Aging in a free-energy landscape model for glassy relaxation

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The aging properties of a simple free-energy landscape model for the primary relaxation in supercooled liquids are investigated. The intermediate scattering function and the rotational correlation functions are calculated for the generic situation of a quench from a high temperature to below the glass transition temperature. It is found that the re-equilibration of molecular orientations takes longer than for translational degrees of freedom. The time scale for re-equilibration is determined by that of the primary relaxation as an intrinsic property of the model.

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I. Introduction

If glassy materials are quenched from above their glass transition temperature deep into the glassy state, they usually do not reach equilibrium on experimentally accessible time scales. The dynamics in this out-of-equilibrium situation, the so-called aging phenomena, have been investigated for a long time, for reviews see e.g. refs. [1, 2]. If the system reaches equilibrium, i.e. if the quench is not performed at too low temperature, the aging behavior often can be well described in terms of the Tool-Narayanaswami-Moynihan model [3]. This model takes into account the non-linearity and the time-dependence of the relaxation time via the introduction of a reduced time and a fictive temperature.

In the recent past, many theoretical investigations of the aging behavior of glassy systems have been undertaken and some rigorous results regarding both, the detailed time-dependences of two-time correlation functions (CFs) and the violations of the fluctuation-dissipation theorem (FDT) have been derived for several models [4]. These violations can in favourable cases be used for the definition of a so-called effective temperature [5]. Also some computer simulations on model supercooled liquids have been performed and an effective temperature could be defined [6, 7]. Apart from theoretical considerations a number of experimental investigations of the violations of the FDT have been performed in the recent past, in particular on glassforming liquids [8], polymers [9], colloidal glasses [10] as well as spin glasses [11]. In all these systems, strong violations of the FDT have been observed and in some cases an effective temperature as a function of the time elapsed after the initial quench into the glassy phase has been determined. For glass forming liquids, the effective temperature relaxes to the bath temperature for not too deep quenches [8, 9].
Without referring to an effective temperature explicitly, it has been found experimentally that the aging behavior of volume and enthalpy in a glassy polymer may not be the same\textsuperscript{12}. A detailed study of the aging properties of polystyrene has been performed by Thurau and Ediger\textsuperscript{13}, who clearly showed that probe rotation and probe translation show different behaviors in this example. It was found that after a temperature jump into the glassy phase, the relaxation towards equilibrium of probe rotation takes longer than the corresponding re-equilibration of probe translation, if the final temperature of the quench is low enough. In particular, the temperature dependence of the re-equilibration times for rotations was found to be stronger than that of translational motions. The results could consistently be interpreted in terms of spatially heterogeneous dynamics, which is now well established to be at the origin of many of the peculiar features of the relaxation in glass forming liquids, for reviews see refs.\textsuperscript{14, 15}. Thurau and Ediger did not attempt to quantitatively discuss the relation between the re-equilibration times and the time scale of the primary relaxation at the final temperature of the quench. Such an analysis has been performed in detail for a number of glass forming liquids by dielectric spectroscopy\textsuperscript{16} and it was shown unequivocally that the aging behavior in these examples is determined by the structural $\alpha$-relaxation.

In the present paper, I will discuss the aging properties of glass forming liquids within a simple free-energy model that has been used previously to describe the heterogeneous relaxation in equilibrium\textsuperscript{17, 18, 19}. The idea of this model is simple. It is assumed that the primary relaxation in a supercooled liquid is thermally activated and proceeds via transitions among a large number of metastable states, characterized by their free-energy. This idea is in accord with various proposed scenarios of glassy relaxation, such as the one of a random first order transition\textsuperscript{20}. In order to describe the rotational or translational motion of tagged particles, it is assumed that each transition is accompanied by a particle rearrangement, giving rise to changes in both, the orientation and the position of the particle considered. These assumptions along with a mean jump distance and a mean rotation angle are enough to compute relevant CFs, such as the intermediate scattering function or rotational CFs. Due to the different ways various CFs average over the distribution of free-energies a number of hitherto unresolved puzzling features of the $\alpha$-relaxation could be explained in a simple way\textsuperscript{18}. This includes the breakdown of the Stokes-Einstein relation and the differences in the stretching observed in different experiments probing the reorientational or translational dynamics. Here, I will concentrate on a qualitative description of aging experiments and show that the results from model calculations capture the most prominent features observed experimentally.

The paper is organized as follows. In the next section, the free-energy model is briefly reviewed and it is described how to calculate CFs in an aging system. In Section III the aging behavior of the intermediate scattering function and of the rotational CFs is discussed. For comparison, in Section IV the aging-behavior of rotational CFs is discussed in the framework of models for environmental fluctuations\textsuperscript{21} or exchange models\textsuperscript{22}. Finally, the conclusions are presented in Section V.
II. Aging behavior in the free-energy landscape model

The aging behavior of supercooled liquids depends on the final temperature in a temperature jump experiment. This is because if the quench is performed to a temperature not too far below the glass transition temperature, the system can reach equilibrium on an accessible time scale since the glass transition temperature is merely a convenient way of classifying the time scale of the primary relaxation\[23\]. For deep quenches the re-equilibration usually cannot be monitored experimentally because the relaxation time is extremely long. This is one reason why sometimes models exhibiting a true transition into a glassy phase are considered when discussing the aging behavior. As will become clear in the present Section, in the free-energy landscape model the system always reaches equilibrium for long times and the re-equilibration time scale is determined by the $\alpha$-relaxation time at the final temperature of the quench.

In the following, I will utilize the free-energy landscape model for the calculation of translational and the rotational two-time CFs\[18\] after a temperature jump. In case of the reorientational motion, the CF is obtained by correlating the orientation-dependent interactions relevant in the experiment considered at two times. The transformation properties of these interactions determine the so-called rotational CF $g_L(t, t_w)$,

$$g_L(t, t_w) = \langle P_L(\cos(\theta(t)))P_L(\cos(\theta(t_w))) \rangle$$

(1)

Here, $P_L(x)$ denotes the Legendre polynomial of rank $L$. For instance, in dielectric spectroscopy $g_1(t, t_w)$ and in NMR or depolarized light scattering $g_2(t, t_w)$ are measured. Here, $t_w$ denotes the waiting time, i.e. the time that has elapsed after the initial preparation of the system before the beginning of the experiment. In all later calculations, the initial preparation corresponds to a quench from a high temperature to the working temperature.

If one is interested in translational motions of tagged particles, one naturally considers the incoherent intermediate scattering function\[24\]:

$$S_q(t, t_w) = \langle e^{i\mathbf{q} \cdot \mathbf{r}(t)} e^{-i\mathbf{q} \cdot \mathbf{r}(t_w)} \rangle$$

(2)

where $\mathbf{r}(t)$ denotes the position of the particle and $\mathbf{q}$ is the wave-vector. Additionally, I have already assumed that the system is isotropic, $q = |\mathbf{q}|$.

In the free-energy model, a free-energy $\epsilon$ is associated with each of the exponentially large number of basins or metastable states of the system\[4, 25\]. The $\alpha$-relaxation is modeled using a master equation\[26\] for the conditional probability to find the system in a metastable state characterized by $\epsilon$ at time $t$, given that one had $\epsilon_0$ at $t_0$:

$$\dot{G}(\epsilon, t|\epsilon_0, t_0) = -\int d\epsilon'\kappa(\epsilon'|\epsilon)G(\epsilon, t|\epsilon_0, t_0) + \int d\epsilon'\kappa(\epsilon|\epsilon')G(\epsilon', t|\epsilon_0, t_0)$$

(3)

Here, $\kappa(\epsilon'|\epsilon)$ denotes the rate for a $\epsilon \rightarrow \epsilon'$-transition, which is assumed to be time-independent for simplicity. Consequently, $G(\epsilon, t|\epsilon_0, t_0)$ depends only on the difference of the times involved, $G(\epsilon, t|\epsilon_0, t_0) = G(\epsilon, t-t_0|\epsilon_0)$. In ref.\[18\], we considered different choices for the transition rates $\kappa(\epsilon'|\epsilon)$ with only quantitative differences in the results. Therefore, in
the present calculations, I will solely consider the following simple choice for the transition rates, denoted as globally connected model in ref. [15]. It is assumed that every state can be reached by a transition and that the destination state is chosen at random according to a prescribed density of states, denoted by \( \eta(\epsilon) \). The transition out of a given state is assumed to be thermally activated with a rate given by 
\[
\kappa(\epsilon) = \kappa_\infty e^{\beta \epsilon},
\]
where a common activation energy has been absorbed in the prefactor and \( \beta = (k_B T)^{-1} \). This means, all calculations will be restricted to the simple case of transition rates
\[
\kappa(\epsilon|\epsilon') = \kappa_\infty \eta(\epsilon') e^{\beta \epsilon}
\]
(4)
Furthermore, the density of states will be chosen to be Gaussian with zero mean and variance \( \sigma \) throughout, 
\[
\eta(\epsilon) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\epsilon^2/(2\sigma^2)}
\]
The same transition rates have also been used by Dyre in his ‘energy master equation’ [27]. With this choice, the system reaches equilibrium for long times and the equilibrium probabilities are given by:
\[
p^{eq}(\epsilon) = \lim_{t \to \infty} G(\epsilon, t|\epsilon_0, t_0) = \frac{1}{\sqrt{2\pi\sigma}} e^{-(\epsilon - \bar{\epsilon})^2/(2\sigma^2)} \quad \text{with} \quad \bar{\epsilon} = -\beta \sigma^2
\]
(5)
The distribution of equilibrium probabilities thus has a temperature-independent width and a mean that scales like the inverse temperature. In the inherent structure approach to the classification of the potential energy landscapes of supercooled liquids [25] it is usually found that the inherent structure energies are distributed according to a Gaussian [28]. However, the transitions among different inherent structures are more complicated than assumed in eq. (4), see e.g. ref. [29].

The main idea of the present model consists in the coupling of the reorientational and translational motion of a tagged particle to the \( \alpha \)-relaxation as follows. The transitions among the metastable states are the only possible way for particle rearrangements (apart from vibrational motion within a state). Therefore, it is assumed that the particle considered changes its position as well as its orientation by a certain amount whenever a transition takes place. In order to model the dynamics of either translations or rotations, the composite Markov process \( \{\epsilon(t), a(t)\} \) with \( a(t) \) denoting the orientation \( \Omega(t) \) or the position \( r(t) \) is considered [17, 18]. To this end, one has to deal with the master equation for the combined conditional probabilities \( G(\epsilon, a, t|\epsilon_0, a_0, t_0) \) and the transition rates \( W(\epsilon', a'|\epsilon, a) \). For the latter, the simplest possible choice will be considered which means that only reorientations with a mean angle \( \delta \Omega \) and only translations with a mean jump distance \( \delta R \) are allowed.

The solution of the corresponding master equation is outlined in Appendix A for convenience of the reader, for more details see ref. [18]. Here, it suffices to note that it is assumed that initially there are no correlations between the populations \( p(\epsilon, 0) \) and \( p(a, 0) \) and the latter are given by the equilibrium populations \( p^{eq}(a) \), cf. eq. (A.4). The two-time CFs defined in eqns. (1) and (2) are given by:
\[
\begin{align*}
g_L(t, t_w) &= \int d\epsilon \int d\epsilon' G_L(\epsilon, t|\epsilon') p(\epsilon', t_w) \\
S_Q(t, t_w) &= \int d\epsilon \int d\epsilon' G_Q(\epsilon, t|\epsilon') p(\epsilon', t_w)
\end{align*}
\]
Here, the Green’s functions \( G_L(\epsilon, t|\epsilon') \) and \( G_Q(\epsilon, t|\epsilon') \) are solutions of eq.(A.5) and \( Q = (q, \delta R) \). For long waiting times, it is evident from eq.(5) that

\[
p(\epsilon, t_w) \rightarrow p^{\text{eq}}(\epsilon) \quad \text{for} \quad t_w \rightarrow \infty
\]

because of \( p(\epsilon, t_w) = \int d\epsilon' G(\epsilon, t_w|\epsilon') p(\epsilon', 0) \) and \( \int d\epsilon' p(\epsilon', 0) = 1 \). The CFs then reduce to those in equilibrium,

\[
g^{\text{eq}}_L(\tau) = \int d\epsilon \int d\epsilon' G_L(\epsilon, \tau|\epsilon') p^{\text{eq}}(\epsilon') \quad \text{and} \quad S^{\text{eq}}_Q(\tau) = \int d\epsilon \int d\epsilon' G_Q(\epsilon, \tau|\epsilon') p^{\text{eq}}(\epsilon')
\]

the former of which has been discussed in detail in ref.\[18\].

In order to describe an aging experiment, one has to fix the initial populations. Experimentally, one usually performs a temperature jump from a ’high’ temperature above the glass transition temperature \( T_g \) to below \( T_g \). In the present paper, I will consider only quenches from \( \beta = 0 \) (\( T = \infty \)) to the working temperature, which means:

\[
p(\epsilon, 0) = \eta(\epsilon) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\epsilon/(2\sigma^2)}
\]

Due to the fact that equilibrium is reached in the long run, cf. eq.(7), all aging effects are of a transient nature. Note that \( \beta = 0 \) in the present context only means that the transition rates in eq.(4) are no longer thermally activated, i.e. one has \( \kappa(\beta=0)(\epsilon'|\epsilon) = \kappa_\infty \eta(\epsilon') \) independent of the initial state.

A first estimate of the effects that are to be expected can be obtained from the temporal evolution of the populations, \( p(\epsilon, t_w) \). In Fig.1a, I have plotted \( p(\epsilon, t_w) \) as a function of \( \epsilon \) for two final temperatures, \( T = 0.2\sigma \) (upper panel) and \( T = 0.4\sigma \) (lower panel), for various waiting times \( t_w \). For \( t_w = 0 \), one has a Gaussian centered at \( \epsilon = 0 \), cf. eq.(9) and in the long-time limit, the center has moved to \( \bar{\epsilon} = -\beta\sigma^2 \). It is, however, obvious from the figure, that with increasing \( t_w \) the distribution first narrows and then becomes broader again. Furthermore, the form of the distribution is not exactly Gaussian for intermediate times. A similar behavior of the distribution of inherent energies during aging has been found in a recent simulation of a binary Lennard-Jones system\[30\]. In a next step, I determined the various moments of the distributions, the mean value \( \langle \epsilon(t_w) \rangle \), the width \( \sigma(t_w) \) and the skewness \( \gamma_1(t_w) \). The results are shown in Fig.1b. The change in sign of \( \gamma_1(t_w) \) reflects the fact that the distributions are skewed to the high-energy side for small \( t_w \) and to the low-energy side for long \( t_w \). The deviations from a Gaussian are seen to be more pronounced for the lower final temperature. The fact that the distribution of \( p(\epsilon, t_w) \) becomes narrower for intermediate \( t_w \) already gives rise to the expectation that the degree of non-exponentiality of the two-time CFs given in eq.(6) will change with the waiting time. This means that one expects the stretching parameter \( \beta_K \) of Kohlrausch fits (\( \propto \exp\left[-(t/\tau_K)^{\beta_K}\right] \)) first to increase and then to decrease again.

In the following, the evolution of the intermediate scattering function and the rotational CFs after a quench from high temperature to several low temperatures will be discussed.
III. Aging monitored by two-time correlation functions

The equilibrium properties of the rotational CFs \( g^e_L(\tau) \) for different values of \( L \) have been discussed in detail in ref. [18] along with the apparent translational enhancement. Therefore, I will start with a brief discussion of the \( Q \)-dependence of the intermediate scattering function. In Fig. 2a, \( S^e_Q(\tau) \) is plotted versus \( \tau/\tau_Q \) for various values of \( Q \) and \( T = 0.3\sigma \). Here, \( \tau_Q \) is the relaxation time obtained from a fit to a stretched exponential function \( \exp\left(-\left(\tau/\tau_Q\right)^{\beta_Q}\right) \). It is evident that only for small \( Q \) one is in the hydrodynamic limit and the degree of non-exponentiality is a strong function of \( Q \). In the free-energy landscape model, the reason for this behavior is explained by the fact that for small \( Q \) many jumps have to be performed in order for the CF to decay. Therefore, \( S^e_Q(\tau) \) averages over the density of states quite effectively and the decay is very slow and exponential. For large values of \( Q \), any single jump decorrelates the intermediate scattering function and therefore there is no averaging. Consequently, the decay is governed by a broad distribution of effective relaxation rates. The situation thus is similar to the one for the rotational CFs for different values of \( L \), c.f. the discussion on this point in ref. [18]. For rotational CFs, however, the mean rotation angle enters separately, whereas due to \( Q = q \cdot \delta R \) the jump distance \( \delta R \) only multiplies the scattering vector.

In Fig. 2b the relaxation times \( \tau_Q \) and the stretching parameter \( \beta_Q \) from fits of \( S^e_Q(\tau) \) to a stretched exponential function, \( \exp\left(-\left(\tau/\tau_Q\right)^{\beta_Q}\right) \), are shown. For values of \( Q \) smaller than roughly \( 10^{-2} \), the decay is exponential and one can define a diffusion coefficient \( D_T = (\delta R)^2 \langle \kappa \rangle / 6 \), where \( \langle \kappa \rangle \) is the average relaxation rate, \( \langle \kappa \rangle = \int d\epsilon \kappa(\epsilon) p^{eq}(\epsilon) \). For larger \( Q \), \( \beta_Q \) decreases and the relaxation time deviates from the \( Q^{-2} \)-scaling. For \( Q > 10 \), neither \( \tau_Q \) nor \( \beta_Q \) change any further, because here one is in the limit of the 'jump correlation function' [17].

In Fig. 2c, I have plotted the fitted relaxation times scaled to those at \( T = 0.9\sigma \) versus inverse temperature. The reason for the different behavior again lies in the different averaging over the transition rates for different \( Q \). The maximum discrepancy between the relaxation times, however, does not exceed a factor of roughly two (three, if the average times are considered). The values of \( Q \) were chosen, because if \( \delta R \) is chosen between twenty and fifty percent of the van der Waals radius of a tetracene molecule, they are comparable to the scattering vector used in the mentioned experiment by Thurau and Ediger [13].

Next, the CFs \( S_Q(t_w + \tau, t_w) \) and \( g_L(t_w + \tau, t_w) \) are calculated according to eq. (6), where now \( t = t_w + \tau \) is used as the time-variable. Results for different waiting times \( t_w \) are shown in Fig. 3a for \( T = 0.3\sigma \). In case of the rotational CF, I used \( L = 1 \), corresponding to dielectric relaxation. The results for other values of \( L \) are quite similar, apart from minor quantitative differences that are relevant at equilibrium, cf. ref. [18]. In all calculations, a mean rotation angle of \( \Theta = 10^\circ \) is used. This is on the order of magnitude as found experimentally for supercooled liquids [31]. For long \( t_w \), both CFs are independent of \( t_w \) and coincide with those in equilibrium. It is evident, that the relaxation time as a function of \( t_w \) changes much more for the rotational CF than for the intermediate scattering function. Also this finding is explained by the different inherent averaging over the density of states.
As already pointed out above, for small $Q$, many $\epsilon \rightarrow \epsilon'$-transitions have to take place in order for $S_Q$ to decay. The same transitions are responsible for the approach of equilibrium. Therefore, the $t_w$ dependence of $\tau_Q$ is less pronounced than the corresponding one for $\tau_1$, the relaxation time describing $g_1$. This is because in the latter case fewer $\epsilon \rightarrow \epsilon'$-transitions are required for $g_1$ to decay and the system exhibits less re-equilibration during the decay.

In Fig.3b, the results of Kohlrausch fits $\exp(-(t/\tau_z(t_w))^\beta_z(t_w))$, where $z$ denotes either $L=1$ or $Q$, to the CFs as shown in Fig.3a are collected. Two features are evident immediately. The values of $\tau_1(t_w)$ change by about 1.5 decades from $t_w=0$ to $t_w=\infty$, whereas this change is much smaller for $\tau_Q(t_w)$ (0.7 decades for $Q=0.1$ and 0.07 decades for $Q=0.01$). The stretching parameters show an increase for small $t_w$ and then decrease as equilibrium is reached. This 'hump' for intermediate $t_w$ has its origin in the narrowing of the distribution of the populations $p(\epsilon, t_w)$, cf. Fig.1. Thurau and Ediger[13] found that $\tau_{rot}(t_w)$ changes by a larger amount as a function of $t_w$ than $\tau_{trans}(t_w)$ does. In their interpretation of the experimental results, the value of the stretching parameter for the rotational CF was assumed to also show a slight increase followed by a decrease as a function of $t_w$. Both effects are much more pronounced in the present model calculations, which might have its origin partly in the high initial temperature used here. It should be mentioned, that the ratio $\tau_1(t_w=\infty)/\tau_1(t_w=0)$ strongly depends on the final temperature of the quench, for instance this ratio is roughly 15 and 6 for $T=0.32\sigma$ and $T=0.35\sigma$, respectively. As already mentioned, it will not be attempted to provide a quantitative description of existing experimental data. The overall qualitative features are, however, very similar to what is observed experimentally.

Another important feature of the experiment, which supports the view of a spatially heterogeneous aging scenario is the fact that probe rotation needs longer to reach equilibrium than probe translation, at least for low final temperatures[13]. In Fig.3c, $\tau_1(t_w)$ and $\tau_Q(t_w)$ are plotted in a scaled way. It is evident that the intermediate scattering function reaches equilibrium much faster than the rotational CF. In order to have a measure of the re-equilibration time, to be denoted as $\tau_{eq}$, I have determined the $(1-1/e)$-points of the curves, cf. Fig.3c. These are plotted versus inverse temperature in Fig.3d, where I scaled them to their value at $T=0.5\sigma$. It is seen that the temperature-dependence of the re-equilibration times is somewhat different for translation and rotation. For lower temperatures, $\tau_{eq}(rot.)$ is longer than $\tau_{eq}(trans.)$ in qualitative agreement with the experimental results. The explanation of this finding again lies in the fact that the two CF’s average in different ways over the density of states. Therefore, $S_Q(t_w + \tau, t_w)$ reaches equilibrium faster than $g_1(t_w + \tau, t_w)$. It should be pointed out that in the framework of the present model it is the same difference in the averaging over the density of states that gives rise to the apparent translational enhancement[13]. Furthermore, the re-equilibration of course is determined by the $\alpha$-relaxation in the free-energy model as there is no other time scale.
IV. Aging in environmental fluctuation models

In the free-energy model the lifetime of the dynamic heterogeneities is on the same time scale as the $\alpha$-relaxation time. This is because there is no other time scale in the model. In terms of Heuer’s more general concept of a rate memory parameter $Q$ (not to be confused with a scattering vector) the free-energy model intrinsically corresponds to $Q=1$. It has to be noted, however, that the free-energy model in the simple form presented here, cannot describe the finding of an exchange time much longer than the $\alpha$-relaxation time observed in a photobleaching experiment near $T_g$ in ortho-terphenyl. In this section, therefore, I will consider so-called environmental fluctuation models that allow for an extra time scale for exchange or arbitrary rate memory. In such models it is assumed that the molecular dynamics are faster in some part of the sample and slower in another. When applied to supercooled liquids the dynamic heterogeneities are related to a distribution of the correlation times and their lifetime is limited by exchange among the regions of different mobility. Therefore, one would interpret the dynamic exchange as the structural relaxation of the system.

Such models can also be used for the calculation of the aging properties of the relevant CFs. Here, I will concentrate on the rotational CF $g_1(t, t_w)$ and consider the following variant of an exchange model. It is assumed, that a reorientation rate $\Gamma(\epsilon)$ corresponds to each value of the variable $\epsilon$. Therefore, the variable $\epsilon$ in the present context characterizes a given environment and the value of the corresponding reorientation rate $\Gamma(\epsilon)$. These rates for simplicity are chosen according to

$$\Gamma(\epsilon) = \Gamma_\infty e^{\beta \epsilon}$$

The transition rates $\kappa(\epsilon|\epsilon')$ for $\epsilon' \rightarrow \epsilon$-transitions are again chosen according to eq.(11). As mentioned above, it are these transition rates that are responsible for the exchange among the various reorientation rates in the sense that with every $\epsilon' \rightarrow \epsilon$-transition a change from $\Gamma(\epsilon')$ to $\Gamma(\epsilon)$ is accompanied. According to eq.(5), one has a Gaussian distribution of $\epsilon$-values and therefore a broad distribution of reorientation rates $\Gamma(\epsilon)$. This ‘bare’ distribution is narrowed somewhat due to exchange, if the latter takes place on a similar time scale as the reorientational dynamics. Note that the choice of $\Gamma(\epsilon)$ and $\kappa(\epsilon|\epsilon')$ are of a purely phenomenological nature. However, the details of the form of the distributions of reorientation rates and of exchange rates are of minor importance for the following qualitative discussion.

The solution of the master equation for such exchange models is outlined in Appendix B where again it is assumed that reorientations proceed via rotational jumps with a mean jump angle $\Theta = 10^\circ$. In the following, I will restrict myself to the assumption that each ‘exchange-transition’ is accompanied by a randomization of the molecular orientation. In this case, the solution of eq.(B.2) is trivial (because of $c_L = \delta_{L,0}$) and the corresponding rotational CF is given by $g_L(t, t_w) = \int d\epsilon e^{-\left(\Gamma_L(\epsilon) + \kappa(\epsilon)\right)(t-t_w)} p(\epsilon, t_w)$ with the reorientation rates $\Gamma_L(\epsilon) = [1 - P_L(\cos \Theta)] \Gamma(\epsilon)$, cf. eq.(B.3). The aging behavior of $g_1(t, t_w)$ is reflected solely in the populations $p(\epsilon, t_w)$ which evolve in time according to the master equation.
These populations decay with effective reorientation rates \( \Gamma_L(\epsilon) + \kappa(\epsilon) \), reflecting the fact that both, a reorientation as well as an 'exchange-transition' depletes the population \( p(\epsilon, t_w) \). In order to allow for different time scales of reorientations and exchange, I will use the following simple relation between the attempt frequencies:

\[
\frac{\Gamma'_\infty}{\kappa'_\infty} = x \quad \text{with} \quad \Gamma'_\infty = [1 - \cos \Theta] \Gamma_\infty
\]  

(11)

Here, \( x \) is a free parameter and the scaling to \( (1 - \cos \Theta) \) assures that the reorientational geometry has no further impact on the relative time scales. For \( x = 1 \), the time scale of molecular reorientation coincides with the time scale of dynamic exchange, whereas for larger \( x \), the average exchange rates are smaller than the reorientation rates. Note that the assumption of a randomization of the molecular orientation means that also exchange gives rise to a decay of the rotational CF, which has some influence on its form for \( x \sim 1 \) but not for large \( x \) (slow exchange).

The rotational CFs \( g_1(t, t_w) \) for \( x = 1 \) behave very similar to those obtained in the free-energy landscape model. For large \( x \), however, the re-equilibration takes very long. This is a consequence of the fact that the aging behavior is determined by the time scale of exchange in this model. The \( \epsilon \rightarrow \epsilon' \)-transitions are responsible for both, the re-equilibration of the system and the exchange among the reorientation rates. For large \( x \), the re-equilibration is still determined by the exchange time but the time scale for reorientations is faster. This behavior is summarized in Fig. 4, where I have plotted the rotational correlation times \( \tau_1 \) as a function of the waiting time for \( T = 0.4\sigma \) and \( \Theta = 10^\circ \). The re-equilibration for \( x = 10^3 \) is much longer than for \( x = 1 \). This behavior scales exactly with \( x \) and it shows that in this model the re-equilibration is determined by the dynamic exchange and not by the reorientations.

These model calculations show that within such an approach the assumption of an exchange time much longer than the \( \alpha \)-relaxation, as obtained in the mentioned optical experiments\(^{33, 15} \) near \( T_g \), cannot be reproduced by assuming that dynamic exchange is governed by a structural relaxation which also determines the aging behavior of the system. This is because the re-equilibration time scale has been found to be determined by the \( \alpha \)-relaxation\(^{16} \). Therefore, one would have to include still another time scale, an 'aging-time', in such exchange models. This 'aging-time', however, would have to coincide with the \( \alpha \)-relaxation time.

As already noted above, also the free-energy model in the simple form presented here cannot describe both features. It is not clear at present, whether the reason for this lies in the oversimplified assumptions regarding the geometry of molecular reorientations and if a more realistic description using a distribution of jump-angles\(^{34} \) would allow to obtain longer exchange times.
V. Conclusions

In the present paper I have examined the out-of-equilibrium behavior of the two-time CFs for translational and rotational degrees of freedom within the framework of a free-energy model for relaxation in glass-forming liquids. The system has been prepared in an off-equilibrium situation by performing a quench from a high temperature to a low 'working temperature'. Instead of trying to obtain quantitative agreement with existing experimental data the focus has been on a qualitative description of the physics inherent in the model. Therefore, all model calculations were performed using the simplest choices possible for the various parameters involved. For instance, the transition rates were chosen according to a simple-minded rule, cf. eq.(4), and the density of states was chosen to be Gaussian with a temperature-independent width. Both choices would have to be improved in order to obtain quantitative agreement with experimental results. In addition, I solely considered the generic situation of a quench from an infinitely high temperature.

When considering the behavior of the intermediate scattering function and of the rotational CFs after a quench from a high temperature to a rather low temperature it is found that the correlation times of both functions increase continuously as a function of the waiting time that has elapsed between the quench and the measurement. For long waiting times, both correlation times reach their equilibrium values at the final temperature. However, the absolute change in correlation time is much larger in case of rotational motion than for translations monitored with small scattering vectors. In addition, the time needed to re-equilibrate, i.e. to reach equilibrium at the final temperature, also is longer for rotations than for translations. When considered as a function of the final temperature, the re-equilibration times \( \tau_{eq} \) behave differently. For rotations, \( \tau_{eq} \) shows a stronger temperature-dependences than for translational motions. These findings along with a waiting-time dependent stretching parameter are in qualitative agreement with experimental results by Thurau and Ediger[13].

In the present model, the re-equilibration is determined solely by the \( \alpha \)-relaxation, as there exists no other time scale. This feature is in accord with recent dielectric experiments on a variety of supercooled liquids[15]. To allow for two distinct time scales I considered a so-called exchange model in addition to the free-energy landscape model. Such a model naturally provides two distinct time scales, one for on-site relaxation and one for dynamical exchange. It is found in the model calculations that \( \tau_{eq} \) coincides with the equilibrium 'exchange time' if the exchange is associated with the structural relaxation responsible for the aging properties. Therefore, if the exchange time is much longer than the correlation time, \( \tau_{eq} \) is much longer, too. This means, in order to reproduce \( \tau_{eq} \) on the order of \( \tau_{\alpha} \) in such models, yet another time scale has to be introduced.

In summary, the free-energy model that has been introduced in order to describe the primary relaxation of supercooled liquids in equilibrium[17, 18] can also reproduce the experimentally observed features in out-of-equilibrium situations, at least on a qualitative level. The comparison with the exchange models shows, that aging experiments might also yield additional information about the nature of the dynamic heterogeneities in supercooled
liquids. In particular, it appears an open question what the exact relation between the life-time of these heterogeneities and the re-equilibration time after a quench is. In the free-energy model the differences in the time scales, the correlation times, the life-time of the dynamic heterogeneities and $\tau_{eq}$ can unequivocally be attributed to the different averaging over the density of states for different dynamical variables. The underlying intrinsic time scale is determined solely by the $\alpha$-relaxation.

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Appendix A: Solution of the master equation for the free-energy landscape model

In this Appendix I will give the relevant formulae that are needed for the solution of the master equation for the composite Markov process \( \{\epsilon(t), a(t)\} \), where \( a(t) \) has to be identified with the orientation \( \Omega \) or the position \( r \). Because the solution of the master equation proceeds in the same way for both cases, the treatment can be formulated quite generally. The transition rates can be written in the form

\[
W(\epsilon', a'|\epsilon, a) = \kappa(\epsilon'|\epsilon)\Lambda(a'|a)
\]

(A.1)

Here, I neglected possible dependencies of \( \Lambda(a'|a) \) on the initial and final states of the transition. In the text, only the special case \( \Lambda(a'|a) = \delta(a' - (a + \delta a)) \) is considered explicitly. To solve the corresponding master equation for this case one defines the matrix of the eigenvectors of \( \Lambda(a|a') \), \( U(a, p) \) corresponding to the eigenvalue \( \Lambda(p) \), i.e. \( \Lambda(p) = \int da fda' U^{-1}(a', p) \Lambda(a'|a) U(a, p) \). Next, the conditional probability is expanded in terms of these eigenvectors,

\[
G(\epsilon, a, t|\epsilon_0, a_0) = \int dp U(a, p)G_p(\epsilon, t|\epsilon_0)U^{-1}(a_0, p)
\]

(A.2)

The Green’s functions \( G_p(\epsilon, t|\epsilon_0) \) are then found from the solution of

\[
\dot{G}_p(\epsilon, t|\epsilon_0) = -\kappa(\epsilon)G_p(\epsilon, t|\epsilon_0) + \Lambda(p) \int d\epsilon' \kappa(\epsilon'|\epsilon)G_p(\epsilon', t|\epsilon_0)
\]

(A.3)

where the sum rule \( \kappa(\epsilon) := \int d\epsilon' \kappa(\epsilon'|\epsilon) \) was used for the diagonal element.

The initial populations are chosen as described in the text, i.e.:

\[
p(\epsilon, a, t=0) = p^eq(a)p(\epsilon, t=0)
\]

(A.4)

If one considers isotropic rotational motions with a fixed mean jump angle \( \delta \Theta = \Theta \), one has to identify \( a \) with \( \Omega \). In this case one has \( p^eq(a) = \frac{1}{4\pi} \), \( U(a, p) = \sqrt{\frac{2L+1}{2\pi}} D_{\frac{L}{2}}(\Theta) \), \( \Lambda(p) = P_L(\cos(\Theta)) \) and the integration over \( p \) is now a sum over \( L \). In case of translational jumps onto all positions of a sphere with a radius \( \delta R \) (jump length), the corresponding substitutions in the general formulae are \( p^eq(a) = V^{-1} \) with \( V \) denoting the volume. Furthermore, one has \( U(a, p) = \sqrt{\frac{2L+1}{2\pi}} e^{i\mathbf{q} \cdot \mathbf{r}} \) and \( \Lambda(p) = j_0(q\delta R) \), where \( j_0(x) \) denotes the Bessel function of zeroth order.

In eq. (A.3) one has to identify \( p = L \) for rotations and \( p = Q \) with \( Q = (q \cdot \delta R) \) for translations and thus eq. (A.3) explicitly reads:

\[
\text{Rotation : } \quad \dot{G}_L(\epsilon, t|\epsilon_0) = -\kappa(\epsilon)G_L(\epsilon, t|\epsilon_0) + P_L(\cos(\Theta)) \int d\epsilon' \kappa(\epsilon'|\epsilon)G_L(\epsilon', t|\epsilon_0)
\]

\[
\text{Translation : } \quad \dot{G}_Q(\epsilon, t|\epsilon_0) = -\kappa(\epsilon)G_Q(\epsilon, t|\epsilon_0) + j_0(Q) \int d\epsilon' \kappa(\epsilon'|\epsilon)G_Q(\epsilon', t|\epsilon_0)
\]

(A.5)

Note that due to \( P_0(x) = j_0(0) = 1 \), there is one eigenvalue, \( p = 0, \Lambda(0) = 1 \). Therefore, for \( p = 0 \), from eqns. (A.3), (A.5) the original master equation for the transitions in the free-energy landscape, eq. (3), is obtained, i.e. \( G_0(\epsilon, t|\epsilon_0) \equiv G(\epsilon, t|\epsilon_0) \). This is in full accord
with the idea underlying the model that the variable $a$ is allowed to change only in case of a $\epsilon \rightarrow \epsilon'$ transition\[18]. Once the $G_p(\epsilon,t|\epsilon_0)$ are obtained from the (numerical) solution of the equations (A.5), all quantities of interest can be calculated and one finds for the normalized correlation function:

$$C_p(t, t_w) = \int \! d\epsilon \int \! d\epsilon' G_p(\epsilon, t - t_w|\epsilon')p(\epsilon', t_w)$$

(A.6)

where $p(\epsilon, t_w) = \int \! d\epsilon' G(\epsilon, t|\epsilon')p(\epsilon', 0)$, i.e. only $p = 0$ is relevant here. This is easy to understand from the fact that according to the chosen initial conditions, eq.(A.4), the variable $a$ was in equilibrium in the beginning, $t_w = 0$. In case of reorientational motions the normalization eliminates a factor $(2L + 1)^{-1}$.

In general, the behavior of the correlation functions is obtained from a numerical solution of the equations for the Green’s functions, eq.(A.5)\[17, 18]. For this purpose, the transition rates $\kappa(\epsilon'|\epsilon)$ have to be chosen in a prescribed way, e.g. as done in the text, cf. eq.(4). It is, however, possible to give some general results valid in specific situations.

Consider the case of rotational random jumps, for which one has $\Lambda(\epsilon > 0) = 0$. Similarly, if the incoherent scattering function is observed for large wave-vectors, $Q \gg 1$ (or $q \gg (\delta R)^{-1}$), one has $j_0(Q) \simeq 0$.

In the limit $\Lambda(p) \to 0$, the general expression for the Green’s function, eq.(A.5), approximately reads as $\dot{G}_p(\epsilon, t|\epsilon_0) = -\kappa(\epsilon)G_p(\epsilon, t|\epsilon_0)$ and therefore one has $G_p(\epsilon, t|\epsilon_0) \simeq \delta(\epsilon - \epsilon_0)e^{-\kappa(\epsilon)t}$. Using this expression, one easily finds from eq.(A.6):

$$C_p(t, t_w) \simeq \int \! d\epsilon e^{-\kappa(\epsilon)(t-t_w)}p(\epsilon, t_w)$$

(A.7)

which is independent of $p$ and gives the probability that the system has not left the metastable state with free-energy $\epsilon$ occupied at $t = t_w$ in the time interval $(t - t_w)$.

In the other extreme, namely very small wave-vectors or rotational diffusion, one has $\Lambda(p) = 1 - \eta_p$ with $\eta_Q = Q^2/6$ and $\eta_L = L(L + 1)(\Theta/2)^2$. As has been shown in ref.\[18], in equilibrium in the limit of small wave-vectors the model predicts an exponentially decaying intermediate incoherent scattering function, $S_q^{\text{eq}}(\tau) \simeq \exp(-q^2 D_T \tau)$, with an apparent diffusion coefficient $D_T = (\delta R)^2\langle \kappa \rangle/6$. In case of the rotational diffusion of molecules one accordingly has $g_L^{\text{eq}}(\tau) \simeq \exp(-L(L + 1)D_R \tau)$ with $D_R = (\Theta/2)^2\langle \kappa \rangle$.

### Appendix B: Environmental fluctuation model

Such models can be defined by transition rates of the type\[22]

$$W(\epsilon', \Omega'|\epsilon, \Omega) = W_c(\Omega'|\Omega)\delta(\epsilon' - \epsilon) + \kappa(\epsilon'|\epsilon)\Lambda(\Omega'|\Omega)$$

(B.1)

where now the on-site reorientations are modelled via finite $W_c(\Omega|\Omega')$. Translational motions can be modeled in a similar way. In the following, it is assumed that the reorientations proceed via rotational jumps with a mean jump angle $\Theta$ as in the free-energy landscape model. In addition, it has to be quantified what happens to the molecular orientation
in case of $\epsilon \rightarrow \epsilon'$ transition. As in the original model of Beckert and Pfeifer\cite{35}, it will be assumed that either no change at all, $\Lambda(\Omega|\Omega') = 1$, or a random rotation, $\Lambda(\Omega|\Omega') = 1/(8\pi^2)$, takes place. Proceeding exactly in the same way as in Appendix A, the Green’s functions are obtained from:

$$\dot{G}_L(\epsilon, t|\epsilon_0) = -[\Gamma_L(\epsilon) + \kappa(\epsilon)] G_L(\epsilon, t|\epsilon_0) + c_L \int d\epsilon'\kappa(\epsilon|\epsilon')G_L(\epsilon', t|\epsilon_0)$$  \hspace{1cm} (B.2)

where the reorientation rates $\Gamma_L(\epsilon)$ are given by

$$\Gamma_L(\epsilon) = [1 - P_L(\cos \Theta)] \Gamma(\epsilon)$$  \hspace{1cm} (B.3)

Additionally, I defined $c_L = 1$, if $\Lambda(\Omega|\Omega') = 1$ and $c_L = \delta_{L,0}$ if $\Lambda(\Omega|\Omega') = 1/(8\pi^2)$\cite{22}. As in the case of the energy landscape model, the relevant quantities are given by eqns.(A.6) if again it is assumed that there is no correlation initially.
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**Figure captions**

**Fig.1:**

**a:** The distribution of populations $p(\epsilon, t_w)$ as a function of free-energy $\epsilon$ for different values of the waiting time $t_w$ after a quench from $T = \infty$ to $T = 0.2\sigma$ (upper panel) ($t_w = 0, 10^{-15}, 10^{-13}, 10^{-11}, 10^{-9}, 10^{-7}, 10^{-5}, 10^{-3}, 10^{-1}, 10^2, 10^4$) and $T = 0.4\sigma$ (lower panel) ($t_w = 0, 10^{-5}, 10^{-3}, 10^{-1}, 10, 10^4$).

**b:** The mean value (upper panel), the width (middle panel) and the skewness (lower panel) of the distributions shown in (a). The skewness is defined as $\gamma_1(t_w) = \kappa_3(t_w)/\kappa_2(t_w)^{3/2}$ where $\kappa_2$ and $\kappa_3$ are the time-dependent cumulants.

**Fig.2:**

**a:** The intermediate scattering function in equilibrium ($t_w \to \infty$) for $T = 0.3\sigma$ and different values of the reduced scattering vector $Q = q \cdot \delta R$.

**b:** Results of fits to a Kohlrausch function ($\exp(-t/\tau_Q)^{\beta_Q}$) at $T = 0.3\sigma$ as a function of $Q$. It is evident that $Q^2 \tau_Q = const.$ and $\beta_Q = 1$ holds only for small $Q$. 

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c: The parameters \( \tau_Q \) (upper panel) and \( \beta_Q \) (lower panel) as a function of temperature. The values of \( \tau_Q \) are scaled to their value at \( T = 0.9\sigma \), \( \tau_Q(T)_{\text{scaled}} = \frac{\tau_Q(T)}{\tau_Q(0.9)} \).

**Fig.3:**

a: \( S_Q(t_w + \tau, t_w) \) and \( g_1(t_w + \tau, t_w) \) versus \( \tau_{\text{scaled}} = (\tau/\tau_Q) \) and \( \tau_{\text{scaled}} = (\tau/\tau_1) \), respectively. Both panels show the correlation functions for reduced \( t_w = 10^{-7}, 10^{-1}, 1, 10, 10^6 \tau_Q(\tau_1) \). For the longest waiting time, the system has reached equilibrium.

b: Results of Kohlrausch fits to \( S_Q(t_w + \tau, t_w) \) and \( g_1(t_w + \tau, t_w) \) as a function of the waiting time.

c: The time scales \( \tau_Q(t_w) \) and \( \tau_1(t_w) \) versus \( t_w \) are shown in a scaled way such that \( \tau_x(0) = 0 \) and \( \tau_x(\infty) = 1 \) for \( x = Q, 1 \).

d: The re-equilibration time, i.e. the time needed for the correlation time to reach its equilibrium value. The values of \( \tau_{eq} \) are determined as the \( (1 - 1/e) \)-values of the curves shown in part (c).

**Fig.4:** The rotational correlation time \( \tau_1(t_w) \) versus \( (t_w/\tau_1) \) for the exchange model showing that for \( x = 10^3 \) the re-equilibration takes much longer than the rotational correlation time.
G. Diezemann, Fig. 1a
G. Diezemann, Fig. 1b
G. Diezemann, Fig.2a
G. Diezemann, Fig.2b
G. Diezemann, Fig.2c
G. Diezemann, Fig.3a
G. Diezemann, Fig.3b
\[ \tau_Q(t_w), \tau_1(t_w) \]

\[ (t_w / \tau_Q), (t_w / \tau_1) \]

G. Diezemann, Fig.3c
G. Diezemann, Fig. 4