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Minimal Model for Beta Relaxation in Viscous Liquids

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Contrasts between beta relaxation in equilibrium viscous liquids and glasses are rationalized in terms of a double-well potential model with structure-dependent asymmetry, assuming structure is described by a single order parameter. The model is tested for tripropylene glycol cooled through the glass transition and subsequently reheated [26]. In the glassy phase (at low temperatures) the loss peak frequency is strongly temperature dependent while the maximum loss varies little. On the other hand, the loss is strongly temperature dependent in the equilibrium liquid phase. Here we even see the loss peak frequency decreasing upon heating. How is one to understand these findings? A clue is provided by Fig. 1(b), which shows the maximum loss as a function of time after an “instantaneous” temperature step, i.e., instantaneous on the time scale of structural (alpha) relaxation. This experiment utilizes a special-purpose setup with a cell consisting of two aluminum disks separated by three capton spacers (layer distance ~20μ, empty capacitance 30 pF). One disk, where temperature is measured via a negative temperature coefficient resistor, is placed on a Peltier element. Less than 6 s after a 0.672 K temperature jump is initiated, temperature is stable within 1 mK. In this setup we measure at 10 kHz, which is the loss peak frequency (changes of loss peak frequency lead only to second-order corrections of ε''\(_{\text{max}}\)). The sampling time is 2 s. Figure 1(b) shows a very fast change of the maximum loss, followed by relaxation toward the equilibrium value taking place on the structural (alpha) relaxation time scale. The existence of an instantaneous increase of the loss clearly indicates a pronounced asymmetry of the relaxing entity. Inspired by this fact we adopt the standard asymmetric double-well potential model (Fig. 2) with transitions between the two free energy minima described by rate theory [2,27–30]. In terms of the small barrier U and the asymmetry Δ, loss peak frequency f\(_{\text{max}}\) and maximum loss ε''\(_{\text{max}}\) are given [29] by

\[
f_{\text{max}} = f_0 \exp\left( -\frac{2U + \Delta}{2k_BT} \right) \cosh\left( \frac{\Delta}{2k_BT} \right)
\]

\[
\varepsilon''_{\text{max}} = \varepsilon''_0(T) \cosh^{-2}\left( \frac{\Delta}{2k_BT} \right).
\]

The prefactor f\(_0\) is assumed to be structure and temperature independent while ε''\(_0(T) \propto 1/T\) [29] is assumed to be structure independent: ε''\(_0(T) = T_0/T\). The free energy differences U and Δ are expected to change with
Structure is parameterized by just one variable, \( s \). Equation (2) follows from minimal assumptions: Suppose terms of the fictive temperature changing structure, but freeze at the glass transition. Working from this picture the simplest possible assumptions are that (1) Structure is parameterized by just one order parameter, and (2) first order Taylor expansions apply in the relatively narrow temperature range studied.

![Figure 1](image1.png)

**FIG. 1.** Data for tripropylene glycol. (a) Observation of beta relaxation in the liquid phase and around the glass transition. Consequently, structure varies only little and, changing structure, but freeze at the glass transition. In terms of the fictive temperature \( T_f \) our model is based on

\[
U = U_0 + a k_B T_f, \quad \Delta = \Delta_0 - b k_B T_f. \tag{2}
\]

Equation (2) follows from minimal assumptions: Suppose structure is parameterized by just one variable, \( s \). Only a rather narrow range of temperatures is involved in studies of beta relaxation in the liquid phase and around the glass transition. Consequently, structure varies only little and, e.g., \( U(s) \) may be expanded to first order: \( U(s) = c_0 + c_1 (s - s_0) \). For the equilibrium liquid, \( s = s(T) \) which may also be expanded to first order. By redefining \( s \) via a linear transformation we obtain \( s = T \) at equilibrium while \( U(s) \) is still linear in \( s \). A single variable describing structure, which at equilibrium is equal to temperature, is — consistent with Tool’s 1946 definition [31] — to be identified with the fictive temperature: \( s = T_f \). Thus one is lead to Eq. (2) where signs are chosen simply to ensure \( a, b > 0 \) in fit to data.

The model has six parameters: \( f_0, T_0, U_0, \Delta_0, a, \) and \( b \). These were determined by measuring the instantaneous changes of \( f_{\text{max}} \) and \( \varepsilon_{\text{max}}'' \) upon a temperature step, as well as their thermal equilibrium changes. Figure 1(b) allows determination of the instantaneous change of the loss. It is not possible to determine the instantaneous change of \( f_{\text{max}} \). Instead we extrapolated measurements obtained by the standard cell [26] as follows (Fig. 3): Beta loss is monitored by first annealing at 183.0 K, subsequently changing temperature to 181.0 K. The latter data show a reversal so that the loss peak frequency decreases with increasing temperature. (b) Beta loss peak maximum measured after a temperature increase of 0.672 K starting from equilibrium at 184.0 K. After 6 s temperature is stable within 1 mK of the final temperature.

![Figure 2](image2.png)

**FIG. 2.** Asymmetric double-well potential as a simple model for beta relaxation. The two free energy differences \( U \) and \( \Delta \) vary as structure changes with temperature in the equilibrium liquid phase, but freeze at the glass transition. Working from this picture the simplest possible assumptions are that (1) Structure is parameterized by just one order parameter, and (2) first order Taylor expansions apply in the relatively narrow temperature range studied.

In the data analysis it is convenient to eliminate \( \alpha; b > 0 \) in fit to data.
Having determined the instantaneous changes of $\epsilon''_{\text{max}}$ and $f_{\text{max}}$, Eqs. (1) and (4) provide four equations for the six model parameters. The last two equations come from the temperature dependence of loss and loss peak frequency at thermal equilibrium where $U(T)$ and $\Delta(T)$ are given by Eq. (2) with $T_f = T$, leading to

$$\frac{d \ln Y}{d \ln T} \bigg|_{\text{eq}} = \frac{2U_0 + \Delta_0}{k_B T},$$

$$\frac{d \ln \epsilon''_{\text{max}}}{d \ln T} \bigg|_{\text{eq}} = \frac{\Delta_0}{k_B T} \ln \left(1 - \frac{\epsilon''_{\text{max}}(T)}{\epsilon''_{\text{max}}(T)} - 1\right).$$

Using Eq. (4) for the data of Figs. 1(b) and 3, and using Eqs. (1) and (5) for equilibrium state measurements at 183 and 185 K, the six parameters determined for tripropylene glycol are $f_0 = 6.2 \times 10^{11}$ Hz, $T_0 = 130$ K, $U_0/k_B = -1107$ K, $\Delta_0/k_B = 3039$ K, $a = 23.28$, $b = 12.77$. $U_0 < 0$ reflects the fact that the beta loss peak frequency in the liquid phase decreases as temperature increases [Fig. 1(a)]. Physically, this anomalous behavior is caused by the barrier $U$ increasing more than $T$ upon heating.

Once all parameters are fixed the model predicts how $f_{\text{max}}$ and $\epsilon''_{\text{max}}$ correlate for the continuous passage through the glass transition of Fig. 1(a). To analyze these

![Graph](image)

FIG. 3. Reversible temperature jump experiment for tripropylene glycol monitoring beta loss peak frequency and loss peak maximum. Starting at 185.0 K (not shown) temperature is first lowered to 183.0 K and kept there for 60 h; the last point, $a$, was obtained after further 24 h. Then temperature is changed to 181.0 K where it is kept constant for 140 h (initially 20 min between measurements, later 12 h). The point $b$ is found by extrapolating to zero time after the quench utilizing the data of Fig. 1(b). This series ends at point $c$, thereafter temperature is changed back to 183.0 K where it is kept for 140 h (all points except the final point $e$ refer to times up to 70 h; $e$ was measured after further 70 h). Equilibrium at 183.0 K is somewhere between points $a$ and $e$.

![Graph](image)

FIG. 4. Data for tripropylene glycol from Fig. 1(a) replotted to test the model. The variable $Z$ defined in Eq. (6) is calculated using parameters obtained by independent experiments.
merging temperature is fundamental, a symmetry is somehow broken below this temperature.

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[25] This explains the apparent paradox that in some cases annealing below the glass transition brings out an otherwise invisible beta peak, while in other cases annealing makes the beta peak disappear: If $T_g$ is above the merging temperature where alpha and beta peaks merge in the equilibrium liquid phase no beta peak is visible in the liquid, and only annealing will bring out the beta peak. On the other hand, if $T_g$ is below the merging temperature the beta peak is visible in the liquid and its magnitude is more or less frozen at the glass transition. In this case, however, annealing below $T_g$ decreases the magnitude of the beta peak because the equilibrium magnitude is strongly temperature dependent. Sometimes the magnitude decreases so much upon annealing that the beta process eventually ends up below the resolution limit.

[26] The experimental setup is identical to that used in Ref. [24], except for an improved noncommercial 14-bit cosine-wave generator at 16 fixed frequencies per decade used for frequencies below 100 Hz. To eliminate the influence from the high frequency alpha tail the data were subjected to the following procedure: First, we obtained the equilibrium shape of the beta peak by annealing for 100 h at 184 K. Then, assuming invariance of the shape of the beta peak, the alpha tail influence was eliminated by subtracting a term $\alpha^{-1/2}$ [20] with constant of proportionality adjusted to obtain the invariant shape of the beta peak. This procedure is unique. The subtraction procedure mainly affects $f_{\text{max}}$ and only influence measurements at the highest temperatures. The observed hysteresis effects are much larger than the corrections from subtracting the alpha tail [24].

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[32] Whenever $U, \Delta \gg k_BT$ the present model predicts the empirical relation reported in Ref. [24] with $\gamma = a/b$. 