is limited by the cut-off at V_c , so it is conceivable that some dielectric polarization remains, which should appear as an additional Debye relaxation at the Debye relaxation time. In fact, dielectric measurements in the monoalcohols [19] look as if most of the reorientation happened in a Debye-like process long after the Maxwell time.

We conclude that the Eshelby model for the highly viscous flow, though it raises more questions than it answers, provides a new way to tackle an old and difficult problem on a quantitative level.

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