A pragmatical access to the viscous flow

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Within the recently published pragmatical model of the flow process in undercooled liquids, a relation for the viscosity is derived which is in excellent agreement with measured data. According to this relation, most of the viscous flow is due to the reaction of a relaxing core to the flow of the surroundings.

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The shearing response of undercooled liquids is much better understood [1, 2] than it is theoretically understood [11, 12].

The problem is that one needs a theory which describes the crossover from thermally activated back-and-forth jumps at short times to viscous flow at long times. Such a theory does not yet exist. For the time being, one can make use of the pragmatical model [13], which has been devised to fill this theoretical gap.

The pragmatical model [13] describes the crossover in terms of asymmetric double-well potentials with a finite lifetime \( \tau_c \), of the order of the Maxwell time. Each double-well potential stands for a local cooperative rearrangement. The rearranging region changes its volume and its shape in the rearrangement, coupling to the surrounding elastic matrix according to the Eshelby theory [14].

The concept of a double-well potential with a finite lifetime has the advantage that one can calculate the ratio between the viscous response from no-return jumps and the retardational response from the back-and-forth jumps.

For an ensemble of potentials which reproduces the short-time Kohlrausch behavior \( t^\beta \) with a Kohlrausch exponent \( \beta \approx 1/2 \), one finds \( f_r = 1/(1 + \beta) \approx 2/3 \) retardational response and \( 1 - f_r \approx 1/3 \) viscous response. This implies [15] a fraction of one third viscous response also in the dielectric spectra. It turns out to be possible to find a consistent description of dielectric and shear spectra on this basis in several molecular glass formers [13].

This consistent description requires a whole distribution of lifetimes, with a full width at half maximum \( W_r \approx \ln 10 \) in \( \ln \tau_c \), about a decade. So one has a double dynamical heterogeneity [16], not only in the local relaxation times, but also in the local structural lifetimes.

The usefulness of the pragmatical model is clearly demonstrated in the mono alcohols, where the molecules form long-lived chains or rings [16], with a lifetime two decades longer than the one of the cooperatively rearranging regions. Postulating a large number \( n_r \) of cooperatively rearranging regions which have to grow and decay before the long-lived structures change their dipole moment, the pragmatical model is not only able to explain the size, position and width of the Debye line [13], but even gives a quantitative description [15] of nonlinear dielectric data in two mono alcohols [16, 20].

The present paper derives a relation for the viscosity in order to reduce the number of parameters of the pragmatical model by one.

The derivation starts with the contribution of the no-return jumps to the viscosity \( \eta \), which is completely analogous to the calculation of the viscous fraction \( 1 - f_r \) of the response in dielectric spectra [13]. Under an applied external shear stress \( \sigma \), the total retardation response due to the back-and-forth jumps is \( (J_0 - 1/G)\sigma \), where \( J_0 \) is the recoverable compliance [15] and \( G \) is the infinite frequency shear modulus. Ascribing the viscous flow to the no-return part of the jumps, one arrives at

\[
\frac{\tau_c}{\eta} \mid_1 = \beta(J_0 - 1/G) = \frac{1 - f_r}{f_r} (J_0 - 1/G). \tag{1}
\]

The alternative formulation in terms of \( f_r \) is only needed for cases with excess wings and secondary relaxations.

The contribution has been given the index 1, because there is a second contribution, which is absent in the dielectric case: the relaxing region is surrounded by a flowing liquid. The flow of the surroundings induces additional jumps in the relaxing core, which have to be added to the inverse viscosity (the fluidity).

In order to calculate the second contribution, note first that the decay of the cooperatively rearranging region is a continuous process, induced by many rearrangements in the surroundings. After the time \( dt \), the state can be considered to consist of a fraction \( dt/\tau_c \) of a new state and a fraction \( 1 - dt/\tau_c \) of the old one. In the flowing liquid, the new state is created in equilibrium with the actual shear state at the given time. This continuous creation process implies a back-lag of the equilibrium shear position \( \epsilon_\text{eq} \) of the state by \( \sigma \tau_c/2\eta \).

If one takes the external shear stress away at time zero and shear strain zero, the sample relaxes immediately to the shear strain \( \epsilon(\infty) = -\sigma/G \). Then, as the local relaxations proceed, the sample relaxes gradually to \( \epsilon(\infty) = -\sigma J_0 \), where \( J_0 \) is the recoverable compliance [13].
To fulfill this, the actual average equilibrium shear position \( \epsilon_\text{eq}(0) \) of the local relaxations must be at a negative value

\[
\epsilon_\text{eq}(0) = -\frac{\sigma(J_0 - 1/G)}{f_r},
\]

where the factor \( 1/f_r \) accounts for the fraction of local relaxations decaying without a back-jump.

Equating the two expressions for \( \epsilon_\text{eq} \), one finds

\[
\frac{\tau_c}{\eta} |_2 = 2 \frac{f_r}{f_r} J_0 = (2 + 2\beta)(J_0 - 1/G).
\]

(3)

Adding the two contributions, one gets the full fluidity

\[
\frac{\tau_c}{\tau_M} = \frac{3 - f_r}{f_r} (GJ_0 - 1) = (2 + 3\beta)(GJ_0 - 1)
\]

(4)

where \( \tau_M \) is the Maxwell time \( \eta/G \). For a Kohlrausch \( \beta = 1/2 \), the flow is seven times larger than the effect of the no-return jumps of eq. (4) alone, so the reaction of the relaxing core to the flow of the surroundings provides \( 6/7 \) of the fluidity.

Mechanical recoverable compliance measurements (1, 2) determine \( J_0 \) directly and thus allow a stringent check of the validity of eq. (4). At a given temperature, the recoverable compliance measurement supplies the parameter \( G, J_0 \) and \( \eta \). \( \tau_c \) is calculated from \( \beta \) via eq. (4). Fig. 1 shows that this procedure, with only \( \beta \) and \( W_r \) as free parameters, supplies excellent fits.

A second check of the relation is provided by the recently measured (10) high accuracy shear data of DC704 in Fig. 2 (a). They allow to fit all six parameters with reasonable accuracy, giving a correction factor for eq. (4) of \( 1.1 \pm 0.2 \).

The high accuracy of the data is illustrated in Fig. 2 (b), which shows the residuals of the best fit, comparing it to the residuals obtained assuming a sharp \( \tau_c \), i.e. \( W_r = 0 \). Though the fit curves in Fig. 2 (a) are practically the same, the residuals show very clearly that the measurement is able to decide whether one has a distribution of lifetimes or not.

The measurement is also able to decide whether one has an excess wing or not.

For the proper description of the excess wing, it is necessary to go a bit deeper into technical detail (13). The retardation part of the shear is described by the relaxation time density \( l(\tau) \). In the retardation spectrum, the contribution of a given potential does not appear at \( \tau_r \), but at

\[
\tau = \frac{\tau_r \tau_c}{\tau_r + \tau_c}
\]

(5)

so there is no contribution beyond \( \tau_c \), even if \( \tau_r \) is longer than \( \tau_c \).

The Kohlrausch time dependence \( t^\beta \) is described by \( l(\tau) = l_0(\tau/\tau_c)^\beta \), which has the logarithmic slope \( \beta \) at \( \tau_c \). If one wants to go a step further, one needs to introduce a logarithmic curvature \( \beta_2 \) by

\[
l(\tau) = l_0 \exp(\beta v + \beta_2 v^2),
\]

(6)

where \( v = \ln(\tau_r/\tau_c) \).

One can introduce \( \beta_2 \) as a seventh parameter into the fits. But in DC704 and in PPE, the fit to the data (10) does not improve. The fitted value is small and as often positive as negative.

This is different in propylene carbonate, where a good fit requires a small positive excess wing (9, 11).

For eq. (4), similar correction factors as the one in DC704 are obtained from the high accuracy measurements of PPE (10) and propylene carbonate (9). PPE supplies \( f_{\text{corr}} = 1.17 \pm 0.2 \) and propylene carbonate \( f_{\text{corr}} = 0.84 \pm 0.2 \).

![FIG. 1: Fit of recoverable compliance data (1, 2) in terms of the pragmatically model, assuming the validity of eq. (4).](image1)

![FIG. 2: (a) Fit of \( G(\omega) \)-data of the diffusion pump oil DC704 (10) in terms of the pragmatically model, testing the validity of eq. (4) (b) Comparison of residuals for a sharp lifetime \( \tau_c \) (open symbols) to the ones for a distribution of \( \tau_c \) over a whole decade.](image2)
For \( G(\omega) \)-data of lesser accuracy, eq. \( \text{[4]} \) is a gift from heaven, because the terminal recoverable compliance \( J_0 \) is always clouded by the viscous flow (see Fig. 3). Fixing it by eq. \( \text{[4]} \) in terms of the other parameters reduces the uncertainty considerably, not only for the product \( GJ_0 \), but also for the other parameters.

A rather convincing example for the validity of eq. \( \text{[4]} \) is glycerol \( \text{[8]} \). Fig. 3 shows the \( G(\omega) \)-data converted to compliance \( J(\omega) = 1/G(\omega) \) (a) real part \( J' \) (b) imaginary part \( J'' \), also showing the retardational part \( J'' = 1/\omega \eta \).

![FIG. 3: Fit of \( G(\omega) \)-data of glycerol \( \text{[8]} \), assuming the validity of eq. \( \text{[4]} \), with data and fit both converted to compliance \( J(\omega) = 1/G(\omega) \) (a) real part \( J' \) (b) imaginary part \( J'' \), also showing the retardational part \( J'' = 1/\omega \eta \).](image)

In all examples of Table I, secondary relaxation peaks or excess wings were so small that one can reckon with the validity of \( f_e = \beta/(1 + \beta) \). For this reason, \( f_e \) is not specified in Table I. The fit to propylene carbonate, which has an excess wing \( \text{[9]} \), has been described elsewhere \( \text{[18]} \).

Let us begin the discussion of the results in Table I with the recoverable compliance data \( \text{[1, 2]} \), where the three parameters \( G, \eta, \) and \( J_0 \) are known. Fitting \( \tau_c \), one finds eq. \( \text{[4]} \) fulfilled within ten percent in all four cases.

Assuming eq. \( \text{[4]} \) to be valid, the lifetime distribution width \( W_r \) turns out to be small. In tri-naphtyl benzene \( \text{[1]} \), it is even zero within the error bar of 1, so the lifetime distribution width must be smaller than half a decade.

In the other three substances, it is about two thirds of a decade, a bit smaller than the average value, but nonzero within the error bar.

What is remarkable, however, is that the four \( \beta \)-values are all close to 1/3, the value which Plazek \( \text{[1, 2]} \) believed to be universal at short times. In these four cases, it is shown to hold up to the terminal relaxation time \( \tau_c \). But other cases in Table I have larger values of the Kohlrausch parameter \( \beta \), so it cannot be universal at \( \tau_c \).

Next comes a large group of \( G(\omega) \)-data for van-der-Waals-bonded molecular liquids \( \text{[6–8, 10]} \), beginning with the diffusion pump oils DC704 (see Fig. 2) and 5-PPE, where a comparison of fits at two different temperatures shows how accurately the parameters are determined.

Silica and a sodium silicate, the two next examples, show the lowest \( GJ_0 \)-values found so far, which implies that they have the lowest ratio \( \tau_c/T_M \). Their \( W_r \)-values are only defined with a large error bar.

The same is true for the following two metallic glasses. But their \( GJ_0 \)-values are well defined and similar to those of the van-der-Waals-bonded molecular liquids.

Finally, the two hydrogen-bonded examples glycerol and propylene glycol have much larger \( GJ_0 \)-values than all the others. Their cooperatively rearranging regions are like strong rocks, which can withstand the viscous flow for much longer times than the ones in van-der-Waals bonded substances. It seems consistent that such a longer lifetime is accompanied by a narrower distribution width \( W_r \).

| substance       | \( T \) | \( G \) | \( GJ_0 \) | \( \beta \) | \( \tau_c \) | \( \tau_c/T_M \) | \( W_r \) |
|-----------------|------|-----|--------|------|--------|---------------|------|
|                 | \( K \) | \( GPa \) |               |      |        |               |      |
| TNB \[1\]       | 337  | 1.18| 3.05   | 0.33 | 1572   | 8.12          | 0    |
| aroclor \[2\]   | 232.8| 2.36| 2.42   | 0.34 | 1541   | 6.51          | 1.5  |
| OTP \[2\]       | 240.8| 2.22| 2.64   | 0.33 | 735    | 7.02          | 1.6  |
| 6-PPE \[2\]     | 248.2| 2.37| 3.37   | 0.36 | 2231   | 6.48          | 1.5  |
| DC704 \[10\]    | 210  | 1.16| 2.51   | 0.46 | 133.5  | 5.05          | 2.7  |
| DC704 \[10\]    | 222  | 0.96| 2.74   | 0.45 | 0.013  | 5.81          | 2.8  |
| 5-PPE \[10\]    | 242.5| 1.18| 2.33   | 0.54 | 892    | 4.76          | 2.7  |
| 5-PPE \[10\]    | 260  | 0.88| 2.67   | 0.44 | 0.007  | 5.52          | 2.5  |
| DGEBA \[6\]     | 256.3| 0.95| 3.18   | 0.44 | 30.1   | 7.19          | 2.5  |
| TPE \[7\]       | 258  | 1.16| 2.56   | 0.51 | 0.95   | 5.48          | 2.9  |
| DEP \[8\]       | 183  | 1.30| 3.18   | 0.41 | 50.8   | 7.00          | 1.5  |
| DEP \[8\]       | 197  | 1.02| 3.10   | 0.40 | 0.003  | 6.66          | 1.6  |
| silica \[3\]    | 1449 | 29.4| 1.89   | 0.38 | 284.3  | 2.77          | 2.8  |
| NaSiO \[3\]     | 728  | 14.4| 1.72   | 0.36 | 214.4  | 2.21          | 0.7  |
| met1 \[4\]      | 371  | 28.1| 2.71   | 0.39 | 45.0   | 5.42          | 2.9  |
| met2 \[4\]      | 318  | 33.3| 3.19   | 0.38 | 2.05   | 6.86          | 2.7  |
| glycerol \[9\]  | 192.5| 3.48| 5.83   | 0.43 | 38.2   | 14.1          | 0.4  |
| PG \[8\]        | 171  | 3.95| 5.95   | 0.42 | 6.85   | 15.7          | 1.3  |
| PG \[8\]        | 180  | 3.36| 6.40   | 0.43 | 0.092  | 18.0          | 0.8  |

TABLE I: Fit parameters for dynamical shear data in fifteen glass formers. TNB is tri-naphtyl benzene, OTP is ortho-terphenyl, 6-PPE is 6-polyphenylether, DGEBA is an epoxy resin, DC704 is a vacuum pump oil, 5-PPE is 5-polyphenylether, TPE is triphenylethylene, DEP is diethyl phthalate, NaSiO is (SiO2)0.67(NaO)0.33, met1 is Zr0.65Al0.35Cu0.175Ni0.10, met2 is Pd0.4Ni0.4P0.2, PG is propylene glycol.
In view of the very large ratio $\tau_c/\tau_M$ in these last two examples, the question arises whether such a large ratio is compatible with the Green-Kubo relation for the viscosity

$$\eta = \frac{V}{kT} \int_0^\infty dt < \sigma(0)\sigma(t) >,$$  \hspace{1cm} (7)

the only reliable recipe for the calculation of the viscosity that we have. In fact, the question is whether eq. (4) itself is compatible with the Green-Kubo relation.

But if one calculates the shear compliance $J(\omega)$ from the equations [13], inverts to $G(\omega)$, Fourier-transforms to $G(t)$ and determines $< \sigma(0)\sigma(t) >$ with $\sigma(0)^2 = kT/G(0)V$ in thermal equilibrium, one does indeed get the correct viscosity. Obviously, the concept of a double-well potential with a finite lifetime is compatible with the linear response rules.

To conclude, the relation between viscosity and lifetime derived from the pragmatical model concept of a relaxing Eshelby core with a finite lifetime is corroborated by the collected experimental evidence on the viscous flow. This encourages the hope that the pragmatical model will turn out to be the appropriate predecessor of a full theory.

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