

Pragmatical access to the viscous flow of undercooled liquids

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The paper derives a relation for the viscosity of undercooled liquids on the basis of the pragmatical model concept of Eshelby relaxations with a finite lifetime. From accurate shear relaxation data in the literature, one finds that slightly less than half of the internal stresses relax directly via single Eshelby relaxations; the larger part dissolves at the terminal lifetime, which is a combined effect of many Eshelby relaxations.

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The shear response of undercooled liquids is much better measured [1–10] than it is theoretically understood [11,12].

The problem intimately is related to the existence of a terminal lifetime τ_c . The existence of such a lifetime, after which the final relaxation is exponential, has been shown in aging experiments [13]. It is experimentally well established [13,14] that this lifetime is markedly longer than the Maxwell time $\tau_M = \eta/G$.

At shorter times, the shear relaxation proceeds with the Kohlrausch time dependence t^β with a Kohlrausch β close to 1/2. The relaxation processes behind this Kohlrausch behavior must be back-and-forth jumps because one finds a recoverable compliance J_0 which is more than a factor of 2 larger [1,2] than the elastic recoverable compliance $1/G$ alone.

Thus there must be a crossover from back-and-forth jumps at short times to no-return jumps at the terminal lifetime τ_c for which, here, there is a theory [11,12].

A first attempt to attack this problem is the pragmatical model of Eshelby relaxations with a finite lifetime [15]. The present paper develops this model further and derives a relation for the ratio τ_c/τ_M between terminal and Maxwell times.

With this relation, accurate shear relaxation data allow for determining the fraction f_c of the internal stresses which are not relaxed by any single Eshelby relaxation but dissolve in the collective terminal process. The recognition of the fraction f_c is important for the description of dielectric and other nonshear relaxation data because it increases their viscous components. In particular, f_c is crucial for the understanding of nonlinear dielectric data [16].

The pragmatical model [15] has six parameters: The infinite frequency shear modulus G , the viscosity η , the recoverable compliance J_0 , the Kohlrausch β , the structural lifetime τ_c , and, finally, the full width W_r at half maximum of the distribution of local structural lifetimes on a logarithmic scale.

Since measured data are only rarely accurate enough to fix six parameters, this implies an undesirable arbitrariness in the results of the fitting procedure [15].

On the other hand, none of the six parameters is avoidable. In the case of the shear modulus G , the viscosity η , and the Kohlrausch β , this is generally agreed. The recoverable compliance J_0 , although no longer in the focus of the attention of the community, is an acknowledged textbook [17] material constant.

Finally, since one has dynamical heterogeneity in undercooled liquids [18], one must also reckon with a distribution of local structural lifetimes.

In the pragmatical model [15], 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 [19].

In the Eshelby theory, the structural jump of the central core couples to the stress not to the strain [19]. This implies that the effects of different structural jumps do not add in the shear modulus but in the elastic shear compliance [17],

$$J(\omega) = \frac{1}{G} + \int_{-\infty}^{\infty} \frac{L(\tau)}{1 + i\omega\tau} d \ln \tau - \frac{i}{\omega\eta}. \quad (1)$$

The retardation function $L(\tau)$ defines the zero-frequency recoverable compliance J_0 , the infinite-frequency elastic compliance, plus the integral over the retardation processes,

$$J_0 = \frac{1}{G} + \int_{-\infty}^{\infty} L(\tau) d \ln \tau. \quad (2)$$

In the absence of a secondary relaxation peak, the density of local cooperative rearrangements in the logarithm $\ln \tau_r$ of their relaxation time is given by

$$l(\tau_r) = l_0(\tau_r/\tau_c)^\beta, \quad (3)$$

in order to reproduce the rise in the shear response with the Kohlrausch t^β .

A given local rearrangement with relaxation time τ_r does not exist forever because the surroundings flow, providing it with a decay time τ_c .

The rates $r = 1/\tau_r$ and $r_c = 1/\tau_c$ add up to the total decay rate $1/\tau = r + r_c$, so

$$\tau = \frac{1}{r + r_c} = \frac{\tau_r \tau_c}{\tau_r + \tau_c}, \quad (4)$$

which is always shorter than both τ_r and τ_c .

The total response probability of the rearrangement within its lifetime is given by

$$\frac{r}{r + r_c} = \frac{\tau_c}{\tau_c + \tau_r} \quad (5)$$

(in the first version [15], this was mistakenly taken to be the retardational response probability).

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This probability divides into a probability for viscous response,

$$\frac{r r_c}{(r + r_c)^2} = \frac{\tau_r \tau_c}{(\tau_c + \tau_r)^2}, \quad (6)$$

and a probability for the retardation response,

$$\frac{r^2}{(r + r_c)^2} = \frac{\tau_c^2}{(\tau_c + \tau_r)^2}. \quad (7)$$

Integrating both components over τ_r , one finds the total integral I_β (in reasonable approximation),

$$I_\beta = l_0 \pi [1 + 13.27(\beta - 1/2)^2 + 135(\beta - 1/2)^4], \quad (8)$$

with the exact retardation fraction,

$$f_r = 1 - \beta. \quad (9)$$

The resulting retardation function is

$$L(\tau) d \ln \tau = \frac{\tau_c^2}{(\tau_r + \tau_c)^2} \frac{l(\tau_r)}{G} d \ln \tau_r, \quad (10)$$

which evaluates to

$$L(\tau) = \frac{l_0}{G} \frac{\tau_c - \tau}{\tau_c} \left(\frac{\tau}{\tau_c - \tau} \right)^\beta. \quad (11)$$

A fraction f_r of the relaxation shear response goes into the retardation $J_0 - 1/G$, and a fraction $1 - f_r$ is the viscous response at the average relaxation time τ_c .

This implies a contribution to the viscosity from the no-return processes,

$$\frac{\tau_c}{\eta} \Big|_1 = \frac{\beta}{1 - \beta} (J_0 - 1/G) = \frac{1 - f_r}{f_r} (J_0 - 1/G). \quad (12)$$

The formulation in terms of f_r is needed for cases with excess wings and secondary relaxations.

Note that this part of the viscosity is not a collective effect; it is due to individual Eshelby jumps which are not followed by a backjump.

The collective effect of all Eshelby jumps leads to the finite structural renewal lifetime τ_c , the decay time for all internal stresses, even in those shear stress directions for which the local rearrangement does not couple. Defining f_c as the fraction of internal stresses released by the collective effect, only the fraction $1 - f_c$ is left for the direct effect of the Eshelby jumps. This in turn implies a fraction $(1 - f_c)f_r$ responsible for the retardation $J_0 - 1/G$.

With this normalization, the collective contribution to the viscous flow is

$$\frac{\tau_c}{\eta} \Big|_2 = \frac{f_c}{(1 - f_c)f_r} (J_0 - 1/G). \quad (13)$$

There is a third contribution: 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 third 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/τ_c of a new state and a fraction $1 - dt/\tau_c$ of the old one.

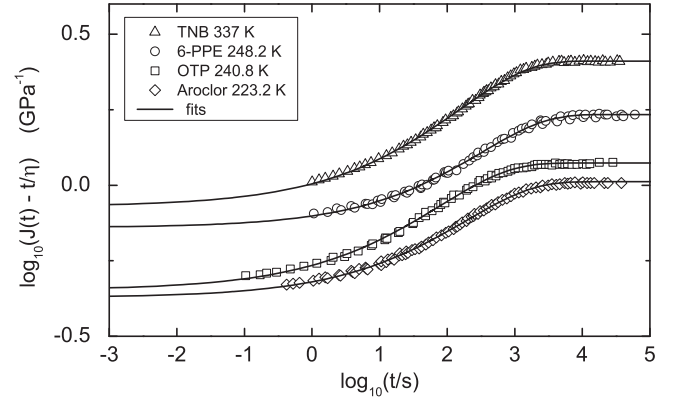


FIG. 1. Fit of recoverable compliance data [1,2] in terms of the pragmatical model.

In continuous flow, the new state is created in equilibrium with the actual shear state at the given time. This continuous creation process implies a backlog of the equilibrium shear position ϵ_{eq} of the state by $\sigma \tau_c / 2\eta$.

Thus, if one interrupts the continuous flow by taking the external shear stress away at time zero and shear strain zero, the sample relaxes within a few picoseconds (the adaptation time of the vibrations) to the shear strain $\epsilon(0) = -\sigma/G$. Then, as the local relaxations proceed, the sample relaxes gradually to $\epsilon(\infty) = -\sigma J_0$, where J_0 is the recoverable compliance [17].

To fulfill this, the actual average equilibrium shear position $\epsilon_{eq}(0)$ of the local relaxations must be at a negative value,

$$\epsilon_{eq}(0) = -\frac{\sigma(J_0 - 1/G)}{f_r}, \quad (14)$$

where the factor $1/f_r$ accounts for the fraction of local relaxations decaying without a backjump.

Equating the two expressions for ϵ_{eq} , one finds

$$\frac{\tau_c}{\eta} \Big|_3 = \frac{2}{f_r} (J_0 - 1/G) = \frac{2}{1 - \beta} (J_0 - 1/G). \quad (15)$$

Adding all three contributions, one gets the full fluidity,

$$\frac{\tau_c}{\tau_M} = \frac{3 - f_r}{f_r} (G J_0 - 1) + \frac{f_c}{f_r(1 - f_c)} (G J_0 - 1), \quad (16)$$

where τ_M is the Maxwell time η/G .

Fitting the pragmatical model parameters τ_c , τ_M , $G J_0$, and f_r to shear relaxation data, one can determine the ratio f_c .

The ratio f_c is obtained most accurately from mechanical recoverable compliance measurements [1,2], which determine G , η , and J_0 directly. W_r has little influence on the curves, so one has essentially only τ_c and β as free parameters. Figure 1 shows the fits.

Table I compiles the determinations of the collective viscous flow fraction f_c from recoverable compliance and $G(\omega)$ data. The most accurate results in Table I are the first four recoverable compliance measurements [1,2], which fix f_c within a few percent.

A helpful result from these fits is that the width W_r of the lifetime distribution is comfortably small on the order of half a decade (remember that a simple Debye relaxation peak already has a width of about a decade). This conclusion is

TABLE I. Determination of the collective fraction f_c of the viscous shear response by applying Eq. (16) to recoverable compliance data (TNB is tri-naphthyl benzene, OTP is ortho-terphenyl, 6-PPE is 6-polyphenyleneether) and to high accuracy $G(\omega)$ -data (DC704 is a vacuum pump oil, 5-PPE is 5-polyphenyleneether, PC is propylene carbonate, and PG is propylene glycol). Values marked with asterisks are taken from fits of dielectric data. PC has an excess wing $f_{1/6}(\tau_r/\tau_c)^{1/6}$ with $f_{1/6} = 0.035$, and PG has an excess wing with $f_{1/6} = 0.027$ (see the text).

Substance	T (K)	G (GPa)	GJ_0	β	W_r	τ_M (s)	τ_c/τ_M	f_c
TNB [1]	337	1.18	3.03	0.37	0.0	195.0	14.2	0.67
Aroclor [2]	232.8	2.36	2.42	0.37	0.6	236.6	12.4	0.75
OTP [2]	240.8	2.22	2.64	0.37	0.9	104.7	13.2	0.73
6-PPE [2]	248.2	1.38	2.37	0.39	0.3	344	12.7	0.78
DC704 [10]	214	1.09	2.49	0.46	1.8	0.79	11.7	0.65
DC704 [10]	216	1.05	2.43	0.46	2.0	0.16	11.2	0.62
DC704 [10]	218	1.02	2.44	0.47	2.6	0.041	13.3	0.66
5-PPE [10]	250	1.03	2.33	0.50	2.0*	0.69	9.5	0.53
5-PPE [10]	252.5	0.98	2.39	0.48	2.0*	0.13	10.3	0.58
5-PPE [10]	255	0.95	2.45	0.47	2.0*	0.022	11.0	0.61
PC [9]	159	1.48	2.96	0.47	1.7	0.34	12.5	0.54
PC [9]	161	1.42	2.97	0.49	2.0	0.037	12.1	0.50
PC [9]	163	1.39	3.14	0.55	2.8	0.006	13.0	0.39
PG [8]	171	4.08	6.39	0.53	1.6*	0.45	35.9	0.48
PG [8]	174	3.85	6.68	0.54	1.6*	0.088	38.9	0.48
PG [8]	177	3.69	6.78	0.54	1.6*	0.020	41.1	0.52

corroborated independently by fits of dielectric data in terms of the pragmatism model where the viscous component is seen directly at the peak.

$G(\omega)$ data give much less accurate f_c values because the viscous component overshadows the retardational one at the crossover. Nevertheless, very accurate data, such as those in DC704 and 5-PPE [10], determine f_c within an error of about 20%. In some of these fits, W_r was taken from fits of dielectric data from the same substance.

Another new accurate data set exists for propylene carbonate [9]. Like many other strong dielectric substances, propylene carbonate shows an excess wing with a logarithmic slope of about $-1/6$ at high frequencies in its dielectric response [see Fig. 2(b)]. In the new measurement [9], the authors demonstrated that the same excess wing slope also appears in the shear response.

The excess wing requires the relaxation density,

$$l(\tau_r) = l_0[(\tau_r/\tau_c)^\beta + f_{1/6}(\tau_r/\tau_c)^{1/6}] \quad (17)$$

with the same $f_{1/6}$ of 0.03 in propylene carbonate [9] and glycerol [15].

With Eqs. (8) and (9), it is straightforward to calculate the retardation fraction f_r for this relaxation density. Inserting f_r and the other fit parameters into Eq. (16), one can again determine f_c (see Table I).

With the retardation density $L(\tau)$ obtained from the $l(\tau_r)$ in Eq. (17), one can calculate the normalized dielectric susceptibility,

$$\Phi(\omega) = \frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty}, \quad (18)$$

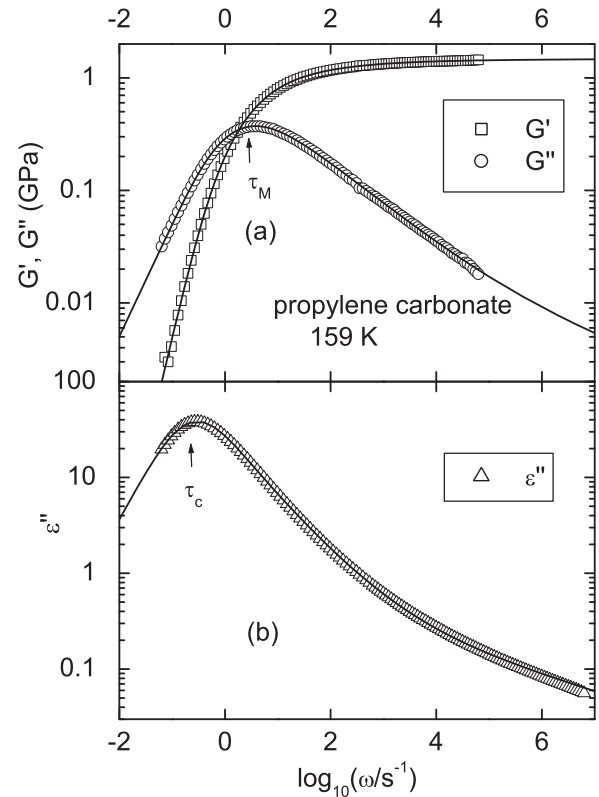


FIG. 2. Fit of (a) $G(\omega)$ data and (b) dielectric relaxation data of propylene carbonate [9] in terms of the pragmatism model.

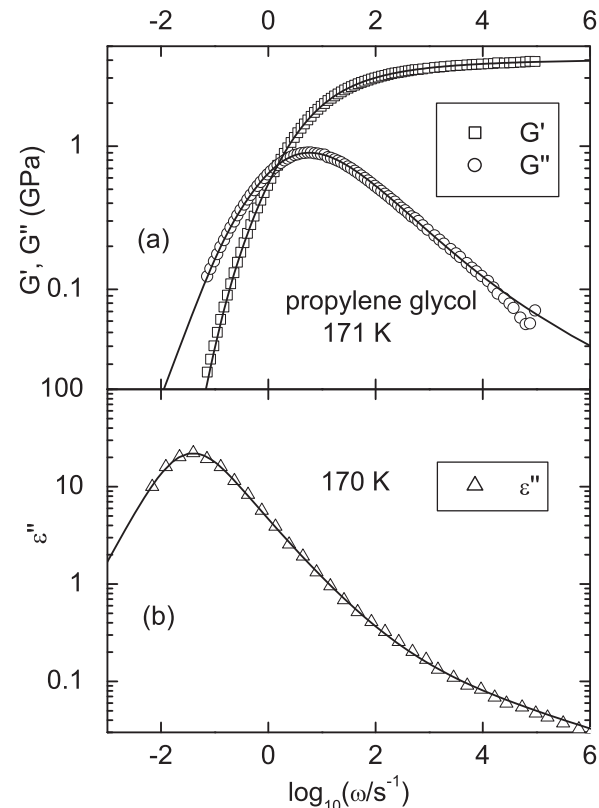


FIG. 3. Fit of (a) $G(\omega)$ data [8] and (b) dielectric relaxation data [20] of propylene glycol in terms of the pragmatism model.

where ϵ_s is the static dielectric susceptibility and ϵ_∞ is its high-frequency limit.

To perform the calculation, one has to normalize $L(\tau)$ to $f_r(1 - f_c)$ and add a viscous component at τ_c with weight $1 - f_r(1 - f_c)$, a Gaussian distribution of Debye processes with the width W_r .

Although the dielectric fits do not determine f_c very accurately, one gets generally smaller f_c values (about 1/3) than the average shear f_c of 5/9 from Table I. This is understandable: An Eshelby relaxation couples to one of the three electric polarization components but only to one out of five shear stress components. Thus a factor of 5/3 more shear equilibration is left for the terminal process.

Applying this fit procedure to shear and dielectric data obtained by measuring a propylene carbonate sample from the same charge in the same cryostat [9], one finds not only the same terminal relaxation time τ_c , but also the same excess wing coefficient $f_{1/6}$ within experimental accuracy. Figures 2(a) and 2(b) show the shear and dielectric measurements at 159 K.

The same procedure has been followed to evaluate the high accuracy shear data of propylene glycol [8] in Fig. 3(a). The

evaluation of dielectric data [20] [see Fig. 3(b)] supplies an excess wing coefficient of $f_{1/6} = 0.027$, which was taken to be the right one for the fit of the shear data.

In this case, shear and dielectric data, although measured in different laboratories, show essentially again the same τ_c for the dielectric data. Since the dielectric relaxation peak coincides with the dynamic heat capacity one [21], the results support the concept of a terminal relaxation time.

This is no longer true for DC704. In fact, the correction of the pragmatistical model destroys the seemingly perfect agreement between shear and dielectrics reported in the first paper [15] for DC704. The shear τ_c of the corrected version is now a factor of 2.4 larger than the dielectric one and lies close to the ones suggested by the peak positions of heat capacity and thermal expansion data [14] of DC704.

To conclude, the paper derives a relation between the structural lifetime and the Maxwell time, which allows for calculating the collective fraction of the viscous response (the one resulting from the cumulative effect of all Eshelby relaxations together) from accurate shear relaxation data.

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