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Relaxation Times at the Rate-Dependent Glass Transition

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The structural relaxation time near the cooling rate dependent glass transition is determined self-consistently within the Moynihan-Narayanaswami formalism. In order to illustrate the method we analyze scanning calorimetry data from amorphous calcium-rubidium nitrate. A characteristic time scale of about 250 s is obtained at the conventionally defined glass transition. The occurrence of decoupled, faster relaxation modes is briefly discussed.

Glasses are often prepared by cooling a liquid sufficiently fast through its viscous regime. But exactly when the glassy state is arrived at depends on such factors as the cooling rate q or generally on quantities which are related with the observation time scale t. The glass transition is then commonly defined to take place at that temperature at which the characteristic time scale, τ, in the sample is about equal to t. Thus it is useful to define a quantity $DN = d\tau/dt$ which should be ≈ 1 at T_g. The parameter has variously been called Lillie number or Deborah number, for a review see.[1] The condition $DN \approx 1$ has often been used to estimate $\tau(T_g)$ to be of the order of 10–1000 s[1),2)] for typical cooling rates of 10 K/min in diverse types of glass formers.

Viewed from a related perspective the glass transition is signaled by the freezing of quantities such as entropy S or volume V. These typically exhibit a pronounced temperature dependence in the liquid but not so in the solid state. Such a situation is schematically depicted in Fig. 1 for the fictive temperature a quantity which can be thought of to represent S or V, say, and which in any case couples to the structural state of the glass former. Figure 1 represents the situation at a given cooling rate. The use of smaller (larger) q would correspond to shift of the curve to the left (right).

In this article we will try to give more accurate estimates for the Deborah number. Our computations will be based on a phenomenological model that has often been used for the description of quantities measured near the glass-transition in rate-cooling or heating experiments. In order to illustrate our considerations we present results from scanning calorimetry on the ionic calcium-rubidium-nitrate system. This substance is chosen because it provides a good example for the discussion of the term characteristic time scale that we have used above. There are several models that describe the temperature dependence of structural state variables.[1),3)] Since these only differ in the way they parameterize the experimental data in the glass transformation regime, any model could be used as long as no specific interpretation is attached to the phenomenological parameters entering into these models. For our considerations here we have employed the time-honored Moynihan-Narayanaswami formalism.[2),4)]

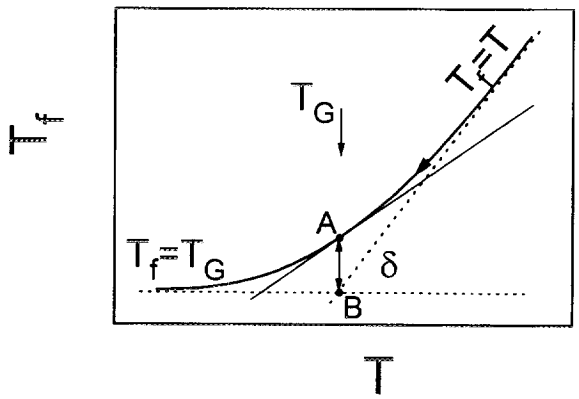

Fig. 1. Schematic representation of the temperature dependence of the fictive temperature in the vicinity of the calorimetric glass transition. The dotted lines are extrapolations of the approximately linear (or constant) behavior outside the transformation regime.

$$T_f(T) = T - \int_{T_0}^{T} dT' \exp\left\{ -\left(\int_{T'}^{T} \frac{dT''}{q\tau(T'', T_f)} \right)^{\beta} \right\} , \tag{1}$$

$$\tau(T, T_f) = \tau_0 \exp\left(\frac{\Delta H x}{T} + \frac{\Delta H (1-x)}{T_f} \right) , \tag{2}$$

where is x the so-called non-linearity parameter, β is a stretching exponent, τ_0 is a pre- exponential factor, and ΔH is an effective activation energy associated with the structural relaxation. These coupled expressions are quite complicated and therefore it is of interest to derive a set of simple relationships, helpful in the understanding that aspect of the glass transition that we address here. To begin with, we reproduce the expression derived by Moynihan et al.[5] for the cooling rate dependence of the glass transition temperature.

$$\frac{d \ln |q|}{d(1/T_g)} \approx -\Delta H . \tag{3}$$

A second expression states that the characteristic time scale is inversely proportional to the cooling rate[3]

$$\frac{d \ln \tau_e}{d \ln |q|} = -1 , \tag{4}$$

where the index e denotes the relaxation time value in the thermodynamical equilibrium.

Consider now a cooling process with the constant rate q from a temperature T_0 far above the glass transition point to the temperature T_1 far below T_g. In this case the left-hand side of Eq. (1) is simply $T_g = T_f(T_1)$ and the upper integration limit is extended up to T_1. We approximate the real temperature dependence of the fictive temperature by a linear function at the point, where $T(t)$ equals T_g. This point is marked as A in Fig. 1. Thus we have

$$T_f(t) = T_g + \delta + c[T(t) - T_g] \,, \tag{5}$$

where δ and c are constants, which can be determined self-consistently. δ is connected with the width of the glass transformation range and c is simply $(dT_f/dT)_{T=T_g}$.

From Eq. (2) with $\delta << T_g$ within the same linear approximation we have

$$\tau(T'', T_f) \approx \tau_1 \exp[-k(T'' - T_g)] \tag{6}$$

with τ_1 being a constant and k is defined as

$$k = \frac{x\Delta H}{T_g^2} + \frac{c(1-x)\Delta H}{(T_g + \delta)^2} \,. \tag{7}$$

The result of the first integration of Eq. (1) over T'' then reads:

$$\frac{1}{q\tau_1 k}[\exp k(T_1 - T_g) - \exp k(T' - T_g)] \,. \tag{8}$$

The first term in the square brackets can be neglected compared to the second, except for the case, when $T' \sim T_1$. But for such values of T' the relaxation time τ becomes very large, thus the expression (8) tends exponentially to zero. If the first term in square brackets is thus neglected, Eq. (1) reads:

$$T_g = T_1 - \int_{T_0}^{T_1} dT' \exp\left\{-\frac{1}{(q\tau_1 k)^\beta} \exp[k\beta(T' - T_g)]\right\} \,. \tag{9}$$

Using $a = (q\tau_1 k)^\beta$ this equation can be rewritten as

$$\int_{T_g}^{T_1} dT' = \int_{T_0}^{T_g} dT' \exp\left\{-\frac{1}{a} \exp[k\beta(T' - T_g)]\right\} + \int_{T_g}^{T_1} dT' \exp\left\{-\frac{1}{a} \exp[k\beta(T' - T_g)]\right\} \,. \tag{10}$$

Now we introduce the new variable $z = k\beta(T' - T_g)$ and extend the integration range from (T_0, T_g) and (T_g, T_1) to $(+\infty, 0)$ and $(0, -\infty)$ respectively. This is justified by the exponential temperature dependence of the functions under the integral. Eq. (10) can thus finally be written as

$$\int_0^\infty \exp\left(-\frac{\exp z}{a}\right) dz = \int_{-\infty}^0 \left[1 - \exp\left(-\frac{\exp z}{a}\right)\right] dz \,. \tag{11}$$

This equation can be solved self-consistently to yield $a \approx 1.78$. On the other hand, according to Eq. (6) one has

$$\left.\frac{d\tau(t)}{dt}\right|_{T=T_g} = q\tau_1 k = a^{1/\beta} \,. \tag{12}$$

As a result, within the approximation used, a, i.e. the effective Deborah number, does not depend on the material parameters, such as τ_0, β, x and ΔH. Using the latter expression, in conjunction with Eqs. (6) and (7), one can thus estimate $\tau_e(T_g)$.

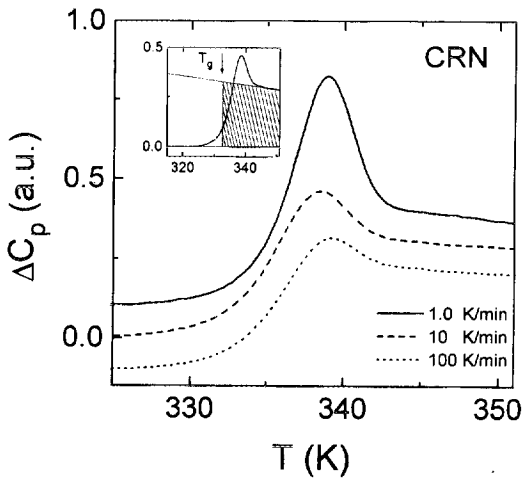

Fig. 2. Excess specific heat ΔC_p as measured using a Perkin Elmer DSC-4 calorimeter. Some data are displaced vertically for clarity. The inset illustrates the determination of the calorimetric T_g at $q = 10$ K/min using the method of equal areas.

Alternatively one can avoid the approximations and solve the problem numerically. Then it is advisable to restrict discussion to a specific value of the effective energy barrier ΔH. We will use data on glass-forming metal nitrate mixtures as examples in our considerations.

In Fig. 2 we present calorimetric data taken at a heating rate of 10 K/min after prior cooling with 1,10, and 100 K/min on $2Ca(NO_3)_2 - 3RbNO_3$ (CRN). From the DSC traces the calorimetric T_g was determined using the method of equal areas[6] as illustrated in the inset. For $q = 10$ K/min we obtain $T_g = 332.5$ K which is virtually identical to the corresponding transition point in CKN.[7]

In Fig. 3 we show $T_g(q)$ in an Arrhenius representation. A linear relationship

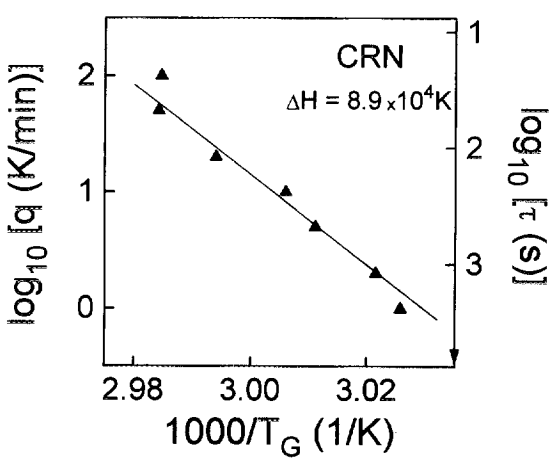

Fig. 3. Arrhenius plot of the logarithm of the cooling rates versus the inverse glass transition temperature. The solid line represents an effective energy barrier ΔH of 89000 K.

between $\ln q$ ($\propto -\ln \tau_e$) and $1/T_g$ is obtained within experimental uncertainty. From the slope of the line drawn in Fig. 3 an effective barrier ΔH of 8.9×10^4 K is obtained. This is slightly larger than the activation energy from several other metal nitrate mixtures.[8),9)] Therefore in the following we will work with $\Delta H = 8 \times 10^4$ K. The non-linearity parameter x was varied between 0 and 0.6 and the stretching exponent β between 0.2 and 1. This covers the parameter range relevant for many glass formers including the metal-nitrate materials.[1),10)]

Dropping the approximations (except the one represented by Eq. (4)) we have calculated the parameters a and k_τ, the latter explicitly defined via

$$\tau_e|_{T=T_g,T_f=T_g} = k_\tau(\beta, x)\frac{T_g^2}{q\Delta H} \,. \tag{13}$$

The results of the computer simulation are shown in Fig. 4. As can be clearly seen, a is not really a universal constant, but keeping in mind the exponential temperature dependence of τ, $a \sim 2$ is a good approximation in the parameter range covered.

As shown in Fig. 4 the coefficient k_τ lies in quite a broad range from $k_\tau \sim 6$ at $\beta = 1$ and $x = 0.5$ to $k_\tau > 10^4$ at $\beta, x < 0.2$. For the parameters $x = 0.31$ and $\beta = 0.5$ found for CKN[8)] and CRN[10)] one has $k_\tau \sim 30$. This gives $\tau_e = (250 \pm 10)$ s for $q = 10$ K/min.

It is clear that the relaxation times thus obtained can only be regarded as a

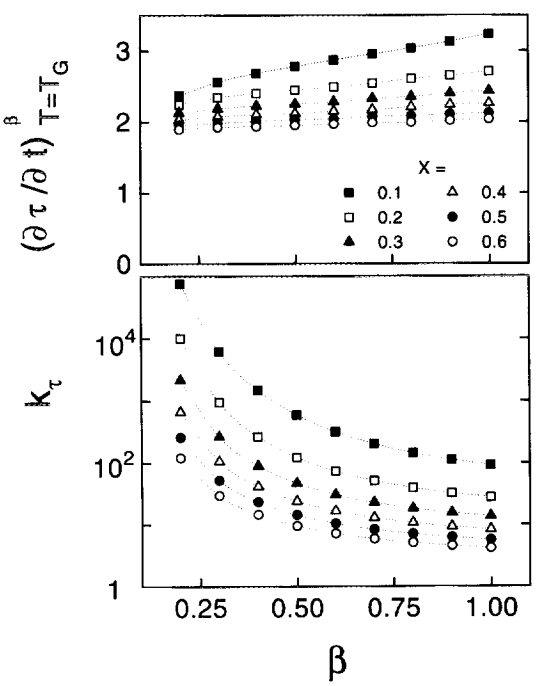

Fig. 4. (upper frame) Effective Deborah number $a = (DN)^\beta$ estimated within the Moynihan-Narayanaswami formalism for various combinations of stretching exponents β and non-linearity parameters x. Except for very small x, the coefficient a is relatively insensitive against parameter variations. (lower frame) Proportionality constant k_τ connecting the characteristic structural relaxation time and the term $T_g^2/q\Delta H$ via Eq. (13).

rough indicator of the dynamical processes within the glass former. This is on the one hand due to the fact that the structural relaxation is stretched with a typical distribution of τ_e spanning about two decades. One the other hand apart from the slowest (primary) relaxation mode which we have considered so far, there can be a wealth of other faster modes. This is not only true for the molten nitrates [11] but also for amorphous polymers. Of course, due to the differences in the types of bonding and of mesoscopic structures in these two classes of materials the nature of these faster modes can be quite different. In polymers one usually encounters various kinds of side group motions, while one prominent decoupled mode in the molten and vitreous salts is the electrical conductivity due to the mobile ions.

To summarize we have considered various time scales relevant at the calorimetric glass transition, primarily focusing on the structural relaxation. We have outlined some arguments leading to a justification for the frequently cited order of magnitude for the Deborah number $DN = a^{1/\beta}$. On the basis of self-consistent computations employing the Moynihan-Narayanaswami formalism we have estimated from our DSC data a characteristic time of about 250 s at the conventionally defined calorimetric glass transition of CRN.

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