On the nature of slow β-relaxation in supercooled liquids

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Abstract. We propose a model for reorientational motions of molecules associated with secondary beta-relaxation in supercooled liquids. The secondary relaxation is attributed to relaxation within a given local minimum, while the primary relaxation is attributed to transitions between distinct free-energy minima. We find that (i) at the temperature where the peak frequency of the extrapolated beta-relaxation intersects the alpha-relaxation, the actual and the extrapolated spectra differ in their time constants by approximately one decade; (ii) there is no clear division between the imaginary part of the dielectric susceptibility for the alpha- and the beta-relaxation for temperatures larger than $1.1\,T_g$. Thus, one must proceed with caution to extrapolate low temperature data of beta-relaxation to higher temperatures in order to estimate the temperature at which the time scales for the two processes cross. The relaxation times for the alpha- and the beta-processes cannot cross except at high temperature, where only the primary relaxation remains.

1. Introduction

Since a detailed understanding of the origin of the slow beta-process is lacking, there has been renewed experimental and theoretical interest in elucidating the characteristics of the beta-process in glass-forming liquids [1–15]. The β-relaxation is generally viewed to be an inherent property of the glassy state of matter [3, 4] and has been attributed not only to intramolecular reorientation [5, 6], but also to the packing statistics of the molecules in the inherent structure description of supercooled liquids [1, 2, 10].

Near the glass transition temperature, the time scale of the β-relaxation process in dielectric loss experiments is in the kHz range, while that of the alpha-relaxation is a few hundred seconds. A partition of the β- and the α-peaks is usually observed at low temperatures. At high temperatures, however, the β- and the α-peaks tend to merge if the analysis is based on low temperature extrapolated data of the β-peak frequency. Various scenarios have been advanced to explain the crossing of the β- and the α-time-scales [6, 11–13].

In this paper, we review a recently proposed generalization of the free-energy landscape model to the β process [14, 15]. In section 2, we describe the essential features of the free-energy landscape model for activated β-processes. In section 3, we briefly present a model calculation for dielectric loss and discuss its implications.

2. Model for β-relaxation

Reorientation dynamics inside an individual minimum of the free energy defines the β-process. Structural relaxation occurs by transitions amongst the various free-energy minima. Note that

the various minima are not due to all coarse grained degrees of freedom. In this model, not all degrees of freedom are to be coarse grained but mainly the centre of mass positions of the molecules. The reorientational processes are very restricted in the sense that they are not isotropic. The underlying idea is that steric hindrance within an amorphous minimum is responsible for such barriers.

Let be $\kappa(\varepsilon'|\varepsilon)$ the rate of transition between an initial minimum (state) ε and a final minimum, ε', $\varepsilon \to \varepsilon'$, which obeys a detailed balance. In the model, the orientation as well as the translation degrees of freedom of a labelled molecule are linked to the α-relaxation process through $(\varepsilon|\varepsilon)$. The dynamics of the system at a given temperature is governed by a master-like equation for the Green function $G(\varepsilon, t|\varepsilon_0)$ and can be expressed in terms of the attempt frequency, κ_∞^α, the mean activation energy E_α, the density of states of the minimum ε', $\eta(\varepsilon')$, and the activation energy for escape out of a given valley $E_\alpha - \varepsilon$ [14, 15].

At time t, the orientation of a tagged molecule changes as a result of relaxation; this orientation is denoted by $\Omega_\alpha(t)$. Similarly, $\omega_\beta(t)$ denotes the orientation of the molecule at time t due to relaxation. Our goal is to describe the rate equation for the combined Markov set $(\Omega_\alpha, \omega_\beta, \lambda)$, where $\lambda = (\varepsilon, \mu)$, and μ is the activation energy of the β-process.

A molecular fixed coordinate system (M) is introduced as shown in figure 1. The z-axis of system M, z_M, is in coincidence with the axis of interaction being studied [15]. By axis of interaction one means, in the case of a dielectric, the axis of the dipole moment, while in deuteron NMR, it is the principal axis system of the electric field gradient tensor. The β-process is described as angular jumps, on a cone of fixed polar angle θ, with azimuthal jump angle $\delta(t)$ about some axis A, relative to M, chosen such that its z-axis is parallel to A [15]. The angle $\delta(t)$ is time dependent and can acquire only two values. We assume equilibrium populations of the two orientations, $\omega_1 = (\alpha_{AM}(\varepsilon), \theta(\varepsilon), \delta(\varepsilon))$ and $\omega_2 = (\alpha_{AM}(\varepsilon), \theta(\varepsilon), 0)$, $p_{eq}(\omega_i) = 1/2$, $i = 1, 2$ [15]. The assumption that $p_{eq}(\omega_i) = 1/2$ means that the two orientations are equally probable. This and the choice of only two orientations is the simplest one. Other scenarios give rise to quantitatively more complex behaviour, but the qualitative features remain unchanged. We do not specify the angles $\alpha_{AM}(\varepsilon)$ as they turn out not to be relevant for evaluation of two-time correlation functions.
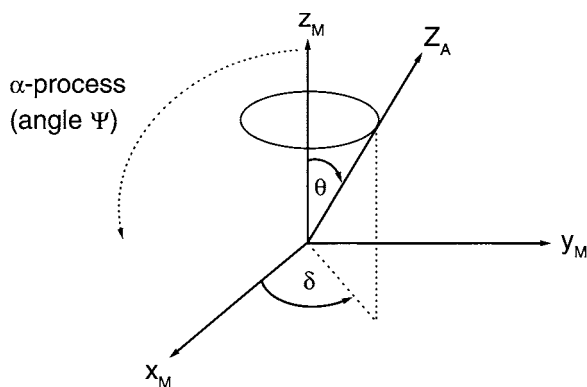

Figure 1. The molecular fixed coordinate system (M). The α-relaxations are due to isotropic reorientations of the molecular axis. The β-process is described by angular jumps, on a cone of fixed polar angle θ, with azimuthal jump angle $\delta(t)$ around some axis A, relative to M, chosen such that its z-axis is parallel to A. Adapted from [15] (1999 copyright, American Physical Society).

In this model, the α-relaxations are due to isotropic reorientations of the molecular axis (M) relative to the laboratory coordinate axis (L): $\Omega_\alpha(t) = (\alpha_{ML}(t), \beta_{ML}(t), \gamma_{ML}(t))$, where

$\Omega = (\alpha, \beta, \gamma)$ are the Euler angles [15].

We make the assumption that the transition rates between distinct minima do not depend on the activation free energy μ [15]. The dependence of ε on μ is, however, complicated. We have analysed the case in which ε and μ are not correlated and hence have independent distribution $p_{eq}(\varepsilon)$ and $g(\mu)$ respectively [15]. Another possibility that has been investigated is a strong correlation between the alpha- and the beta-processes defined by $\mu = f(\varepsilon)$ [15].

The conditional probability of the Markov process $(\Omega_\alpha(t), \omega_\beta(t), \lambda(t))$ satisfies an appropriate master equation with the transition probability expressed in terms of a parameter c. If c is unity, no correlation exists between the processes $\varepsilon(t)$ and $\omega_\beta(t)$. If c is zero, then the transition $\varepsilon \rightarrow \varepsilon'$ randomizes ω_β [15].

To solve the master equation, the conditional probability is expanded in terms of Green functions G and the Wigner rotational matrices $D_{mn}^{(1)}(\Omega)$; the latter quantities are eigenvectors of the transition matrix [15, 16]. Two-time orientational correlation functions $C_{n_1 n_2}^{(1)}(t) = \langle D_{n_1 n_2}^{(1)}(\Omega_{AL}(t)) D_{n_1 n_2}^{(1)*}(\Omega_{AL}(0)) \rangle$ are calculated from the conditional probability, where AL denotes the relative orientation between the A-axis system and the laboratory fixed frame [15]. From $C_{n_1 n_2}^{(1)}(t)$, all experimental observable quantities are obtained.

3. Results and discussion

3.1. Model parameters

For computational convenience we have taken the density of states to be a Γ-distribution [15]

$$\eta(\varepsilon) = \mathfrak{T}(\delta\varepsilon)^p \, e^{-q(\delta\varepsilon)} \tag{1}$$

where $\mathfrak{T}$ is a normalization constant, and $\delta\varepsilon$ denotes the deviation of ε from its maximum value, ε_{max}. We used a gamma-distribution mainly because it is flexible enough to give either a Gaussian or an exponential distribution for some choice of the parameters. In the results presented below, we have taken $p = 10$ and $q = 0.3$ [15].

As mentioned above, the β-relaxation is modelled as activated jumps between two orientations. Since we assume the activation free energy μ and ε are not correlated, the values for μ are selected from the distribution $g(\mu)$, assumed to be a Gaussian, whose mean and variance are E_β and σ, respectively [15]. We use a symmetric distribution of activation energies which automatically gives rise to an approximately symmetric dielectric loss and the spread is just a question of the width. As will be seen below, the important point in our model is that the peak becomes asymmetric when the time scales of alpha- and beta-relaxation are no longer separated in a clear-cut way. The temperature dependence of the reorientation rate is Arrhenius: $\Gamma(\mu) = \kappa_\infty^\beta e^{-\beta\mu}$, where $\beta = 1/k_B T$, k_B is the Boltzmann constant and T is the absolute temperature [15]. The parameters κ_∞^β and E_β have been assigned the values 10^{15} s^{-1} and 24 T_g respectively [7, 15].

For the α-process, the parameters in the model are the activation free energy E_α and the quantities p and q that appear in the density of states. The value of E_α is fixed by imposing the constraint that the correlation time at temperature $T \approx 1.2\, T_g$ is 10^{-8} s [15]. Since the overall time scale is dictated by the attempt frequency, we choose the combination $\kappa_\infty^\alpha e^{-\beta_g E_\alpha}$ to define the glass transition temperature T_g. The value for this temperature is such that the orientation time correlation function for the first rank Legendre polynomial decays in approximately 100 s [15]. We have varied the activation free energy E_α from 108 to 114 T_g and the corresponding variance σ from 4.5 to 7 T_g. Thus, the parameter $X(T_g) = \kappa_\infty^\alpha e^{-\beta_g E_\alpha} / \kappa_\infty^\beta e^{-\beta_g E_\beta}$ acquires values between 10^5 at $T = 108\, T_g$ and 22.8 at $T = 22.8\, T_g$ [15].
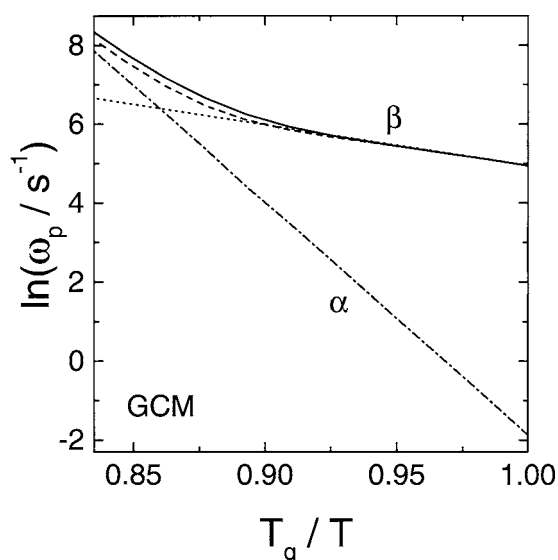
Figure 2. $\text{Log}(\omega_p)$ versus inverse temperature scaled by the glass transition temperature. The continuous and the dashed lines are the peak frequency of $\Phi_1^{(\beta)}(\omega)$ for the case $c = 0$ and $c = 1$ respectively. The dotted line represents the extrapolated low temperature characteristic of the peak frequency for the beta-relaxation. The dashed–dot line is the peak frequency for the alpha relaxation $\Phi_1^{(\alpha)}(\omega)$. Adapted from [15] (1999 copyright, American Physical Society).

Next we turn our attention to the determination of the jump angles (ϕ, ψ, δ). Since the alpha-relaxation is viewed as isotropic reorientation of the molecule, $\phi = \psi/\sqrt{8}$ [17]. NMR studies on tolune, glycerol and *ortho*-terphenyl indicate an approximate value of $10°$ for ψ [18–20].

The jump angle δ is determined as follows. The mean-squared displacement and the jump distance r_{jump} in the two-site model are related by $\langle r^2 \rangle = p_{eq;1} p_{eq;2} \{2 r_{jump} \sin(\delta/2)\}^2$ [15]. Near, T_g the mean squared displacement increases in an exponential manner with temperature. Thus, its temperature dependence is through the equilibrium distribution and the azimuthal angle. We take the temperature dependence of $\delta(T)$ to be Arrhenius: $\delta(T) = \delta_0 e^{-\beta E_\delta}$ [8]. We have varied δ_0 between 10 and $3°$ at $0.8 \, T_g$ [15].

3.2. Dielectric susceptibility

In the model, the imaginary part of the dielectric susceptibility is found to be of the form [15]

$$\Phi(\omega) = f_\alpha^{(10)} \Phi_1^{(\alpha)}(\omega) + \left(1 - f_\alpha^{(10)}\right) \Phi_1^{(\beta)}(\omega) \tag{2}$$

where the amplitudes $f_\alpha^{(ln)}$ are strongly dependent on the angle θ—the angle between the z_M-axis and the interaction under consideration (see figure 1). For dielectric relaxation, the values of l and n are 1 and 0, respectively. Here, $\Phi_1^{(x)}(\omega)$ is the Laplace transform of $-\left[d\Phi_1^{(x)}(t)/dt \right]$ and the functions $\Phi_1^{(\beta)}(t)$ and $\Phi_1^{(\alpha)}(t)$ are explicitly given in [15].

We have varied the angle θ between 20 and $60°$ in intervals of $10°$. Numerical results show that the amplitude $f_\alpha^{10}(\theta \approx 60°)$ is approximately that determined by experiments [6, 7, 15]. The various Green functions are numerically solved by diagonalizing the discrete form of the various matrices and applying 50–100 values of ε. Both $\Phi_1^{(\alpha)''}(\omega)$ and $\Phi_1^{(\beta)''}(\omega)$ as a function

of frequency (ω) were evaluated for a range of temperatures from 0.8 to 1.2 T_g in intervals of 0.04 T_g [15]. The peak position of $\Phi_1^{(\alpha)''}(\omega)$ and $\Phi_1^{(\beta)''}(\omega)$, ω_p, as well as the full width at half maximum were then calculated as a function of temperature.

The logarithms of ω_p—the peak positions for both the alpha- and the beta-processes—are plotted as a function of reduced temperature T/T_g in figure 2. In this figure, we have also depicted the extrapolated behaviour of the low temperature characteristic of the response function $\Phi_1^{(\beta)''}(\omega)$, i.e. $\Phi_1^{(\beta,0)''}(\omega)$—a quantity which does not depend on the correlation parameter c [15].

Several comments are in order. First, the peak frequency of the extrapolated beta-relaxation intersects the alpha-relaxation at $\ln(\omega_p) \approx 6.5$ [15]. At the cross-over temperature, the actual and the extrapolated spectra differ in the time constant by a decade or so [15]. Second, the actual spectra of $\Phi_1^{(\beta)''}(\omega)$ deviate from the extrapolated spectra at temperature above $T \approx 1.1 \, T_g$, where the two peak frequencies vary by two decades. Third, there is no clear division between the imaginary parts of the dielectric susceptibility spectra for the alpha- and the beta-relaxation for temperatures larger than 1.1 T_g [15]. Fourth, the width of $\Phi_1^{(\beta)''}(\omega)$ deviates even at low temperatures from the width of the low temperature extrapolated spectra, $\Phi_{10}^{(\beta,0)''}(\omega)$ [15]. Fifth, what the results mean is that care must be taken to extrapolate low temperature data of beta-relaxation to higher temperatures in order to estimate the temperature at which the time scales for the two processes cross [15]. The relaxation times for the alpha- and the beta-processes cannot cross except at high temperature, where only the primary relaxation remains [15]. Finally, note that the temperature dependence of the peak position of the alpha-process, contrary to experiments, shows Arrhenius-like behaviour [15]. This is due to our assumption that the density of states $\eta(\varepsilon)$ is temperature independent [15]. However, the curvature can be made steeper by assuming the variance σ of $\eta(\varepsilon)$ to be temperature dependent. Since the goal of this work is the description of the beta-process, we have not explored the consequences of a temperature dependent width to the density of states.

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