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Slow secondary relaxation in a free-energy landscape model for relaxation in glass-forming liquids

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Within the framework of a free-energy landscape model for the relaxation in supercooled liquids the primary (α) relaxation is modeled by transitions among different free-energy minima. The secondary (β) relaxation then corresponds to intraminima relaxation. We consider a simple model for the reorientational motions of the molecules associated with both processes and calculate the dielectric susceptibility as well as the spin-lattice relaxation times. The parameters of the model can be chosen in a way that both quantities show a behavior similar to that observed in experimental studies on supercooled liquids. In particular we find that it is not possible to obtain a crossing of the time scales associated with α and β relaxation. In our model these processes always merge at high temperatures and the α process remains above the merging temperature. The relation to other models is discussed. [S1063-651X(99)07002-6]

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I. INTRODUCTION

Despite considerable efforts, a detailed understanding of the glass transition is still missing (for reviews see [1–3]). There are several aspects of the relaxation behavior of supercooled liquids, which have been subject to extensive discussions in the last few years. Apart from the question of the applicability of mode coupling theories (MCT) [4], the question concerning heterogeneity of the α relaxation has been addressed in many recent studies [5]. At present it seems that the α relaxation can be viewed as heterogeneous, although the relation to a characteristic length scale still poses a question [5,6], as many of the applied experimental techniques are sensitive to molecular reorientational dynamics. Concerning the temperature dependence of the dynamic heterogeneities, little is known at present as most studies are carried out at temperatures slightly above the calorimetric glass transition temperature T_g [7].

Several models have been formulated to treat the problem of dynamical heterogeneities, most of which rely on the existence of long-lived domains or regions in the supercooled liquid, see, e.g., Refs. [3] and [8]. One of us in collaboration with others recently introduced a free-energy landscape model for the α relaxation in strongly supercooled liquids [10–12]. In this model molecular reorientation is assumed to be coupled intrinsically to the structural relaxation, which in turn is modeled as transitions among an extensive number of free-energy minima. When interpreted in terms of domains, in this model the restructuring of domains is responsible for α relaxation. We note that in the low-temperature regime of relevance here MCT is of little use since the idealized version does not give rise to any structural relaxation at all and the dynamical equations occurring in more sophisticated models have not been solved so far [9].

Another aspect of glassy relaxation, which has attracted much attention, is the (slow) β relaxation. This relaxation process is thought to be an intrinsic property of glassy relaxation by many [13–15]. However, there still is some discussion about its molecular origin [16–18]. Whereas in some cases, an intramolecular reorientation [16,17] has been suggested as the origin of the β process, this process has also been observed in rigid molecules like toluene [18,20] and fluorocarbon mixtures [21,22]. We note that Goldstein remarked already in his seminal paper on the energy landscape picture of glassy relaxation [19] that one should not rule out the possibility that the β process may be related to the packing of the molecules in the amorphous phase. It is to be mentioned that this process is much slower than the (fast) β process playing a central role in the two-step decay of density correlation functions within the framework of MCT.

Some aspects of the dielectric loss in the glassy state seem to show universal behavior. The spectra are symmetric on a logarithmic frequency scale and the peak position changes with temperature according to a simple Arrhenius law. This behavior can be modeled excellently by the assumption of a Gaussian distribution of activation energies with an approximately temperature-independent width. Recently, it has been emphasized that the mean activation energy correlates with the calorimetric glass transition temperature T_g, $E_\beta \sim 24 T_g$ [18]. Typically, the time scale of the β process is in the kHz regime at T_g to be compared with about 100 s for the α process. Therefore, at temperatures not too high, a clear-cut separation of the α and β peaks is possible. At higher temperatures, the peaks seem to merge and the typically shown schematic plots of a merging or crossing of the timescales of α and β relaxations heavily rely on extrapolations of the β peak frequency from low temperatures.

Concerning the merging of the α and β process, several interpretations have been put forward so far. Some authors suggest that at temperatures higher than the merging temperature, T_{merge}, the α process dies out due to vanishing intensity [23]. Rössler [24] argues that the merging of the processes takes place at the temperature where a change in

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the transport mechanism in supercooled liquids can be observed. Similar observations have been reported by Hansen *et al.* [25]. This means that there should be a relation between the MCT critical temperature and T_{merge}. As pointed out by Arbe *et al.* [17], a note of caution is appropriate in the interpretation of the merging of the α and β peaks. Most of the data are analyzed in terms of two distinct peaks and a subsequent extrapolation of the peak frequency of the β process to higher temperatures. These authors used a more sophisticated data analysis and were able to resolve some puzzles concerning the time scale of the dielectric α process of polybutadiene as compared to the viscosity. However, this analysis relies on a specific model for the β process and the assumption of statistical independence of the two processes.

Apart from the time scale, a more or less similar behavior is found for the intensity of the β peaks. When corrected for the Curie behavior, it usually is found to increase with increasing temperature. This increase is very weak below T_g but becomes much more pronounced above T_g. Correspondingly, the intensity of the α peak decreases with increasing temperature [17,18].

It is the purpose of the present paper to generalize the above-mentioned free-energy landscape model [10,11,12] in order to take into account the β process in addition to the α relaxation. As already mentioned, the fundamental assumption of this model is an intrinsic coupling of the orientational (and translational) degrees of freedom of a tagged molecule to the α relaxation. Denoting the rates of transitions $\epsilon' \rightarrow \epsilon$ among connected states (minima) ϵ by $\kappa(\epsilon|\epsilon')$, the model assumption of an intrinsic coupling states that molecular reorientations are completely determined by the $\kappa(\epsilon|\epsilon')$. In other words, any transition from a molecular orientation Ω to a different orientation Ω' is associated with a corresponding transition among the states ϵ, which define the minima in the free-energy landscape. Here Ω denotes the orientation of the relevant interaction in a laboratory axes system, specified by the Euler angles $\Omega=(\alpha,\beta,\gamma)$ [26]. The model starts from a composite Markov process [27] $(\Omega(t),\epsilon(t))$ from which the non-Markovian process of molecular reorientation $\Omega(t)$ is obtained as a projection by integrating over all states ϵ. In this model, reorientational time correlation functions decay to their equilibrium value only after a number of transitions have taken place. This, for instance, allows a simple interpretation of several experiments monitoring higher-order correlation functions [10]. The same model can be applied to the translational motion and the diffusion constant obtains. It has been shown that a number of so far unresolved features related to the α relaxation can be understood naturally within the framework of this model, including the different stretching of rotational correlation functions as obtained by different experimental techniques, the similarity in their time scales, and the apparent enhancement of translational diffusion [11]. Since the orientation Ω is associated with the α process, the reorientational motions are modeled by finite isotropic angular jumps. It then appears natural to identify the β relaxation with processes taking place inside the minima of the free-energy landscape. Physically, one would assume that the associated reorientational motions will be neither isotropic nor of large scale. In the following we will consider the simplest possible model for such a scenario. We will formulate the rate equations for a simple reorientation among two sites around some prescribed axis. This gives rise to dielectric loss as well as to spin-lattice relaxation due to the β process. The eventual decay to zero of the considered correlation function is achieved by the α process at high enough temperatures.

The outline of the paper is the following. In the next section we briefly recall the essential features of the free-energy landscape model and set up the rate equations for the generalized model. This section, therefore, is of a more formal nature. Readers only interested in the physical aspects of the model may skip and go directly to Sec. III, where we present the results of model calculations for both the dielectric loss and the spin-lattice relaxation times. Section IV contains a discussion of our results and some remarks on the treatment of experimental data. Finally, we close with some conclusions in Sec. V.

II. ACTIVATED α AND β RELAXATION IN A FREE-ENERGY LANDSCAPE MODEL

In this section we set up the rate equations for the composite Markov process used to describe both the primary and slow secondary relaxation in supercooled liquids and glasses. Concerning the α process, the procedure is identical to the one used in Refs. [10] and [11], which we briefly review here for completeness.

If we assume that the structural relaxation in a supercooled liquid near T_g is governed by activated dynamics, i.e., by transitions among an extensive number of free-energy minima (or valleys in the spin-glass notation), we can set up a master equation for the Green's function $G(\epsilon,t|\epsilon_0)$:

$$\dot{G}(\epsilon,t|\epsilon_0)=-\kappa(\epsilon)G(\epsilon,t|\epsilon_0)+\int d\epsilon'\,\kappa(\epsilon|\epsilon')G(\epsilon',t|\epsilon_0), \tag{1}$$

with $\kappa(\epsilon):=\int d\epsilon'\,\kappa(\epsilon'|\epsilon)$. The rates $\kappa(\epsilon'|\epsilon)$ for a transition $\epsilon\rightarrow\epsilon'$ obey detailed balance and we have defined the decay rate $\kappa(\epsilon)$. As in Ref. [11] we will consider two different models for the transition rates. One is defined by a global connectivity among the free-energy minima and referred to as a *globally connected model* (GCM) in what follows. In addition to the global connectivity we assume that once an escape from the initial minimum ϵ has taken place, the destination minimum ϵ' is chosen at random that is corresponding to the density of states (DOS) $\eta(\epsilon')$. We then have

$$\kappa(\epsilon'|\epsilon)=\eta(\epsilon')(\kappa_\infty^\alpha e^{-\beta(E_\alpha-\epsilon)}), \tag{2}$$

where $\beta=(k_BT)^{-1}$, E_α is a common activation free energy, and κ_∞^α denotes an ''attempt frequency.'' This choice represents a mean-field-like random trap model. If we switch from the values of the free energy in a given minimum ϵ to the corresponding activation free energy, $E_\alpha-\epsilon$, we have a random barrier model. We do not distinguish among these choices, since there is a linear relation among them. The other choice for the transition rates is a *locally connected model* (LCM), where only transitions between minima of similar values of ϵ are allowed. Whereas the GCM might seem more plausible on first sight, the LCM may be relevant if the value of ϵ is among the relevant order parameters as

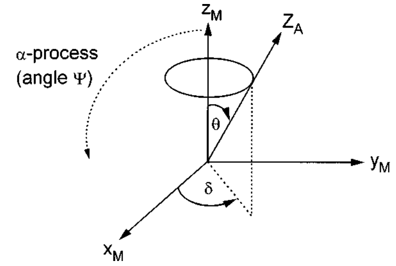

FIG. 1. The definition of the relative orientation of the axis **A** in a molecular fixed coordinate system. The axis **A** coincides with the z axis of the coordinate system (A), $\mathbf{A} \| Z_A$, and is assumed to change due to reorientations about an angle δ and its polar angle relative to the axis of the relevant interaction (z_M) is denoted by θ, cf. text. Also indicated is the isotropic reorientation of the M system due to the α process (dotted arrow).

used, for example, by Stillinger [28]. In this case one ends up with a Fokker-Planck equation for the Green's function and one has activated transport governed by entropic barriers [29]. In the simplified version used here, the ϵ-dependent diffusion coefficient is given by $D(\epsilon)=\kappa_\infty^\alpha e^{-\beta(E_\alpha-\epsilon)}$ and the entropic force stems from a potential $U(\epsilon)=\beta^{-1}\ln[\eta(\epsilon)]$ [10]. In both cases the equilibrium population of the minima or states is given by

$$p^{\mathrm{eq}}(\epsilon)=Z^{-1}\eta(\epsilon)e^{-\beta\epsilon} \quad \text{where} \quad Z=\int d\epsilon\, \eta(\epsilon)e^{-\beta\epsilon}. \tag{3}$$

For a further discussion of the master equation and the physical picture underlying the proposed scenario, we refer to Refs. [10] and [11]. There also the procedure to treat the composite Markov process $(\Omega_\alpha(t),\epsilon(t))$ is described.

We now set up the rate equations for the composite Markov process $(\Omega_\alpha(t),\omega_\beta(t),\hat{\epsilon}(t))$. Here Ω_α denotes the orientation of the tagged molecule that is to be changed in the course of time due to α relaxation, ω_β that orientation associated with the β process, and $\hat{\epsilon}\equiv(\epsilon,\mu)$ now is a two-dimensional variable with μ denoting the activation free energy of the β process. The β process is viewed as a small amplitude reorientational process defined *within* a single minimum of the free energy. We do not specify the interrelation between ϵ and μ now, except for the physically reasonable choice that the rates for transitions among *different* minima are independent of μ. Two possible relations between ϵ and μ are as follows.

(i) The values of ϵ and μ are completely uncorrelated, which means they are chosen from independent distribution functions $p^{\mathrm{eq}}(\epsilon)$ and $g(\mu)$. There is no correlation between the escape rate from state ϵ and the activation energy for the β process in that state.

(ii) The value of ϵ determines the value of μ. In practical calculations one might choose μ to be given as a function $\mu=f(\epsilon)$. Here one has a strong correlation among the activation energies for the α and β process in a given state.

The process $\epsilon(t)$ is viewed as the fundamental stochastic process responsible for the primary relaxation in the system.

In order to model both the α and β processes, we proceed in the following way (cf. Fig. 1): We assume that the β process can be modeled as a simple two-site angular jump of jump angle δ around some axis. Since this axis does not necessarily coincide with the orientation of, e.g., the molecular dipole moment (as is relevant for dielectric relaxation) or one of the principal axes of an electric field gradient tensor (which is relevant for deuteron NMR) we assume that the axis **A** has an arbitary but defined orientation relative to a molecular axis system (M). The latter is defined in a way that the z_M axis coincides with the axis of the relevant interaction under consideration. The β process is now modeled in assuming that **A** performs two site jumps on a cone around z_M with fixed cone angle θ and so far unspecified jump angle δ. Consequently **A** becomes time dependent. This means that the orientation of the coordinate system (A), where Z_A coincides with **A**, relative to the M system Ω_{AM} constitutes our process $\omega_\beta(t)$. Here only δ is time dependent in accord with our assumption. We thus have

$$\omega(t)=(\alpha_{AM}(\epsilon),\theta(\epsilon),\delta(\epsilon,t)),$$

$$\omega_1=(\alpha_{AM}(\epsilon),\theta(\epsilon),\delta(\epsilon)), \quad \omega_2=(\alpha_{AM}(\epsilon),\theta(\epsilon),0), \tag{4}$$

where we have allowed for an additional dependence of the relevant angles on ϵ. This assumption is physically reasonable since different molecular configurations corresponding to different minima in the free-energy landscape might in particular differ in local density, allowing for different mean-squared displacements. Additionally, we assume that the equilibrium populations of the two orientations ω_1 and ω_2 are equal, $p^{\mathrm{eq}}(\omega_i)=\frac{1}{2}$, $i=1,2$, thus neglecting any bias. We mention that for our present purposes the angles $\alpha_{AM}(\epsilon)$ need not be further specified as they do not enter in the calculations of the time correlation functions considered in this paper.

Having defined the reorientational model we will use for the β relaxation, the only thing remaining is the definition of the corresponding α process. In view of the above consideration, this is straightforward: The isotropic reorientations giving rise to α relaxation are just the tumbling motions of the M system relative to a well-defined laboratory (L) system,

$$\Omega_\alpha(t): \quad \Omega_\alpha(t)=(\alpha_{ML}(t),\beta_{ML}(t),\gamma_{ML}(t)), \tag{5}$$

where we (as in all following relations) use the convention of Rose [26].

Before analyzing the corresponding master equations, let us summarize the physical picture of the above definitions. We view the complex reorientational motion in supercooled liquids as a composite process of two distinct motions: There are ‘‘fast’’ restricted angular fluctuations (but still much slower than any microscopic time scale) associated with β relaxation, which we model by a simple two-site angular jump model. (The reason for assuming only two orientations ω_1 and ω_2 is simply that the corresponding master equation can be solved easily.) Superimposed on these we have the (isotropic) tumbling of the jump axis corresponding to the α relaxation. In terms of the free-energy landscape picture setting the overall frame for all considered relaxation processes, the β relaxation $[\omega_\beta(t)]$ corresponds to *intravalley* relaxation and the α relaxation $[\Omega_\alpha(t)]$ corresponds to *intervalley* relaxation.

Since the assumption of a two-site jump model for the β process is rather restrictive, we relax this in the formal development that follows and assume a continuous range for ω_β. When returning to a discrete notation all integrals in the following expressions simply have to be replaced by the corresponding summations. The same holds, of course, for the variable $\hat{\epsilon}=(\epsilon,\mu)$.

The master equation for the conditional probability [27] of the composite Markov process $(\Omega_\alpha(t),\omega_\beta(t),\hat{\epsilon}(t))$ reads

$$\begin{aligned}\dot{P}_{1|1}(\Omega_\alpha,\omega_\beta,\hat{\epsilon},t|\Omega''_\alpha,\omega''_\beta,\hat{\epsilon}'')&=\int d\Omega'_\alpha\int d\omega'_\beta\int d\hat{\epsilon}'\,W(\Omega_\alpha,\omega_\beta,\hat{\epsilon}|\Omega'_\alpha,\omega'_\beta,\hat{\epsilon}')\\&\quad\times P_{1|1}(\Omega'_\alpha,\omega'_\beta,\hat{\epsilon}',t|\Omega''_\alpha,\omega''_\beta,\hat{\epsilon}'')\end{aligned}\tag{6}$$

along with the initial condition

$$\begin{aligned}P_{1|1}(\Omega_\alpha,\omega_\beta,\hat{\epsilon},t=0|\Omega''_\alpha,\omega''_\beta,\hat{\epsilon}'')&=\delta(\Omega_\alpha,\Omega''_\alpha)\,\delta(\omega_\beta,\omega''_\beta)\,\delta(\hat{\epsilon},\hat{\epsilon}''),\end{aligned}\tag{7}$$

where $\delta(x,y)$ denotes a Dirac delta function in the case of continuous variables and the Kronecker symbol in the discrete case. For the equilibrium population we neglect correlations among the different processes and approximate

$$\begin{aligned}P_1(\Omega_\alpha,\omega_\beta,\hat{\epsilon})&\simeq p^{\mathrm{eq}}(\Omega_\alpha)p^{\mathrm{eq}}(\omega_\beta)p^{\mathrm{eq}}(\hat{\epsilon})\\&=p^{\mathrm{eq}}(\Omega_\alpha)p^{\mathrm{eq}}(\omega_\beta)p^{\mathrm{eq}}(\epsilon)g(\mu).\end{aligned}\tag{8}$$

According to our model, we now choose the transition matrix W in the following way:

$$\begin{aligned}W(\Omega_\alpha,\omega_\beta,\hat{\epsilon}|\Omega'_\alpha,\omega'_\beta,\hat{\epsilon}')&=[\mathbf{K}(\epsilon|\epsilon')\mathbf{\Pi}_{(\epsilon,\epsilon')}(\Omega_\alpha|\Omega'_\alpha)\{c\,\delta(\omega_\beta,\omega'_\beta)\\&\quad+(1-c)p^{\mathrm{eq}}(\omega_\beta)\}+\mathbf{\Pi}_{(\epsilon,\mu)}(\omega_\beta|\omega'_\beta)\\&\quad\times\delta(\Omega_\alpha,\Omega'_\alpha)\,\delta(\epsilon,\epsilon')]\,\delta(\mu,\mu').\end{aligned}\tag{9}$$

With the definition $\nu(x,y)=1-\delta(x,y)$ the various operators (matrices) are explicitly given by

$$\mathbf{K}(\epsilon|\epsilon')=-\kappa(\epsilon)\,\delta(\epsilon,\epsilon')+\kappa(\epsilon|\epsilon')\,\nu(\epsilon,\epsilon'),\tag{10}$$

$$\begin{aligned}\mathbf{\Pi}_{(\epsilon,\epsilon')}(\Omega_\alpha|\Omega'_\alpha)&=\delta(\Omega_\alpha,\Omega'_\alpha)\,\delta(\epsilon,\epsilon')\\&\quad+\Lambda_{(\epsilon,\epsilon')}(\Omega_\alpha|\Omega'_\alpha)\,\nu(\Omega_\alpha,\Omega'_\alpha)\,\nu(\epsilon,\epsilon'),\end{aligned}\tag{11}$$

and

$$\begin{aligned}\mathbf{\Pi}_{(\epsilon,\mu)}(\omega_\beta|\omega'_\beta)&=-\Pi_{(\epsilon,\mu)}(\omega_\beta)\,\delta(\omega_\beta,\omega'_\beta)\\&\quad+\Pi_{(\epsilon,\mu)}(\omega_\beta|\omega'_\beta)\,\nu(\omega_\beta,\omega'_\beta),\\\Pi_{(\epsilon,\mu)}(\omega_\beta)&=\int d\omega'_\beta\Pi_{(\epsilon,\mu)}(\omega'_\beta|\omega_\beta).\end{aligned}\tag{12}$$

The transition rates among two orientations Ω_α are chosen to be

$$\Lambda_{(\epsilon,\epsilon')}(\Omega_\alpha|\Omega'_\alpha)=\delta(\Omega_\alpha-(\Omega'_\alpha+\Delta\Omega_\alpha))$$

$$\text{where}\quad\Delta\Omega_\alpha=(\phi_{(\epsilon,\epsilon')},\psi_{(\epsilon,\epsilon')},\phi_{(\epsilon,\epsilon')}).\tag{13}$$

Here, we have assumed that the angular jump angles in the y and z direction are the same. General choice of these angles accounts for anisotropic reorientations. In the following we always stay with isotropic reorientations, which amounts to set $\phi_{(\epsilon,\epsilon')}=(\psi_{(\epsilon,\epsilon')}/\sqrt{8})$ [30]. Note that the above choice of $\Lambda_{(\epsilon,\epsilon')}(\Omega_\alpha|\Omega'_\alpha)$ is more general than the one used in Ref. [11]. However, the results are very similar; see Ref. [30]. In addition, we have already made use of the fact that only the transition rates associated with the β process depend on the activation energies μ.

In the two-site jump model to be utilized in later calculations, the matrix (12) is given by

$$\mathbf{\Pi}_{(\epsilon,\mu)}(\omega_i|\omega_k)=-\Gamma(\epsilon;\mu)\{\delta(\omega_i,\omega_k)-\nu(\omega_i,\omega_k)\},$$

$$i,k=1,2,\tag{14}$$

where $\Gamma(\epsilon;\mu)$ denotes the rate for the reorientational jump.

A couple of comments are in order. The structure of the W matrix in Eq. (9) is the following.

(a) With any transition among the different minima described by the rates $\kappa(\epsilon|\epsilon')$ a transition $\Omega_\alpha\to\Omega'_\alpha$ is associated. The fact that the "diagonal element" in Eq. (11) is unity (instead of the negative sum of the off-diagonal elements) reflects the assumption that Ω_α changes in time *solely* due to $\epsilon\to\epsilon'$ transitions. There is no extra mechanism available for changes. For this reason the matrix $\Pi_{(\epsilon,\epsilon')}(\Omega_\alpha|\Omega'_\alpha)$ does not have the structure of a transition matrix as typically found for master equations; in particular, there is no sum rule.

(b) As we assume that $\omega_\beta(t)$ is a process defined within a free-energy minimum, the corresponding transition matrix (12) occurs on the "diagonal" with respect to ϵ $[\propto\delta(\epsilon,\epsilon')]$ in the transition matrix W. The matrix for transitions among the various possible values of the orientation ω_β, Eq. (12), does obey the sum rule.

(c) As it is still a question of the definition of the particular model whether or not $\omega_\beta(t)$ may change in case of a $\epsilon\to\epsilon'$ transition, we have included the term in the curly brackets in expression (9). The physical meaning of this term is the following. If the parameter c equals unity, there is no correlation among the processes $\epsilon(t)$ and $\omega_\beta(t)$ in which case the value of ω_β after a $\epsilon\to\epsilon'$ transition is the same as before, which is accounted for by the term $c\,\delta(\omega_\beta,\omega'_\beta)$. In the other limit $c=0$ the value of ω_β randomizes completely with every $\epsilon\to\epsilon'$ transition, hence the term $(1-c)p^{\mathrm{eq}}(\omega_\beta)$. A similar ansatz though in a different context has been used in connection with a composite Markov process by Beckert and Pfeifer, and Sillescu [31,32]. Note that other scenarios would of course be possible, but would unnecessarily complicate the physical picture.

Since a (numerical) solution to the master equation, Eq. (6), usually is not feasible in the present form, we proceed in the following way. Since the eigenvectors of the transition matrix $\mathbf{\Pi}_{(\epsilon,\epsilon')}(\Omega_\alpha|\Omega'_\alpha)$ are known to be the Wigner rotation matrices, we expand the conditional probability $P_{1|1}$ in terms of these:

$$P_{1|1}^{(\mu)}(\Omega_\alpha,\omega_\beta,\epsilon,t|\Omega''_\alpha,\omega''_\beta,\epsilon'')$$
$$=\sum_{l,m,n}\left(\frac{2l+1}{8\pi^2}\right)D_{nm}^{(l)}(\Omega_\alpha)D_{nm}^{(l)*}(\Omega''_\alpha)G_{(ln)}^{(\mu)}(\epsilon,t|\epsilon''). \tag{15}$$

Here, we have used the fact that μ does not change in the course of time [cf. Eq. (9)] and denoted the dependence of $P_{1|1}$ and G on μ by a superscript. The latter obeys the following rate equation:

$$\dot{G}_{(ln)}^{(\mu)}(\epsilon,t|\epsilon'')=\int d\omega'_\beta\int d\epsilon'\,\mathbf{W}_{(ln)}^{(\mu)}(\omega_\beta,\epsilon|\omega'_\beta,\epsilon')$$
$$\times G_{(ln)}^{(\mu)}(\epsilon',t|\epsilon''). \tag{16}$$

Here, we have

$$\mathbf{W}_{(ln)}^{(\mu)}(\omega_\beta,\epsilon|\omega'_\beta,\epsilon')$$
$$=\{\mathbf{\Pi}_{(\epsilon,\mu)}(\omega_\beta|\omega'_\beta)-\kappa(\epsilon)\,\delta(\omega_\beta,\omega'_\beta)\}\,\delta(\epsilon,\epsilon')$$
$$+\kappa(\epsilon|\epsilon')\Lambda_{(\epsilon,\epsilon')}(ln)\{c\,\delta(\omega_\beta,\omega'_\beta)$$
$$+(1-c)p^{\mathrm{eq}}(\omega_\beta)\}\,\nu(\epsilon,\epsilon') \tag{17}$$

with

$$\Lambda_{(\epsilon,\epsilon')}(ln)=\frac{2l+1}{8\pi^2}\int d\Omega_\alpha\int d\Omega'_\alpha\,D_{nm}^{(l)*}(\Omega_\alpha)$$
$$\times\Lambda_{(\epsilon,\epsilon')}(\Omega_\alpha|\Omega'_\alpha)D_{nm}^{(l)}(\Omega'_\alpha)$$
$$=\cos(2n\,\phi_{(\epsilon,\epsilon')})d_{n,n}^{(l)}(\psi_{(\epsilon,\epsilon')}). \tag{18}$$

Note that in case of $\mathbf{\Pi}_{(\epsilon,\mu)}(\omega_\beta|\omega'_\beta)=\mathbf{0}$ the above equations reduce to the ones considered in Refs. [10,11].

The next step consists in performing an expansion of the $G_{(ln)}^{(\mu)}(\epsilon,t|\epsilon'')$ in terms of the (as yet unknown) eigenfunctions of $\mathbf{\Pi}_{(\epsilon,\mu)}(\omega_\beta|\omega'_\beta)$. This is most easily achieved formally by using a Dirac notation and introducing the propagator

$$\mathbf{P}_{(ln)}^{(\mu)}(\epsilon,t|\epsilon')=\int d\omega_\beta\int d\omega'_\beta|\omega_\beta\rangle$$
$$\times G_{(ln)}^{(\mu)}(\omega_\beta,\epsilon,t|\omega'_\beta,\epsilon')\langle\omega'_\beta|,$$
$$G_{(ln)}^{(\mu)}(\omega_\beta,\epsilon,t|\omega'_\beta,\epsilon')=\langle\omega_\beta|\mathbf{P}_{(ln)}^{(\mu)}(\epsilon,t|\epsilon')|\omega'_\beta\rangle. \tag{19}$$

We now introduce a representation $\{|q\rangle\}$, which diagonalizes $\mathbf{W}_{(ln)}^{(\mu)}(\omega_\beta,\epsilon|\omega'_\beta,\epsilon')$ with respect to $\{|\omega_\beta\rangle\}$:

$$V(\omega_\beta,q):=\langle\omega_\beta|q\rangle,\quad V^{-1}(\omega_\beta,q):=\langle q|\omega_\beta\rangle. \tag{20}$$

This yields for the resulting Green's function,

$$\dot{G}_{(ln,q)}^{(\mu)}(\epsilon,t|\epsilon'')=\int d\epsilon'\,\mathbf{W}_{(ln,q)}^{(\mu)}(\epsilon|\epsilon')G_{(ln,q)}^{(\mu)}(\epsilon',t|\epsilon''), \tag{21}$$

with

$$\mathbf{W}_{(ln,q)}^{(\mu)}(\epsilon|\epsilon')=-\{\Gamma_{(\epsilon,\mu)}(q)+\kappa(\epsilon)\}\,\delta(\epsilon,\epsilon')$$
$$+\kappa(\epsilon|\epsilon')\Lambda_{(\epsilon,\epsilon')}(ln)$$
$$\times\{c+(1-c)\zeta_q\}\,\nu(\epsilon,\epsilon'). \tag{22}$$

Here, we have defined

$$\Gamma_{(\epsilon,\mu)}(q):=-\int d\omega_\beta\int d\omega'_\beta\,V^{-1}(\omega_\beta,q)$$
$$\times\mathbf{\Pi}_{(\epsilon,\mu)}(\omega_\beta|\omega'_\beta)V(\omega'_\beta,q)$$

and

$$\zeta_q:=\int d\omega_\beta\int d\omega'_\beta\,V^{-1}(\omega_\beta,q)p^{\mathrm{eq}}(\omega_\beta)V(\omega'_\beta,q). \tag{23}$$

In case the eigenvectors $\{|q\rangle\}$ are known, one is left with the problem of the diagonalization of the matrix **K**. This is achieved most easily numerically after symmetrization of this matrix.

In terms of the above-defined eigenvectors and Green's functions the desired conditional probability reads

$$P_{1|1}^{(\mu)}(\Omega_\alpha,\omega_\beta,\epsilon,t|\Omega''_\alpha,\omega''_\beta,\epsilon'')$$
$$=\sum_{l,m,n}\left(\frac{2l+1}{8\pi^2}\right)\int dq\,D_{nm}^{(l)}(\Omega_\alpha)V(\omega_\beta,q)$$
$$\times G_{(ln,q)}^{(\mu)}(\epsilon,t|\epsilon'')D_{nm}^{(l)*}(\Omega''_\alpha)V^{-1}(\omega''_\beta,q). \tag{24}$$

Equation (24) allows the calculation of arbitrary time correlation functions. Here, however, we restrict ourselves to the most general orientational two-time correlation function that is of experimental relevance,

$$C_{n_1n_2}^{(l)}(t)=\langle D_{n_1n_2}^{(l)}[\Omega_{AL}(t)]D_{n_1n_2}^{(l)*}[\Omega_{AL}(0)]\rangle. \tag{25}$$

Using the well-known transformation properties of the Wigner rotation matrices [26] we easily find

$$C_{n_1n_2}^{(l)}(t)=\int d\epsilon\int d\epsilon'\int d\Omega_\alpha\int d\Omega'_\alpha\int d\omega_\beta\int d\omega'_\beta$$
$$\times\int d\mu\,p^{\mathrm{eq}}(\epsilon')g(\mu)p^{\mathrm{eq}}(\Omega'_\alpha)p^{\mathrm{eq}}(\omega'_\beta)$$
$$\times\sum_{n,m=-l}^{l}D_{n_1n}^{(l)}(\omega_\beta)D_{nn_2}^{(l)}(\Omega_\alpha)D_{n_1m}^{(l)*}(\omega'_\beta)$$
$$\times D_{mn_2}^{(l)*}(\Omega'_\alpha)P_{1|1}^{(\mu)}(\Omega_\alpha,\omega_\beta,\epsilon,t|\Omega'_\alpha,\omega'_\beta,\epsilon'). \tag{26}$$

We now give the results that are obtained if the β process is modeled via jumps among two sites. The corresponding transition matrix is given in Eq. (14). The eigenvalues are easily found to be

$$\Gamma_{(\epsilon,\mu)}(q=1)=0 \quad \text{and } \Gamma_{(\epsilon,\mu)}(q=2)=2\Gamma(\epsilon;\mu) \tag{27}$$

and the matrix of the eigenvectors is simply given by

$$V(\omega_i,q)=\frac{1}{\sqrt{2}} \quad \text{for } (i,q)\neq(2,2)$$

$$\text{and } V(\omega_2,q=2)=-\frac{1}{\sqrt{2}}. \tag{28}$$

In this case there are two different Green's functions that occur in the expression for the conditional probability, Eq. (24). Since the $q=1$ eigenvalue of the β process equals zero and the resulting Green's function does not depend on μ at all, we write

$$G_{(ln)}(\epsilon,t|\epsilon'):=G_{(ln,1)}(\epsilon,t|\epsilon'). \tag{29}$$

Similarly, the index 2 is redundant for the other Green's function. Therefore, we denote it by

$$G^{(\mu)}_{(ln)}(\epsilon,t|\epsilon'):=G^{(\mu)}_{(ln,2)}(\epsilon,t|\epsilon'), \tag{30}$$

Using Eqs. (28)–(30) in Eq. (24), we arrive at $(i,k=1,2)$

$$\begin{aligned} P^{(\mu)}_{1|1}(\Omega_\alpha,\omega_i,\epsilon,t|\Omega'_\alpha,\omega_k,\epsilon') &= \frac{1}{2}\sum_{l,m,n}\left(\frac{2l+1}{8\pi^2}\right)D^{(l)}_{nm}(\Omega_\alpha)D^{(l)*}_{nm}(\Omega'_\alpha) \\ &\quad \times\{G_{(ln)}(\epsilon,t|\epsilon')+(-)^{(i+k)}G^{(\mu)}_{(ln)}(\epsilon,t|\epsilon')\}. \end{aligned} \tag{31}$$

The Green's functions obey the following rate equations [cf. Eq. (21)]:

$$\dot{G}_{(ln)}(\epsilon,t|\epsilon'')=\int d\epsilon'\, W_{(ln)}(\epsilon|\epsilon')G_{(ln)}(\epsilon',t|\epsilon'')$$

with

$$W_{(ln)}(\epsilon|\epsilon')=-\kappa(\epsilon)\delta(\epsilon,\epsilon')+\Lambda_{(\epsilon,\epsilon')}(ln)\kappa(\epsilon|\epsilon')\nu(\epsilon,\epsilon'), \tag{32}$$

and analogously

$$\dot{G}^{(\mu)}_{(ln)}(\epsilon,t|\epsilon'')=\int d\epsilon'\, W^{(\mu)}_{(ln)}(\epsilon|\epsilon')G^{(\mu)}_{(ln)}(\epsilon',t|\epsilon'')$$

with

$$\begin{aligned} W^{(\mu)}_{(ln)}(\epsilon|\epsilon') &= -\{2\Gamma(\epsilon;\mu)+\kappa(\epsilon)\}\delta(\epsilon,\epsilon') \\ &\quad +c\Lambda_{(\epsilon,\epsilon')}(ln)\kappa(\epsilon|\epsilon')\nu(\epsilon,\epsilon'). \end{aligned} \tag{33}$$

From the last expression it is obvious that a crucial role is played by the parameter c. If it is set to zero, $c=0$, one simply has

$$G^{(\mu)}_{(ln)}(\epsilon,t|\epsilon')=e^{-\{2\Gamma(\epsilon;\mu)+\kappa(\epsilon)\}t}\delta(\epsilon,\epsilon').$$

The Green's function $G_{(ln)}(\epsilon,t|\epsilon')$ is just the one that is obtained in the absence of any β relaxation and is identical to the one considered in Refs. [10,11]. Its occurence stems from the fact that the total probability for the β process is to be conserved. This in particular means that the general form of $P_{1|1}$, Eq. (31), is unchanged if more complex models for the reorientational motion associated with the β process are considered. One eigenvalue always equals zero and the only thing that changes is the number of Green's functions $G^{(\mu)}_{(ln,q)}$ along with their weight factors [the factor $(-)^{(i+k)}$ in Eq. (31)], as each eigenvalue $\Gamma_{(\epsilon,\mu)}(q)$ gives rise to the occurence of the associated $G^{(\mu)}_{(ln,q)}$.

Inserting the expression for the conditional probability, Eq. (31), into Eq. (26) allows us to write

$$C^{(l)}_{n_1n_2}(t)=\frac{1}{2l+1}\{\mathcal{A}^{(l)}_{n_1n_2}(t)+\mathcal{B}^{(l)}_{n_1n_2}(t)\}. \tag{34}$$

If we replace the actually occurring $G_{(lm)}(\epsilon,t|\epsilon')$ and $G^{(\mu)}_{(lm)}(\epsilon,t|\epsilon')$ in this expression by

$$G_{(l)}(\epsilon,t|\epsilon')\simeq\frac{1}{2l+1}\sum_{m=-1}^{l}G_{(lm)}(\epsilon,t|\epsilon'), \tag{35}$$

and a similar expression for $G^{(\mu)}_{(l)}(\epsilon,t|\epsilon')$, we find

$$\begin{aligned} \mathcal{A}^{(l)}_{n_1n_2}(t) &= \int d\epsilon\int d\epsilon'\, p^{\mathrm{eq}}(\epsilon')f^{(ln_1)}_\alpha(\theta(\epsilon'),\delta(\epsilon')) \\ &\quad \times G_{(l)}(\epsilon,t|\epsilon'), \end{aligned} \tag{36}$$

$$\begin{aligned} \mathcal{B}^{(l)}_{n_1n_2}(t) &= \int d\epsilon\int d\epsilon'\, p^{\mathrm{eq}}(\epsilon')[1-f^{(ln_1)}_\alpha(\theta(\epsilon'),\delta(\epsilon'))] \\ &\quad \times\int d\mu\, g(\mu)G^{(\mu)}_{(l)}(\epsilon,t|\epsilon'). \end{aligned} \tag{37}$$

Note that these expressions are independent of n_2. The amplitudes are defined by

$$f^{(ln_1)}_\alpha(\theta(\epsilon),\delta(\epsilon)):=\frac{1}{2}\left\{1+\sum_m\,[d^{(l)}_{n_1m}\{\theta(\epsilon)\}]^2\cos[m\delta(\epsilon)]\right\}. \tag{38}$$

According to the above remark it should be clear that the amplitudes $f^{(ln_1)}_\alpha(\theta(\epsilon),\delta(\epsilon))$ depend on the model chosen for the β process. We note that the approximation Eq. (35) is excellent for isotropic reorientations, cf. Sec. III, and it is exact for small step reorientations [30]. Without this approximation each term in the sum occurring in Eq. (38) is to be multiplied by $G_{(lm)}(\epsilon,t|\epsilon')$ or $G^{(\mu)}_{(lm)}(\epsilon,t|\epsilon')$, respectively, and the resulting expressions for $\mathcal{A}^{(l)}_{n_1n_2}(t)$ and $\mathcal{B}^{(l)}_{n_1n_2}(t)$ are more complicated.

From the function $C^{(l)}_{n_1n_2}(t)$ all experimentally relevant observables may be calculated. For instance, the correlation function of the first-order Legendre polynomial, which is the observable in dielectric relaxation experiments, is simply given by

$$g_1(t)=\frac{C_{00}^{(1)}(t)}{C_{00}^{(1)}(0)} \tag{39}$$

and the correlation function giving rise to the spectral densities as observed in spin-lattice relaxation experiments is

$$C_m(t)=C_{0m}^{(2)}(t). \tag{40}$$

The above general expressions will be used in the next section, where we present results of model calculations for the imaginary part of the dielectric constant and the average spin-lattice relaxation rates. We end this section by noting that a similar formalism can be applied to translational motions of tagged particles. In this case the transition matrix $\Lambda_{(\epsilon,\epsilon')}(\Omega_\alpha|\Omega'_\alpha)$ in Eq. (11) is to be replaced by a matrix $\Lambda_{(\epsilon,\epsilon')}(\vec{\mathbf{R}}|\vec{\mathbf{R}}')$ and the corresponding eigenvectors (the Wigner rotation matrices) in the expansion (15) by the plane waves $e^{i\mathbf{k}\cdot\mathbf{R}}$, cf. Ref. [11]. Similar arguments then apply for the modeling of the β process, cf. the model of Arbe *et al.* [17].

III. RESULTS OF MODEL CALCULATIONS

Before we show results for the dielectric susceptibilities and the spin-lattice relaxation rates, let us discuss some properties of the expressions obtained in the last section. For the simple model of angular jumps among two sites for the reorientations associated with the β relaxation, the most general orientational two-time correlation function $C^{(l)}_{n_1n_2}(t)$ can be written as a sum of two different terms, cf. Eq. (34). For more complicated models, there would be more terms; however, the Green's function $G_{(l)}(\epsilon,t|\epsilon')$ associated with α relaxation occurring in the term $\mathcal{A}^{(l)}_{n_1n_2}(t)$ [cf. Eq. (36)] will always be present. The reason for this is just given by the fact that the total probability of the stochastic process ω_β is a conserved quantity. This means that orientational correlation functions always will show a decay to a plateau value due to the combined effect of α and β relaxation and then decay to their equilibrium values due to α relaxation. Of course, the plateau value and the form of the initial decay depend on the model chosen for the β relaxation.

When considering the dependence of the jump angles occurring in the expressions of the last section upon the value ϵ, one would assume that they will vary with that value. Consider, for instance, the angle $\delta(\epsilon)$; since it is a reasonable assumption that low-lying free-energy minima correspond to a more close packing or a higher value of some local density, one would expect δ to be a decreasing function of ϵ. Similar arguments may apply to the angles $\phi_{(\epsilon,\epsilon')}$ and $\psi_{(\epsilon,\epsilon')}$ occurring in the expression for $\Lambda_{(\epsilon,\epsilon')}(ln)$, Eq. (18). In all following calculations we neglect these dependencies for simplicity and use single values for these angles, which then correspond to the average jump angles in the system. This simplification allows us to write

$$f_\alpha^{(ln_1)}:=f_\alpha^{(ln_1)}(\theta,\delta)=\frac{1}{2}\left\{1+\sum_m\,[d^{(l)}_{n_1m}(\theta)]^2\cos(m\delta)\right\} \tag{41}$$

and

$$C^{(l)}_{n_1n_2}(t)=\frac{1}{2l+1}\{f_\alpha^{(ln_1)}\Phi_l^{(\alpha)}(t)+(1-f_\alpha^{(ln_1)})\Phi_l^{(\beta)}(t)\}, \tag{42}$$

from which the role of the $f_\alpha^{(ln_1)}$ as amplitudes is most transparent. The definition of the functions $\Phi_l^{(\alpha)}(t)$ and $\Phi_l^{(\beta)}(t)$ is evident from Eqs. (36) and (37).

As already stated in the beginning of Sec. II, there are two possible extreme choices for the interrelation between the value ϵ in a given state and the value for the activation free energy for the β process μ in that state. If we choose μ to be a prescribed function of ϵ, the Green's function $G^{(\mu)}_{(l)}$ does not depend on μ explicitly and the $\int d\mu\, g(\mu)$ occurring in Eq. (37) simply yields unity. In this case all transition rates, in particular $\Gamma(\epsilon;\mu)=\Gamma(\epsilon)$, are determined by the variable ϵ as there is strong correlation between ϵ and μ. In the other extreme case of vanishing correlation among the two variables, one simply has $\Gamma(\epsilon;\mu)=\Gamma(\mu)$ independent of ϵ. This case corresponds to a random choice of the activation energies μ for each state ϵ.

It is illustrative to consider some limits of the equations derived in Sec. II.

(1) If we assume that $\delta=0$ (or also $\theta=0$ for the relevant case $n_1=0$), then we find $f_\alpha^{(ln_1)}=1$ and the correlation function decays solely due to reorientations associated with the α process. The same result is obtained if $\Gamma(\epsilon;\mu)=0$ and $c=1$ is chosen in Eq. (33).

(2) If we choose $\kappa(\epsilon|\epsilon')\rightarrow 0$, only the β process "survives" and the second term in Eq. (42) is of the form $\Phi_l^{(\beta)}(t)=\int d\epsilon\, p^{\mathrm{eq}}(\epsilon)e^{-2\Gamma(\epsilon)t}$ if $\mu=f(\epsilon)$ $[\Gamma(\epsilon;\mu)=\Gamma(\epsilon)]$, and $\Phi_l^{(\beta)}(t)=\int d\mu\, g(\mu)e^{-2\Gamma(\mu)t}$ in case of no correlation among ϵ and μ $[\Gamma(\epsilon;\mu)=\Gamma(\mu)]$. In any case, $\Phi_l^{(\beta)}(t)$ is given as a linear superposition of exponentially decaying functions.

It is clear that the above limit $\kappa(\epsilon|\epsilon')\rightarrow 0$ physically corresponds to low temperatures, well below the glass transition temperature T_g. Since in this case an unsymmetrical choice of the DOS $\eta(\epsilon)$ yields unsymmetrical spectra for the β process, we will neglect any correlation among ϵ and μ in the following calculations. [We will use unsymmetrical $\eta(\epsilon)$ since for a symmetrical DOS the spectra of the α process also will be symmetrical. Only for a symmetrical DOS the β spectra also would be symmetrical.]

A more important remark concerns the choice of the "correlation" parameter c in Eq. (33). If this parameter is chosen to be unity, $c=1$, the two processes $\omega_\beta(t)$ and $\epsilon(t)$ are completely uncorrelated. It then follows from Eq. (33) that for $c=1$:

$$G^{(\mu)}_{(ln)}(\epsilon,t|\epsilon')=e^{-2\Gamma(\mu)t}G_{(ln)}(\epsilon,t|\epsilon'), \tag{43}$$

where $G_{(ln)}(\epsilon,t|\epsilon')$ is just the Green's function for the α process, cf. Eq. (32). This means in this particular case we have

$$C^{(l)}_{n_1n_2}(t)=\frac{1}{2l+1}\{f_\alpha^{(ln_1)}+(1-f_\alpha^{(ln_1)})\Phi^{(\beta,0)}(t)\}\Phi_l^{(\alpha)}(t), \tag{44}$$

where we defined

$$\Phi^{(\beta,0)}(t)=\int d\mu\, g(\mu)e^{-2\Gamma(\mu)t}. \tag{45}$$

We mention that Eq. (44) is exactly of the form, which has a long history in the interpretation of dielectric data [15,17,18]. Note that the assumption $c=1$ means that the orientation ω_β after a $\epsilon\rightarrow\epsilon'$ transition is exactly the same as the one before that transition. This seems a rather unplausible assumption from a physical point of view. The structural relaxation is modeled by the transitions among the different free-energy minima. Therefore, the local configuration of the molecules are assumed to change due to these transitions. In such a picture one always would assume that also the ω_β will change in case of such a transition as ω_β represents a particular orientation within a given configuration.

The choice $c=0$, on the other hand, corresponds to a strong correlation between the processes $\epsilon(t)$ and $\omega_\beta(t)$. In this case ω_β randomizes with every $\epsilon\rightarrow\epsilon'$ transition, i.e., ω_β takes on both values ω_1 and ω_2 with a probability of 50%. In this case we have from Eq. (33), for $c=0$,

$$G^{(\mu)}_{(ln)}(\epsilon,t|\epsilon')=e^{-\{2\Gamma(\mu)+\kappa(\epsilon)\}t}\delta(\epsilon,\epsilon'), \tag{46}$$

and correspondingly,

$$\begin{aligned}C^{(l)}_{n_1n_2}(t)=\frac{1}{2l+1}\{&f_\alpha^{(ln_1)}\Phi_l^{(\alpha)}(t)\\&+(1-f_\alpha^{(ln_1)})\tilde{\Phi}^{(\alpha)}(t)\Phi^{(\beta,0)}(t)\}\end{aligned} \tag{47}$$

with

$$\tilde{\Phi}^{(\alpha)}(t)=\int d\epsilon\, p^{\mathrm{eq}}(\epsilon)e^{-\kappa(\epsilon)t}. \tag{48}$$

Thus, it is seen that although one again has a product of two functions occurring for $\Phi_l^{(\beta)}(t)$ in Eq. (42), the decay function for "the pure β process" is not multiplied by the corresponding one for the "pure α process." Instead, the function $\tilde{\Phi}^{(\alpha)}(t)$ is identical to the one obtained if the α process is modeled by random reorientations, cf. [10]. Only in this unphysical case Eqs. (44) and (47) coincide. Note that $\Phi^{(\beta,0)}(t)$ and $\tilde{\Phi}^{(\alpha)}(t)$ are independent of the rank l of the considered correlation function. Remember, however, that the amplitudes $f_\alpha^{(ln)}$ do depend on this rank.

Before we proceed to present the results of the model calculations, we will fix the model parameters that will be used in all following calculations. In all calculations we use a Γ distribution for the DOS,

$$\eta(\epsilon)=\mathcal{N}(\delta\epsilon)^p e^{-q(\delta\epsilon)}, \tag{49}$$

where $\mathcal{N}$ denotes a normalization constant and $(\delta\epsilon)$ the deviation from the maximum value. This way it is assured that $\eta(\epsilon)$ is centered around zero. We mention that an exponential tail also is characteristic of the energy distributions in mean-field spin glasses. Here, however, we use a Γ distribution just for computational convenience. Since the "attempt frequency" occurring in Eq. (2) merely sets the overall time scale, we choose the product $\kappa_\infty^\alpha e^{-\beta_g E_\alpha}$ to define the temperature $T_g=1/\beta_g$. We set Boltzmann's constant to unity, $k_B=1$, throughout. We always choose this value in such a way that the characteristic decay time constant of the correlation function of the first rank Legendre polynomial $g_1(t)$ is on the order of 100 s.

Additionally, we use the following characterization of the β relaxation. We always assume that the activation free energies μ and ϵ are uncorrelated. We choose the values of μ from a Gaussian distribution $g(\mu)$ of mean E_β and variance σ. The rates for the reorientations are chosen to be of the Arrhenius form,

$$\Gamma(\mu)=\kappa_\infty^\beta e^{-\beta\mu}. \tag{50}$$

This represents the most simple physically reasonable choice. This means, we have the following parameters at our disposal: For the α process we have the values of p and q for the DOS and the overall activation free energy E_α. Since the latter just gives the steepness of the correlation time in an Arrhenius plot, we fix its value by the restriction that this correlation time be on the order of 10^{-8} s at a temperature $T\simeq 1.2T_g$. The time scale κ_∞^α is set according to the above-mentioned requirement. For the β process there are the parameters κ_∞^β, E_β, and σ. We follow Kudlik *et al.* [18] and fix $\kappa_\infty^\beta\simeq 10^{15}\,\mathrm{s}^{-1}$ and $E_\beta\simeq 24T_g$. With these preliminaries the relevant parameters of the model calculations are given by the ratio $X(T_g):=(\kappa_\infty^\alpha e^{-\beta_g E_\alpha})/(\kappa_\infty^\beta e^{-\beta_g E_\beta})$, the parameters p, q, E_α, E_β, and σ. The above choice of $E_\beta=24T_g$ means that the time scales of the α and the β process become comparable at approximately 10^{-7} s.

In addition to the parameters characterizing the shape of the distributions and the time scales of the two processes, we also have to choose the values of the jump angles ϕ, ψ, and δ. Here, we will use an isotropic model for the reorientations associated with α relaxation, $\phi=(\psi/\sqrt{8})$ and use $\psi=10°$ in all model calculations that follow. A mean reorientational angle on the order of 10° has been in found in careful NMR investigations on orthoterphenyl [33], toluene, [34] and glycerol [35]. Concerning the jump angle δ, we proceed in the following way: It has been found in some experiments that the mean-squared displacement increases much stronger than linear—approximately exponential—with temperature for temperatures around T_g [36,37] or higher. For a simple two-site jump model a simple relation between the jump distance r_{jump} and the mean-squared displacement can be given,

$$\langle r^2\rangle=p_1^{\mathrm{eq}}p_2^{\mathrm{eq}}[2r_{\mathrm{jump}}\sin(\delta/2)]^2. \tag{51}$$

In some NMR investigations [37,38], the jump angle in the above expression has been taken as temperature independent and the temperature dependence has been attributed to temperature-dependent equilibrium populations p_i^{eq}. This, however, means that one is concerned with a very asymmetric double-well structure of the minima among which the two-site jumps take place. In the following we use the alternative interpretation that the jump angle δ is temperature dependent in an Arrhenius-like fashion, $\delta(T)=\delta_0 e^{-\beta E_\delta}$, as has also been used by Hinze and Sillescu [39] in their interpretation of NMR relaxation experiments on toluene. Figure 2(a) shows $\langle r^2\rangle$ calculated according to Eq. (51) for two different choices of $\delta(T)$. In one case δ_0 is chosen in a way

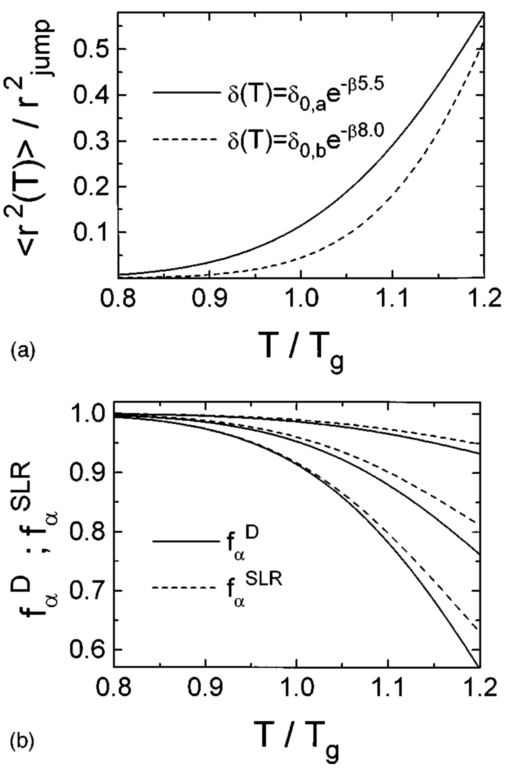

FIG. 2. (a) $\langle r^2\rangle/r^2_{\rm jump}$ as a function of temperature for two choices of the temperature dependence of the jump angle δ. In one example the jump angle is chosen to be 10° at $0.8T_g$ (full curve), which corresponds to the choice $\delta_{0,a}=10°e^{5.5/(0.8T_g)}$ and in the other case it is chosen to be 10° at $0.9T_g$ (broken curve) corresponding to $\delta_{0,b}=10°e^{8.0/(0.9T_g)}$. (b) The amplitudes relevant for the calculations of the dielectric constant (f_α^D) and the spin-lattice relaxation rates ($f_\alpha^{\rm SLR}$) as a function of temperature for the choice $\delta(T)=\delta_{0,a}e^{-\beta 5.5}$ [cf. (a)]. The angle θ is chosen to be 20°, 40°, 60° (from top to bottom) in the case of f_α^D (full lines) and 10°, 20°, 30° for $f_\alpha^{\rm SLR}$ (broken lines).

that $\delta=10°$ at $0.8T_g$ and in the other example $\delta\simeq 3°$ at that temperature. The values are chosen this way only to show that such a temperature dependence can be used in order to show qualitatively the same behavior as found in real supercooled liquids. In particular, it can be seen from Fig. 2(a) that $\langle r^2\rangle$ rises strongly in the temperature range of T_g for both choices. Of course, relations such as Eq. (51) strongly depend on the model considered.

Even more important is the dependence of the amplitudes $f_\alpha^{(ln)}$ on the angle θ. The two amplitudes of interest in the following are $f_\alpha^D\equiv f_\alpha^{(10)}$ in case of dielectric relaxation and $f_\alpha^{\rm SLR}\equiv f_\alpha^{(20)}$ for spin-lattice relaxation. The angle θ between the axis of reorientation and the one of the relevant interaction usually will be different for the two experimental techniques as, e.g., the direction of a relevant carbon-deuteron bond (in case of deuteron NMR) does not necessarily coincide with the direction of the molecular dipole moment. In using the amplitudes f_α^D for the calculation of the dielectric response we have to assume that dielectric relaxation is dominated by single molecule relaxation and that cross terms in the dipolar interaction can be neglected. The dependence of f_α^D and $f_\alpha^{\rm SLR}$ on the angle θ is shown in Fig. 2(b), where we plotted these quantities as a function of temperature for various θ and one choice of $\delta(T)$. The rather strong dependence on θ and the different absolute values of f_α^D and $f_\alpha^{\rm SLR}$ are obvious from that plot. We note that the values of $f_\alpha^D(\theta\simeq 60°)$ are on the order of magnitude of experimentally determined values [17,18].

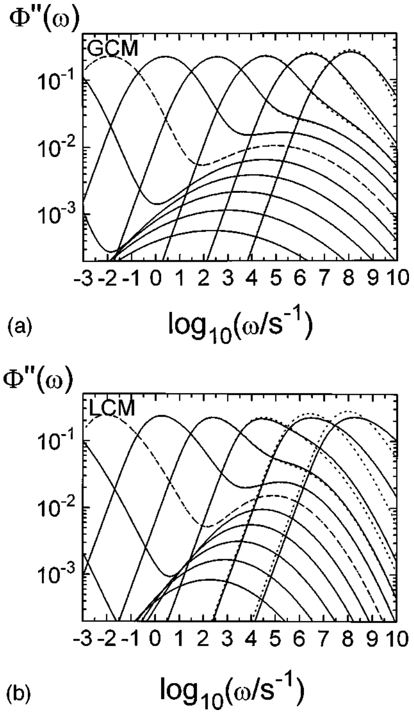

FIG. 3. (a) Dielectric susceptibility $\Phi''(\omega)$ versus frequency according to Eq. (53) for a globally connected model. The parameters are given in the text. Full lines, $c=0$; dotted lines, $c=1$. The temperatures vary from $0.8T_g$ to $1.2T_g$ in equal steps. The dashed line represents the spectrum at T_g. (b) The same as in (a) for a locally connected model.

We now present the results of model calculations for the imaginary part of the dielectric susceptibility,

$$\Phi^*(\omega)=\frac{\epsilon^*(\omega)-\epsilon_\infty}{\epsilon_0-\epsilon_\infty}=\mathcal{L}\left[-\frac{d}{dt}g_1(t)\right], \tag{52}$$

where $\mathcal{L}$ denotes the Laplace transform and ϵ_0 and ϵ_∞ denote the zero and infinitive frequency limits, respectively. According to Eqs. (39) and (42), we have

$$\Phi(\omega)=f_\alpha^D\Phi_1^{(\alpha)}(\omega)+(1-f_\alpha^D)\Phi_1^{(\beta)}(\omega), \tag{53}$$

with $\Phi_1^{(x)}(\omega)$ denoting the Laplace transforms of $[-d/dt\,\Phi_1^{(x)}(t)]$. All calculations are performed by numerical solution of Eqs. (32) and (33) in a similar way as explained in Ref. [11]. Here, we only mention that we numerically diagonalize the matrices defined implicitly in the discrete versions of these equations using 50–100 values of ϵ. From the resulting Green's functions, all observables of interest are obtained easily.

In Fig. 3 we show $\Phi''(\omega)$ versus frequency for the GCM [Fig. 3(a)] and the LCM [Fig. 3(b)]. In both cases a Γ distribution with $p=10$, $q=0.3$ according to Eq. (49) for $\eta(\epsilon)$ is used. The remaining parameters are $\kappa_\infty^\beta=10^{15}$ s^{-1} and $E_\beta=24T_g$ in both cases. Furthermore, we used $X(T_g)=22.8$, $E_\alpha=114T_g$, and $\sigma=7T_g$ in the GCM calculations and

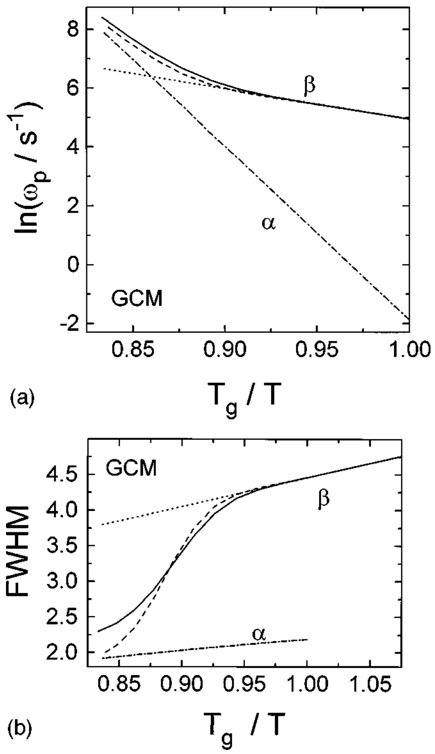

FIG. 4. (a) Logarithm of the peak positions ω_p for the GCM spectra of Fig. 3(a) versus inverse temperature. The peak position of $\Phi_1^{(\alpha)}(\omega)$ is shown as the dot-dashed line. The solid line represents the results for $\Phi_1^{(\beta)}(\omega)$ with $c=0$; the dashed line is the same for $c=1$ [corresponding to the full and dotted lines in Fig. 3(a)]. Finally, the dotted line is obtained by extrapolation from the low temperature behavior of $\Phi_1^{(\beta)}(\omega)$. (b) Full width at half maximum versus inverse temperature for the same calculations as used in (a). The different lines represent the same parameters as in (a).

$X(T_g)=10^5$, $E_\alpha=108T_g$, and $\sigma=4.5T_g$ for the LCM. The amplitude f_α^D was chosen according to the lowest curve in Fig. 2(b). The effect of the different widths chosen for the β process is clearly seen in the spectra, especially below T_g. The full lines represent calculations with the parameter c set to zero, which means that ω_β randomizes with each $\epsilon\rightarrow\epsilon'$ transition and the dotted lines are results for $c=1$. The differences in the spectra are not very pronounced. Only for temperatures larger than roughly $1.1T_g$, a clearly visible discrepancy is apparent. In all cases an apparent merging of the α and the β peak occurs at a temperature of approximately $1.16T_g$–$1.18T_g$ for the parameters chosen. We have also performed calculations for different sets of parameters. As the results qualitatively agree with the ones presented in Fig. 3, we do not show them here. The most prominent differences occur if f_α^D is chosen differently, as this affects the relative weights of the contributions of $\Phi_1^{(\alpha)}(\omega)$ and $\Phi_1^{(\beta)}(\omega)$ in Eq. (53) to the susceptibility.

We now proceed with an analysis of the data presented in Fig. 3. For this purpose we separately determine the peak position ω_p and the width for $\Phi_1^{(\alpha)}(\omega)$ and $\Phi_1^{(\beta)}(\omega)$. The results of this analysis are shown in Fig. 4. Concerning $\Phi_1^{(\alpha)}(\omega)$, we compared the values obtained from a numerical determination of the widths and the position with the results of Kohlrausch fits to the time correlation function $g_1(t)=e^{-(t/\tau)^\beta}$, which were converted to the former via the expressions given by Dixon [40]. The deviations between the two methods did not exceed 5%. The corresponding values of widths and positions in the case of $\Phi_1^{(\beta)}(\omega)$ were determined numerically. The results for ω_p and the full width at half maximum for the calculations according to the GCM [Fig. 3(a)] are plotted versus inverse temperature in Figs. 4(a) and 4(b), respectively. Without showing them here, we mention that the results of the corresponding LCM calculations behave very similar [apart from the smaller width of $\Phi_1^{(\beta)}(\omega)$ due to the smaller σ chosen in those calculations].

Concerning the behavior of the position and the width of the α peak (dot-dashed lines in Fig. 4), we note that the fact that the peak position varies in an almost Arrhenius-like form has its origin in the assumption of a temperature-independent DOS $\eta(\epsilon)$. When calculations with the present model are compared to experimental data, it is usually found that one has to allow for a temperature-dependent width of the DOS [11,12]. In other words, the temperature dependence of the width of the α peak shown in Fig. 4(b) is less pronounced than is often found experimentally. Assuming a temperature-dependent width of the DOS yields a stronger curvature of the peak position and also a steeper rise of the width as a function of inverse temperature. As we are mainly interested in those features associated with slow β relaxation in the present paper, we always used a temperature-independent $\eta(\epsilon)$.

The extrapolated peak frequency of the β process crosses the corresponding one of the α process at $\ln(\omega_p)\simeq6.5$. Note that at low temperatures $\kappa(\epsilon|\epsilon')\simeq0$ and therefore $\Phi^{(\beta)}(\omega)\simeq\Phi_1^{(\beta,0)}(\omega)$, where $\Phi_1^{(\beta,0)}(\omega)$ denotes the response function associated with $\Phi^{(\beta,0)}(t)$ according to Eq. (45). This function represents the low-temperature limit independent of the choice of the correlation parameter c, cf. Eqs. (43) and (46). The effect of averaging due to the α process is evident from the increase of ω_p and the drop in the width of $\Phi_1^{(\beta)}(\omega)$. Note that the time constants of the extrapolated low-temperature data and the real spectra differ by approximately one decade at the temperature where according to the extrapolation a crossing of the two processes would occur. It is evident from these considerations that a crossing of the α and β process cannot occur in our model as the α process leads to an averaging over the distribution of jump rates $\Gamma(\mu)$ for the β relaxation if the mean time constants for reorientations associated with the two processes do not differ too much. In Fig. 4(a), the onset of the deviations between the behavior of $\Phi_1^{(\beta)}(\omega)$ and the extrapolated low-temperature regime first occurs at a temperature $T\simeq1.1T_g$. At this temperature the two peak frequencies differ by more than two decades. This clearly shows that care has to be taken in extrapolating data related to β relaxation to higher temperatures. The effect of the averaging due to the $\Omega_\alpha\rightarrow\Omega_\alpha'$ transitions is seen even more pronounced when comparing the widths of $\Phi_1^{(\beta)}(\omega)$ and $\Phi^{(\beta,0)}(\omega)$ as extrapolated from low temperatures. We note that experimentally, of course, there is no clear-cut separation between $\Phi_1^{(\beta)}(\omega)$ and $\Phi_1^{(\alpha)}(\omega)$ at temperatures higher than roughly $1.1T_g$, as can be seen from the spectra in Fig. 3. If these spectra are analyzed as a single peak, the peak frequency will change only by a negligible amount [cf. Fig. 4(a)] and the width will stay more or less temperature independent as a competition between the decreasing width of $\Phi_1^{(\alpha)}(\omega)$ and the larger one of $\Phi_1^{(\beta)}(\omega)$. When we compare the results for $c=0$ (full lines in Fig. 4) and $c=1$ (dashed lines), we see that they behave quite similarly with some systematic deviations. In the (unphysical) case of $c=1$, $\Phi_1^{(\beta)}(\omega)$ contains a contribution from the Green's function for the α process, cf. Eq. (44). Therefore, the high-temperature limit in this case is a real merging of the two peaks. Of course, the difference between the $c=1$ and the $c=0$ scenarios will be more outspoken if a model with more than two orientations ω_β is considered for the β process, as in this case there are more values the variable ω_β can reach for $c=0$ than the two in the simple two-site model considered here.

We now proceed to calculate the spin-lattice relaxation rates as observed in high-field NMR. This rate is given by the well-known expression [41–44]

$$R_1 := \frac{1}{T_1} = \frac{K_\lambda^2}{3}\{J_1(\omega_L)+4J_2(\omega_L)\}. \tag{54}$$

Here, K_λ denotes the coupling constant, i.e., the quadrupolar beating frequency in case of deuteron NMR and the second moment in case of protons and ω_L is the Larmor frequency. The spectral densities for axially symmetric couplings are given by [43]

$$J_m(\omega)=2\ \mathrm{Re}\int_0^\infty dt\, e^{i\omega t}\langle D_{0m}^{(2)}[\Omega_{\mathrm{PL}}(t)]D_{0m}^{(2)*}[\Omega_{\mathrm{PL}}(0)]\rangle. \tag{55}$$

In this expression Ω_{PL} denotes the orientation of the principal axes system in the laboratory fixed frame. In the latter, the z_L axis coincides with the main magnetic field. One has to be careful in using the above expressions, since in the temperature interval considered in the present context, the NMR spectra undergo a change in line shape from a liquid-like Lorentzian to the typical solid-state spectra. These are given by a Pake spectrum in case of deuterons and often by a Gaussian for protons. At high temperatures in the liquid region, the above correlation function coincides just with the function $C_m(t)$ given in Eq. (40). At lower temperatures, however, this is no longer true in general. If the reorientations due to the α process become slower than the average spin-lattice relaxation time, only the reorientations associated with the β process give rise to relaxation and the above correlation function reads

$$\langle D_{0m}^{(2)}[\Omega_{\mathrm{PL}}(t)]D_{0m}^{(2)*}[\Omega_{\mathrm{PL}}(0)]\rangle$$

$$=\sum_{n,n'} D_{nm}^{(2)}(\Omega_\alpha)D_{n'm}^{(2)*}(\Omega_\alpha)\langle D_{0n}^{(2)}[\omega_\beta(t)]D_{0n'}^{(2)*}[\omega_\beta(0)]\rangle$$

as Ω_α is now time independent and only ω_β gives rise to relaxation. This, in particular, means that the spin-lattice relaxation rate now is a function of the orientation of the considered interaction relative to the magnetic field. Each deuteron contributing to the Pake spectrum (or each pair of protons) has a well-defined R_1 and the decay of the normalized longitudinal magnetization is a superposition of all different decays possible in the system. In principle, the above expression can be used to calculate the relaxation rate for any given line in the inhomogeneous NMR spectrum in a similar way as in Ref. [43]. As the β process in our model gives rise to a broad distribution of relaxation rates, the corresponding magnetization decay will be nonexponential and can be written as

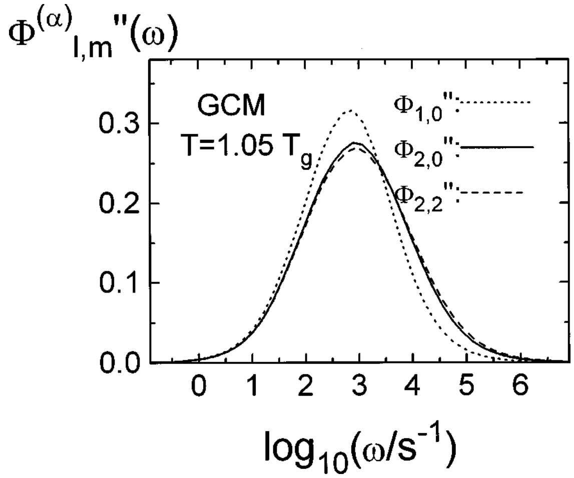

FIG. 5. Spectra $\Phi_{lm}^{(\alpha)}(\omega)$ versus frequency for the GCM at $T=1.05T_g$. The parameters are the same as in Fig. 3. Since $\Phi_{l0}^{(\alpha)}(\omega)$ and $\Phi_{l1}^{(\alpha)}(\omega)$, $l=1,2$ are practically indistinguishable, the latter are not shown. The dependence of the spectra on m is negligible, justifying the approximation Eq. (35).

$$M(t)\propto\int d\mu\, g(\mu)e^{-R_1(\mu)t}, \quad T<T_g. \tag{56}$$

However, Eq. (56) is meaningful only in the absence of any additional averaging processes. In proton NMR usually an exponential decay of the magnetization is found due to fast spin diffusion. When considering deuteron NMR, the magnetization decays nonexponentially in the glassy state. This has been interpreted as a signature of nonergodicity [38]. However, it has also been demonstrated that the effects of spin diffusion cannot be neglected in the case of deuteron relaxation experiments [45]. It can be shown, on the other hand, that the initial decay of the magnetization is free from spin-diffusion effects [46] and this fact has been used to obtain a sound interpretation of deuteron spin-lattice relaxation experiments on toluene [39]. Since the initial decay of the magnetization curves is governed by the average rate $\langle R_1\rangle$, we have, at all temperatures,

$$\langle R_1\rangle=\frac{K_\lambda^2}{3}\{\langle J_1(\omega_L)\rangle+4\langle J_2(\omega_L)\rangle\} \tag{57}$$

in which the average spectral density now reads

$$\langle J_m(\omega_L)\rangle=\langle J(\omega)\rangle=2\ \mathrm{Re}\int_0^\infty dt\, e^{i\omega t}C_m(t) \tag{58}$$

with $C_m(t)$ given by Eq. (40), since the average rate also includes an average over all possible orientations (powder average) [47]. For a discussion of the treatment of experimental data and the ambuigities associated with different average spin-lattice relaxation rates we refer to Ref. [48].

We start with a brief discussion of the response functions for the α process $\Phi_{lm}^{(\alpha)}(\omega)$. As stated in relation to Eq. (35), in principle, different $\phi_{lm}^{(\alpha)}(t)=\int d\epsilon\int d\epsilon' p^{eq}(\epsilon')G_{(lm)}(\epsilon,t|\epsilon')$ contribute to the rotational correlation functions as well as to spin-lattice relaxation. In order to demonstrate the quality of the approximation (35) we plot the spectra $\phi_{lm}^{(\alpha)}(\omega)$ for different m in Fig. 5 as a function of frequency for the GCM at a temperature of $1.05T_g$. In case of $l=1$ only $\phi_1^{(\alpha)}(\omega)\equiv\phi_{10}^{(\alpha)}(\omega)$ is shown as $\phi_{11}^{(\alpha)}(\omega)$ is almost indistinguishable from this. The difference in the width between the spectra for $l=1$ (dotted line) and $l=2$ (full and dashed lines) is clearly visible. The fact that in our model the stretching of $g_1(t)$ is less pronounced than that of $g_2(t)$ has been extensively discussed in Ref. [11]. The width and shape of $\Phi_{21}^{(\alpha)}(\omega)$ and $\Phi_{20}^{(\alpha)}(\omega)$ are almost identical and only $\Phi_{22}^{(\alpha)}(\omega)$ (dashed line) is somewhat broader than $\Phi_{20}^{(\alpha)}(\omega)$. However, the differences among the $\phi_{lm}^{(\alpha)}(\omega)$ for different m are very small. When the same considerations are applied to the spectra $\Phi_{lm}^{(\beta)}(\omega)$ of the β process, one has to keep in mind the dependence on the model chosen. Since at low temperatures $\Phi_{lm}^{(\beta)}(\omega)\simeq\Phi^{(\beta,0)}(\omega)$ according to Eq. (45) is independent of (lm), there is no difference between the various spectra. The same holds for $\Phi_{lm}^{(\beta)}(\omega)$ in the case of $c=0$ for all temperatures, cf. Eq. (47). Only if $c=1$ is chosen, is there a dependence of $\Phi_{lm}^{(\beta)}(\omega)$ on (lm). As this dependence is the same as the one discussed above in the context of the spectrum associated with the α process, we do not show these spectra here. From this discussion it is evident that the approximation (35), which neglects the m dependence of the various spectra, does not represent any problem.

From the above expression for $\langle R_1\rangle$ and the properties of the $C_m(t)$, we have, for the spectral densities,

$$\langle J(\omega_L)\rangle=f_\alpha^{\mathrm{SLR}}\langle J^{(\alpha)}(\omega_L)\rangle+(1-f_\alpha^{\mathrm{SLR}})\langle J^{(\alpha\beta)}(\omega_L)\rangle. \tag{59}$$

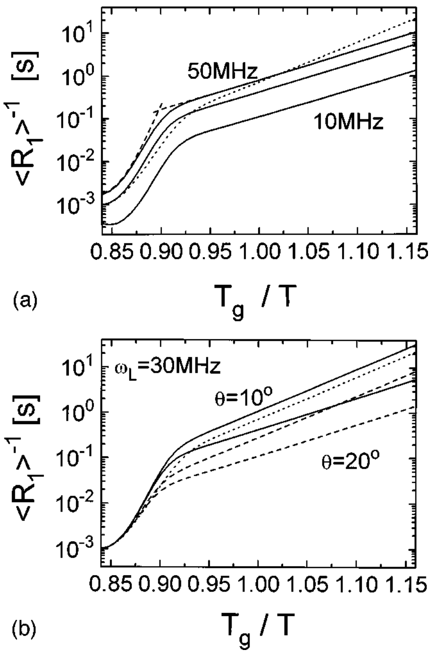

FIG. 6. (a) Average spin-lattice relaxation rates $\langle R_1\rangle$ versus inverse temperature. Here, we used $K_\lambda^2/3=10^9\ \mathrm{s}^{-1}$, which is a value on the order of magnitude typical for the quadrupolar coupling of deuterons. The calculations were performed for the GCM with the same parameters as in Fig. 3(a) and $c=0$, the only difference being the choice of the angle $\theta=10°$ here. The solid lines represent $\langle R_1\rangle$ for 10, 30, and 50 MHz (from bottom to top). The dashed lines are the contributions due to the "pure" α process and the "pure" β process for a 50 MHz. Additionally shown as the dotted line is a calculation for the LCM at 30 MHz. (b) The dependence of the spin-lattice relaxation rates on the angles $\delta(T)$ and θ are shown for two examples at 30 MHz in the GCM. The full lines correspond to $\theta=10°$ and the dashed lines to $\theta=20°$. The lower lying curves are those for the choice $\delta(T)=\delta_{0,a}e^{-\beta 5.5}$ and the upper curves for $\delta(T)=\delta_{0,b}e^{-\beta 8.0}$ according to Fig. 2. The dotted line is the same LCM calculation as in (a).

Spin-lattice relaxation rates calculated according to Eqs. (57) and (59) are shown in Fig. 6(a) for various Larmor frequencies ω_L. In these calculations we used the GCM and $\theta=10°$ in the expressions for f_α^{SLR} (solid lines). The other parameters are the same as those chosen in Fig. 3. Here, we used $c=0$ only. The dashed lines show the individual contributions from the two terms in Eq. (59) for 50 MHz. In addition to these we included one LCM calculation for 30 MHz, where we used the same θ and $\delta(T)$ as in the GCM calculations (dotted line). One clearly sees that the narrower distribution $g(\mu)$ in this case gives rise to a stronger temperature dependence in the glass. However, this does not allow us to determine this distribution due to the very pronounced dependence of $\langle R_1\rangle$ on θ and $\delta(T)$. This is exemplified in Fig. 6(b). Here, we compared $\langle R_1\rangle$ for $\theta=10°$ (full lines) with $\theta=20°$ (dashed lines) for the two different choices for $\delta(T)$ as explained in connection with Fig. 2 and $\omega_L=30$ MHz. It is seen that the variation in the temperature dependence of $\delta(T)$ has a large effect on the temperature dependence of the relaxation rates. Additionally shown as a dotted line is the same LCM calculation as in Fig. 6(a). It is obvious that a variation in the width of the distribution of activation free energy for the β process has a very similar effect as a variation in the temperature dependence of the jump angle $\delta(T)$. Thus, as it appears from the model calculations, it is not possible to determine the parameters for the β relaxation experimentally from spin-lattice relaxation experiments. Here, consideration of the frequency dependence of $\langle R_1\rangle$ may be helpful. If one assumes $\langle R_1\rangle^{-1}\sim\omega_L^d$ [39] and compares experiments performed at different Larmor frequencies, one can estimate the exponent d, which sensitively depends on the width of $g(\mu)$. We find for the data of Fig. 6 an approximately linear temperature dependence of d with $d(0.8T_g)\simeq 1.29$ and $d(T_g)\simeq 1.21$ for the GCM. In the LCM the corresponding values are 1.64 and 1.48 at $0.8T_g$ and T_g, respectively. This clearly shows that for the broader distribution (GCM) there are more fluctuations in the MHz regime, although the mean time scales were taken to be the same in both calculations. The LCM calculations show that one is nearer to the limiting low-temperature value of $d=2$ as obtained for $\Gamma(\mu)\ll\omega_L$. Since a wide variation of Larmor frequencies usually is not feasible in spin-lattice relaxation experiments, a combination of these with dielectric spectroscopy seems to be most advisable. Such a combination may allow the determination of almost all parameters, if the mean and the width of $g(\mu)$ as determined by the dielectric experiment are used as an input for the NMR experiments. Of course, it has to be noted again that particularly the jump angle $\delta(T)$, which results from such an analysis, strongly depends on the model chosen. First, it can depend on the angle θ used in the analysis. This dependence is not very problematic as it merely sets the overall value of $\langle R_1 \rangle$ in the glass, cf. Fig. 6(b). More important is again the fact that we used a two-site jump model, since the dependence of f_α^{SLR} on θ and $\delta(T)$ changes if one considers another model. Nevertheless, the above-recommended combination should give a reliable estimate of the small-angle fluctuations associated with the β process in the glass. This has amply been demonstrated by Hinze and Sillescu [39].

IV. DISCUSSION

Let us start the discussion with a couple of comments concerning the model chosen in the present paper to describe both the slow primary and secondary relaxation in supercooled liquids and glasses. Since the free-energy landscape model presenting the overall framework ceases to make sense in the form used here and in the earlier investigations [10,11] at high temperatures where the number of relevant minima in the free energy is very small, we are restricted to a low-temperature regime. One would expect, that the crossover from a liquidlike dynamics to activated dynamics takes place in a temperature regime around the critical temperature of idealized MCT. Here, we have chosen the parameters in the model calculations in a way that the correlation time for the α process equals approximately 10^{-8} s at $T=1.2T_g$. This also is roughly that temperature where the critical temperature of MCT is located. Therefore, we cannot make any statements about the behavior at higher temperatures.

Concerning the model used for the reorientational dynamics associated with the α relaxation, we stress here only the fact that this dynamics is assumed to be intrinsically coupled to the transitions in the free-energy landscape. The most important point is not represented by a specific choice of the parameters used to model these transitions but by the assumed intrinsic coupling. In all model calculations we used an isotropic small angular jump model for the reorientations due to α relaxation. The jump angle has been fixed to be 10° in all calculations. This means that we neglected any temperature dependence of this angle for simplicity. Also, the existence of a distribution of jump angles, as has been found experimentally [12,34,35], has been neglected. Taking these into account would yield quantitative changes in the calculated spectra. A more dramatic change in the spectra is, however, found if the mean jump angle is changed to larger values, cf. [11].

The slow β process is viewed as local restricted orientational fluctuations. These are modeled in the simplest possible way by a two-site jump model. As has been pointed out in the last section, this restrictive choice can be relaxed in principle. The calculations, however, become somewhat more involved. The qualitative behavior of the spectra does not change in any case as the occurrence of the different terms $\mathcal{A}_{n_1n_2}^{(l)}(t)$ and $\mathcal{B}_{n_1n_2}^{(l)}(t)$ in the expression for the correlation functions $C_{n_1n_2}^{(l)}(t)$ according to Eq. (34) is independent of the special choice for that model. The amplitudes $f_\alpha^{(ln)}$ are the quantities that depend most sensitively on this choice. As in the case of the α process, we neglected any dependence of the jump angle δ on the value of the variable ϵ for simplicity. The most simple generalization of the model used here would be a superposition of more than one two-site jump models. If these are taken to be statistically independent, the resulting amplitudes f_α^D and f_α^{SLR} would just be given by the sum of the individual ones. In that case, however, reorientations about different axes may give rise to different angles θ for both dielectric relaxation and spin-lattice relaxation. It therefore appears most meaningful to interpret our angles δ and θ as effective angles. For the latter, there is no given relation between the value for dielectrics and NMR. A similar comment applies to the mean-squared displacement as shown in Fig. 2(a). The jump distance r_{jump} appearing in Eq. (51) is not determined by the model and it is most likely that the superposition of all local fluctuations will sum up to the observed mean-squared displacement. Also, it is to be noted that if we relax the simplifying assumption that the amplitudes $f_\alpha^{(ln)}$ are independent of ϵ, Eq. (41), we can take into account the fact that there might be molecules not participating in the β relaxation due to vanishing $\theta(\epsilon)$ or, more probably, vanishing $\delta(\epsilon)$. This latter possibility should not be ruled out as one can assume a high local density for small values of ϵ. This decreases the probability of local fluctuations. In this case the relative amplitudes of the α and β peak are not related in any simple manner and Eq. (42) cannot be used to calculate the time correlation functions. Additionally, the fraction of molecules participating in the β process may well be temperature dependent in such a scenario. Thus this could account for the ''islands of mobility'' [13] in principle.

When we consider the dielectric response $\Phi''(\omega)$, it is seen from Fig. 4 that a remarkable difference occurs between the peak frequencies of $\Phi_1^{(\beta)}(\omega)$ and the extrapolated one of $\Phi^{(\beta,0)}(\omega)$. As already pointed out, this difference is on the order of one decade at the crossing temperature as predicted by extrapolation. The influence of the α process on the β peak is already visible at temperatures $\sim 1.1T_g$. This means that even though the mean time scales of the two processes differ by more than two decades, the effect of averaging on the distribution of jump rates $\Gamma(\mu)$ due to α relaxation cannot be neglected at these temperatures. We mention that a similar behavior has been reported by Arbe *et al.* [17]. Thus, it seems that even a slight extrapolation might yield unrealistic estimates of the merging temperature. Therefore, conclusions about a real *crossing* of the two processes as advocated in Ref. [16] seem questionable. From our model, one would assume that the two peaks always merge at high temperatures and that the high-temperature process is the α process, even though this can no longer be modeled with the present approach. This scenario has already been put forward by Williams and Watts [15]. They, however, assumed the α and β processes to be statistically independent. We have commented on this assumed statistical independence already. It is important to recognize what the physical implications of this assumption are. Independent of our concrete model used here, it is plausible to assume that those reorientations associated with the α process are related to structural changes in the supercooled liquid. The β process is viewed as a local fluctuation in orientation within a given structure. Statistical independence of the two processes means that the local fluctuations are not at all affected by rearrangements of the local structure. This seems to be most unrealistic from a physical point of view, in particular, when taking into account the heterogeneous nature [38] of the β process. In the above picture this means that the rates for local fluctuations depend on the local environment, independent of whether these fluctuations are of an intramolecular or intermolecular origin. These rates change in the case of a structural rearrangement. One would not only assume that the relevant orientation of the axis of fluctuations are affected strongly by such a structural change but additionally the amplitude of the fluctuations. The latter corresponds to the jump angle δ in our model. Therefore, a model in which there is a strong correlation among the two processes seems to be much more in accord with physical intuition. Our calculations with the correlation parameter c set to zero, $c=0$, correspond to a complete randomization of the value of the orientation ω_β responsible for β relaxation. Of course, this case of complete correlation also represents an extreme scenario. However, this seems to be more in harmony with the underlying physical picture than the assumption of statistical independence.

The correlation functions $\Phi_l^{(\beta)}(t)$ can be written in the form of a product in all cases, as long as any correlation among the variables ϵ and μ is neglected completely. Also in this case a factorization of the form $\Phi_l^{(\beta)}(t)=\Phi_l^{(\alpha)}(t)\Phi^{(\beta,0)}(t)$ is only possible in the case of $c\equiv1$, as is obvious from Eqs. (33), (37), and (42). In no other choice of the parameters of the model is this kind of factorization possible. On the other hand, if it assumed on the contrary that there is a strong correlation among ϵ and μ, the reorientation rates $\Gamma(\epsilon;\mu)$ are determined (implicitly) by the value of ϵ in a given free-energy minimum, $\Gamma(\epsilon;\mu)\equiv\Gamma(\epsilon)$. In this case it is seen from the same equations that $\Phi_l^{(\beta)}(t)$ is of the form

$$\Phi_l^{(\beta)}(t)\sim\int d\epsilon\, p^{\mathrm{eq}}(\epsilon)e^{-\{\Gamma(\epsilon)+\kappa(\epsilon)\}t};\quad c=0$$

and cannot at all be written as a product. This also is not possible if $c=1$ is chosen in this case. In the model calculations discussed in the last section we always assumed that ϵ and μ are uncorrelated. An argument in favor of a missing correlation is the symmetric form of the β peak independent of the form of the α peak. Realistically, one would assume that a correlation among the two quantities cannot be neglected as can be seen if one assumes that a low value ϵ corresponds to high local density. Therefore, in an environment of high density, one would assume the activation energy for a local process to be higher than in a corresponding low-density environment. Of course, the density changes in a supercooled liquid are not expected to be extraordinarily large and, therefore, the correlation must not be strong. In any case, the assumption of no correlation among ϵ and μ represents a simplification. This discussion shows that the product form for $\Phi_l^{(\beta)}(t)$ is available only as the consequence of a couple of approximations. We mention that we have also performed calculations of $\Phi(\omega)$ with a strong correlation among ϵ and μ, where we chose $\mu\propto(E_\alpha-\epsilon)$ for simplicity. The behavior concerning the peak positions are very similar to the findings of Fig. 4(a). Also the behavior of the width of $\Phi_1^{(\beta)}(\omega)$ is similar to the one shown in Fig. 4(b). The spectra $\Phi_1^{(\beta)}(\omega)$, however, are not symmetric in any temperature regime, also not below T_g. Apart from this contradiction to experimental findings, these calculations again do not show any crossing of the two peaks, as can also be inferred directly by inspection of the above expression for $\Phi_l^{(\beta)}(t)$ for $c=0$. We stress the fact that the behavior of $\Phi_l^{(\beta)}(\omega)$ found here is independent of the input parameters as it is solely a consequence of the averaging of the distribution $g(\mu)$ associated with the $\Gamma(\mu)$ due to the transition rates $\kappa(\epsilon|\epsilon')$. It, therefore, does not rely on any specific form of the chosen distributions (in particular, not on σ and κ_∞^β) let alone a specific form for the correlation functions. In a model like the one proposed here, the β process cannot become slower than the structural relaxation.

When we consider the spin-lattice relaxation rates, it is found that the averaged rates can easily be calculated from our model and the results show the same qualitative behavior as observed experimentally. We pointed out already the strong dependence of these rates on the angles θ and δ. There is, however, one restriction to δ that must be met. If one considers the deuteron NMR spectra below T_g, these are very sensitive to reorientational motions. If reorientations by angles larger than roughly 20° take place on a time scale faster than the inverse quadrupolar coupling constant, the effect of motional narrowing is visible in the spectra. In the examples we chose for the temperature dependence of $\delta(T)$, we have $\delta(T_g)\sim39°$ in one and $\delta(T_g)\sim24°$ in the other example. If all rates $\Gamma(\mu)$ at T_g would be larger than $\sim10^6$ Hz one would observe motional narrowing. Since the fraction of such large rates is quite small in our examples (in the GCM, it is on the order of 5%), the spectra will show only small effects due to narrowing as is compatible with experimental data. [Whether or not motional narrowing is observed in the NMR spectra, of course, delicately depends on the choice for the temperature dependence of $\delta(T)$.] We mention that this problem is overcome in the aforementioned models with a temperature-independent but large jump angle by a very small equilibrium population of the higher level. Since the product of the two equilibrium populations enters in the expression for the amplitudes, again a negligible effect on the NMR spectra is obtained, although the jump angles are chosen to be on the order of 40° [37] or 140° [38]. This especially holds since in these investigations a very fast time scale for the two-site jumps was assumed. We think that the choice of a two-site model without a bias as it is used here is more plausible especially in view of these large jump angles. Additionally it appears more natural that the jump angle increases with temperature as an effect of thermal fluctuations. It has already been pointed out that a determination of the parameters for the dynamics of the β process by means of spin-lattice relaxation experiments is strongly hampered by their sensitivity to the amplitudes. On the other hand, this sensitivity can be used if this type of experiment is combined with dielectric relaxation studies.

Finally, let us discuss the merging scenario of the α and β process in view of the energy landscape model used for the structural relaxation. Since the α process is viewed as activated dynamics, the transitions among the different mimima or metastable states set the scale for the lifetime of the intramimimum reorientation rates $\Gamma(\mu)$. If we use 10° jumps for the isotropic reorientations due to α relaxation, roughly ten transitions $\epsilon\rightarrow\epsilon'$ are necessary in order for the correlation function $g_1(t)$ to decay to zero. This means that a dynamical averaging over the transition rates $\kappa(\epsilon|\epsilon')$ is performed when measuring $g_1(t)$. The effective distribution of reorientation rates is somewhat narrower than the corresponding one of the $\kappa(\epsilon|\epsilon')$. This effect gives rise to different stretching of various time correlation functions as the efficiency of the performed averages are different. For example, if we fit $g_1(t)$ for $\Gamma(\mu)=0$ as calculated with the GCM at $T=1.1T_g$ to a Kohlrausch function, we find stretching exponents $\beta_{KWW}=0.53$ for 10° angular jumps and $\beta_{KWW}=0.44$ for random angular jumps. In the latter example, the dynamical averaging is reduced to a minimum, cf. the extensive discussions in Refs. [10,11].

The averaging effect of the transition rates $\kappa(\epsilon|\epsilon')$ on the distribution of the rates $\Gamma(\mu)$, on the other hand, is much the same as studied in typical environmental fluctuation models [32,49,50]. As soon as some of the $\kappa(\epsilon|\epsilon')$ come on the time scale of the $\Gamma(\mu)$, the distribution of effective reorientation rates starts to get narrowed as compared to $g(\mu)$. This fact explains why the influence of the α process on the β peak is seen already at astonishingly low temperatures in the dielectric susceptibilities. This effect is best seen in the width of the β peak as shown in Fig. 4(b). From that plot one would estimate the temperature where the influence of the α relaxation [i.e., the $\kappa(\epsilon|\epsilon')$] on the β peak sets in even lower than from Fig. 4(a). What is of relevance is not the direct comparison of the peak positions of the α and β peaks. Instead, one has to bear in mind the different character of the averaging for the two processes. When the temperature is increased, the averaging effect becomes more and more pronounced until the time scales of $\kappa(\epsilon|\epsilon')$ and $\Gamma(\mu)$ become similar. Due to the same averaging, the shape of the $\Phi_1^{(\beta)}(\omega)$ becomes asymmetric as the averaging is most effective at low frequencies due to the fact that the $\kappa(\epsilon|\epsilon')$ are smaller than the $\Gamma(\mu)$. Such a behavior has been found experimentally by Garwe *et al.* [23].

Strictly speaking, somewhere in the temperature region of the merging of the two peaks in dielectric spectroscopy the underlying assumptions of the model cease to be valid. The treatment of the structural relaxation by a master equation, Eq. (1), requires that the lifetime of the free-energy minima is much longer than the time spent by the system on crossing the barriers between different minima. A Markovian description of the dynamics is expected to fail if this condition is not met. Concerning the β process, the assumption of a simple relationship of the Arrhenius form (50) for the reorientation rates $\Gamma(\mu)$ makes sense only if the activation energies μ are defined for a time long compared to the residence time of the system in one of the two orientations. If the lifetime of the minima itself is only on that order of magnitude, then the same holds for the μ, as they are defined only within the minima. On the other hand, at a temperature where the lifetime of the extensive number of free-energy minima is too short to allow for activated dynamics, the minima itself become irrelevant for the thermodynamics of the system. In this case, one ends with one thermodynamically relevant free-energy minimum and the dynamics in phase space is diffusive. It may well be described by MCT. We expect that there is a finite temperature interval where this crossover in the dynamics takes place. Regarding the slow β relaxation, this means that at high temperatures only the α relaxation remains, as there is only structural relaxation. It is important to point out that the fast β process as treated by MCT is to be viewed as structural relaxation in the present context. The physical picture emerging from these considerations is very close to the one put forward by Rössler [24]. The occurrence of the slow β relaxation is deeply related to the crossover in the dynamical mechanism in the supercooled liquid state, as in the present model the existence of different minima in the free energy is a prerequisite for the definition of the intraminimum relaxation associated with β relaxation. Though this slow β relaxation appears to be an intrinsic feature of the phase space geometry, the present model is not able to give a resolution to the puzzle that this process is observed in some supercooled liquids but not in others. On the other hand, the spin-lattice relaxation rates in the glass often behave very similar as a function of temperature. It, therefore, is tempting to speculate that the amplitudes play a crucial role with respect to the question of observability of β processes. This may be substantiated by the fact that it appears that in $Ca(NO_3)_2KNO_3$ a secondary relaxation is observable in mechanical relaxation but not in dielectric relaxation studies [51].

As the model used for the primary relaxation is of a heterogeneous nature, it immediately follows that also the β relaxation is heterogeneous. This fact has first been noticed in the NMR investigations of Schnauss, Fujara, and Sillescu [38] and has repeatedly been found afterwards [39].

V. CONCLUSIONS

In the present paper we have generalized a simple free-energy landscape model for primary relaxation in supercooled liquids in order to take into account the slow secondary relaxation observed in many glass-forming liquids. Whereas the primary relaxation is assumed to be intrinsically coupled to transitions among different free-energy minima, this secondary relaxation process is viewed as a local relaxation within a given minimum. We concentrated on the calculation of time correlation functions associated with molecular reorientations, but the generalization to translational motions of tagged particles poses no problem. The slow β process is modeled by simple reorientational jumps among two orientations. The activation energies for these reorientations are assumed to be distributed according to a Gaussian. Several scenarios for the correlations among these activation energies and the values ϵ of the free energy within a given minimum and those among the dynamics of the relevant orientations and the transitions in the free energy landscape have been considered. If no correlation among the energy variables ϵ and μ is assumed, the dielectric susceptibilities for the secondary peak are symmetric at low temperatures in accord with experimental findings. At higher temperatures, they become asymmetric due to the averaging effect of the transitions among different minima.

In the model presented here a crossing of the two peaks associated with α and β relaxation cannot occur, as the determining dynamics are the transitions among different minima. These transitions set the ultimate time scale. The form of the correlation function relevant for dielectric relaxation as a product of α and β correlators is obtained only as a special case for the physically counterintuitive assumption of complete statistical independence of the reorientations associated with the β process and the transitions among the free-energy minima. However, according to the above-mentioned absence of any possibility of a crossing of the two peaks and the concomitant uselessness of extrapolations of the characteristic parameters for the β peak from low temperatures, it seems advisable to analyze experimental data using this assumption, as has been done by Arbe *et al.* [17]. The reason for this is given by the fact that the product used in such an analysis contains the α peak as an input, which reduces the number of parameters. Also, for the simple two-site model considered in this study, we found that the differences between this assumption and the physically more meaningful one of a strong correlation are not very large. However, the conclusions raised from such an analysis should be handled with care.

When considering the spin-lattice relaxation rates as calculated with our model, the results are at least qualitatively in accord with experimental findings. We pointed out that a determination of the parameters characterizing the β relaxation in the glass will usually not be possible by spin-lattice relaxation experiments. Here, the combination of broadband dielectric spectroscopy and NMR might in favorable cases even allow the determination of jump angles due to the high sensitivity of NMR to the amplitudes [39].

Physically, the occurrence of the slow β relaxation in our model is intrinsically related to the often proposed change in transport mechanism in the supercooled liquid [19]. At high temperatures the dynamics is viewed as diffusive in phase space, whereas at low temperatures we are concerned with activated dynamics. The latter is modeled here via a master equation for the transitions among an extensive number of free-energy minima. Only if the existence of the many minima in free energy becomes relevant for the dynamics is it possible to define the slow β relaxation as we have done here as an intraminimum relaxation process. In order to gain a better understanding of the interrelation among the α and β processes, a more detailed picture of the free-energy landscape is necessary.

In conclusion, we have presented a very simplified model for the β relaxation based on a free-energy landscape model that is capable of reproducing both the results of dielectric relaxation experiments and spin-lattice relaxation experiments with the same parameters and is free from physically questionable assumptions.

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