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Information content of multitime correlation functions for the interpretation of structural relaxation in glass-forming systems

Andreas Heuer
Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

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In recent experiments four-time correlation functions have been systematically measured for a polymer near the glass transition via methods of multidimensional NMR [A. Heuer *et al.*, Phys. Rev. Lett. **75**, 2851 (1995)]. In this paper a theoretical analysis of the information content of multitime correlation functions is presented. Having in mind a heterogeneous distribution of relaxation rates, it is demonstrated that multitime correlation functions contain information about temporal fluctuations within the heterogenous distribution. If the relaxation rate distribution is bimodal, the additional information content of the four-time correlation function as compared to the two-time correlation function is given by the exchange rate between both dynamical states. More generally, for arbitrary rate distributions the additional information content of multitime correlation functions can be, to a good approximation, expressed by a single dimensionless parameter Q. This parameter is a measure for the fluctuations within the heterogeneous distribution. It is denoted *rate memory parameter*. It is argued that its value is related to the cooperativity of the dynamics. [S1063-651X(97)08307-4]

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I. INTRODUCTION

The glass transition is often characterized by properties of two-time correlation functions such as the density-density correlation function $\langle f(t_0,t_1)\rangle$ with $f(t_0,t_1) = \cos\{k[x(t_0)-x(t_1)]\}$ [1,2] where $\mathbf{x}(t)$ denotes the positions of the individual molecules at time t and the angular brackets denote the ensemble average. The rate distribution of the α relaxation, which may have a width of several decades, can be extracted from such observables. The properties of this rate distribution have been analyzed extensively [3,4]. In NMR experiments one often uses $f(t_0,t_1)=\cos\{t_p \times[\omega(t_0)-\omega(t_1)]\}$ where t_p is an experimentally adjustable time and $\omega(t)$ the angular-dependent NMR frequency at time t [5]. The corresponding correlation function is sensitive to the reorientational rather than the translational dynamics. In this paper we deal with general correlation functions fulfilling $f(t_0,t_0)=1$ and $\lim_{t_1\to\infty} f(t_0,t_1)=0$.

Recently, experiments have been designed to answer the question on which time scale the mobility of some tagged molecule changes. Since the mobility is determined by the local environment of this molecule, knowledge of this time scale allows us to learn something about typical structural rearrangements on a local scale. Of course, it is interesting to compare this time scale with the time scale on which the tagged molecule relaxes. Here we specifically refer to multidimensional NMR experiments. [6–10]. With this experiment one can determine the four-time correlation functions of the type $\langle f(t_0,t_1)f(t_2,t_3)\rangle$ with four successive times t_i and time intervals $\Delta t_1 \equiv t_1 - t_0$, $\Delta t_2 \equiv t_2 - t_1$, and $\Delta t_3 \equiv t_3 - t_2$. Intuitively, the information content of the four-time correlation function can be described as follows. Let us assume that the two-time correlation function displays nonexponential decay with time and that this nonexponentiality is due to a heterogeneous distribution of relaxation rates in the system [11–13]. Then $\langle f(t_0,t_1)\rangle$ can be viewed as a slow-dynamics filter. Only those subsystems pass that during Δt_1 do not move significantly. Accordingly, only those subsystems pass the double filter $\langle f(t_0,t_1)f(t_2,t_3)\rangle$ that are slow during Δt_1 and Δt_3. Hence, during Δt_1 a slow subensemble is selected that, after waiting for some time Δt_2, is analyzed by the final slow-dynamics filter. Intuitively, one expects that for small values of Δt_2 the majority of the slow subensemble will pass the final filter since the subensemble will keep its slowness for some finite time. However, for very large values of the Δt_2 for reasons of ergodicity the slow subensemble will behave like the full ensemble. This means that in the meantime many particles became fast and hence do not pass the final filter. The situation for some intermediate time Δt_2 is shown in Fig. 1. Therefore, one expects that with increasing Δt_2 and fixed Δt_1 and Δt_3 the correlation function $\langle f(t_0,t_1)f(t_2,t_3)\rangle$ decreases from some starting value to some lower final value, which is given by $\langle f(t_0,t_1)\rangle\langle f(t_2,t_3)\rangle$. The crossover between both limiting values describes after which time a typical element of the slow subensemble "forgets" its dynamical history. The basic idea of the NMR experiment, i.e., the selection of a subensemble and observing its route towards equilibrium has

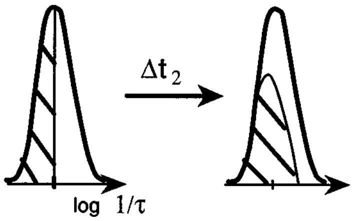

FIG. 1. Sketch of the idea behind the rate memory, which is connected to the time scale Δt_2 on which the selected slow ensemble equilibrates.

been in the meantime also realized by different experimental methods (e.g., photobleaching [14–17] and dielectrics [18]).

Of course, the determination of four-time correlation functions is not restricted only to NMR experiments. As discussed in [13], they can be easily implemented also in computer simulations, yielding so far unknown information about the fluctuations within the heterogeneous rate distribution.

The goal of the present paper is to analyze the information content of the four-time correlation function from a more formal point of view. From the above intuitive description of the four-time correlation function it is clear that this function contains information about a *rate memory*. This term will get a strict meaning during the course of the present analysis. The theoretical results are applied to the case of NMR correlation functions in the following paper [19].

We briefly mention that nonexponential relaxation in time does not automatically indicate the existence of a *heterogeneous* distribution of relaxation rates. Rather it can in principle also be explained by intrinsic non-exponential relaxation (*homogeneous* case). In general one expects that both contributions are present; see the recent Ref. [13] for an extensive discussion. Homogeneous contributions can be uniquely related to the existence of correlated back-and-forth jumps. It is evident that the selection of a slow subensemble as observed in the above NMR experiment is possible only if some heterogeneous contributions are present.

The present problem is very different from the Siegert relation [20,21], which relates the intensity correlation function, a four-particle function, and the intermediate scattering function, a two-particle function. There it turns out that for large scattering volumes the four-particle function can be calculated from the knowledge of the two-particle function. Hence it does not contain additional information.

In Sec. II we develop an appropriate formalism for the description of the correlation functions of interest. Furthermore, we introduce a simple dynamical model together with a specific $f(t_0,t_1)$ correlation function. The subsequent analysis of multitime correlation functions is then performed in the language of this model. However, as will become clear later on, all formal results hold beyond this model. In Sec. III we calculate the relevant four-time correlation function for a bimodal distribution of relaxation rates (*two-state approximation*). Apart from relaxation processes, fluctuations between the fast and the slow state with some *exchange* rate are taken into account. The two-state approximation is analogous to the Beckert-Pfeifer model [22,23]. In Sec. IV we develop a more general approach that allows us to treat a general distribution of relaxation rates. We show that it is possible to define the limits of *minimum* and *maximum rate memory* and to express multitime correlation functions in terms of the two-time correlation function for both limits. This property allows us to introduce a dimensionless rate memory parameter Q that appropriately interpolates between both extreme limits. It is demonstrated that within this theoretical framework the additional information of the four-time correlation function as compared to the two-time correlation function can be expressed by this parameter Q. In Sec. V it is shown that for a bimodal distribution of relaxation rates this interpolation is exact. Section VI contains a discussion and a summary. Among other things, a tentative physical interpretation of the rate memory parameter Q is given.

II. FORMULATION OF THE PROBLEM

A. Formal description of the correlation function

First we introduce a convenient formalism for describing multitime correlation functions. Let us consider $N+1$ subsequent times $t_i (i=0,\ldots,N)$ and a correlation function $\langle f(t_{j_1-1},t_{j_1})\cdots f(t_{j_M-1},t_{j_M})\rangle$ containing M factors $f(t_{j_m-1},t_{j_m})$ with $j_m\in\{1,\ldots,N\}$. All time intervals $[t_{n-1},t_n]$ for which the correlation function contains an f factor are labeled by "0" and all other time intervals by "?." We introduce the notation $p(i_1,\ldots,i_N;\Delta t_1,\ldots,\Delta t_N)$ as an abbreviation of the above correlation function. The $i_n\in\{0,?\}$ denote the labels of the respective time interval $[t_{n-1},t_n]$ and $\Delta t_n=t_n-t_{n-1}$. For example, we have $\langle f(t_0,t_1)\rangle = p(0;\Delta t_1)$ and $\langle f(t_0,t_1)f(t_2,t_3)\rangle = p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)$.

We can immediately formulate three trivial rules for the p's that directly follow from their definition:

$$p(i_1,\ldots,i_{N-1},?;\Delta t_1,\ldots,\Delta t_{N-1},\Delta t_N) = p(i_1,\ldots,i_{N-1};\Delta t_1,\ldots,\Delta t_{N-1}), \tag{1}$$

$$p(?,i_2,\ldots,i_N;\Delta t_1,\Delta t_2,\ldots,\Delta t_N) = p(i_2,\ldots,i_N;\Delta t_2,\ldots,\Delta t_N), \tag{2}$$

and

$$p(i_1,\ldots,?,?,\ldots,i_N;\Delta t_1,\ldots,\Delta t_{n-1},\Delta t_n,\ldots,\Delta t_N) = p(i_1,\ldots,?,\ldots,i_N;\Delta t_1,\ldots,\Delta t_{n-1}+\Delta t_n,\ldots,\Delta t_N). \tag{3}$$

They will be used for our subsequent analysis. Finally we introduce the index "1" via

$$p(i_1,\ldots,1,\ldots,i_N;\Delta t_1,\ldots,\Delta t_n,\ldots,\Delta t_N) \equiv p(i_1,\ldots,?,\ldots,i_N;\Delta t_1,\ldots,\Delta t_n,\ldots,\Delta t_N) - p(i_1,\ldots,0,\ldots,i_N;\Delta t_1,\ldots,\Delta t_n,\ldots,\Delta t_N). \tag{4}$$

A time interval with $i_n=?$ and $1<n<N$ is called the *waiting time*.

B. Simple dynamical model

Now we specify a dynamical model system and an appropriate correlation function $f(t_0,t_1)$. However, this is only for the sake of clarity. Later on we will argue that the results of this paper are independent of these specifications and can be generalized to arbitrary $f(t_0,t_1)$ and to arbitrary underlying dynamics.

The model is defined as follows. We consider an ensemble of units that can orient along M different orientations $m=1,\ldots,M$ $(M\to\infty)$. The dynamical state of a unit is defined by its present reorientation rate, which, however, may vary with time. Furthermore, we define $f(t_0,t_1) \equiv \delta(m(t_0),m(t_1))$. This function is 1 if the orientation is identical at t_0 and t_1 and 0 else. Furthermore, we assume that a unit randomly selects the new orientation after a reorientation process. Since we have chosen $M\rightarrow\infty$, this implies that a unit that started at orientation m_0 will revisit the same orientation only in the limit of infinite time (*random jump model*). Thus there are no units reorienting from m_0 to m_1 during Δt_{n-1} and reorienting back during Δt_n. Formally this can be expressed as

$$p(i_1,\ldots,0,0,\ldots,i_N;\Delta t_1,\ldots,\Delta t_{n-1},\Delta t_n,\ldots,\Delta t_N) \\ = p(i_1,\ldots,0,\ldots,i_N;\Delta t_1,\ldots,\Delta t_{n-1}+\Delta t_n,\ldots,\Delta t_N). \tag{5}$$

For this model the p's can be simply interpreted as probability functions. For example, $p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)$ denotes the probability that a unit does not reorient during Δt_1 and Δt_3. It does not matter whether or not a reorientation takes place during Δt_2. This motivates the use of the symbol "?." In contrast, the probability $p(0,1,0;\Delta t_1,\Delta t_2,\Delta t_3)$ additionally requires that a unit does reorient during Δt_2.

For this model homogeneous contributions may be introduced by a finite probability for correlated back-and-forth jumps, hence by a finite *orientational memory*. One can easily see that the presence of small homogeneous contributions violates Eq. (5). Actually, also beyond this specific model Eq. (5) can be regarded as a condition for purely heterogeneous relaxation [13]. For example, also for purely diffusive dynamics Eq. (5) holds and violation of this equation then indicates some correlation of the direction of motion during two subsequent time intervals [13]. Hence, for many applications one may indeed assume the validity of Eq. (5) to a very good approximation. However, in order to be as strict as possible, the case of finite homogeneous contributions will be considered too.

C. Final description of the problem

We distinguish two classes of correlation functions. To the first class belong correlation functions that contain at least one waiting time. An important member of this class is $p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)$. These correlation functions contain information about the rate memory. To the second class of correlation functions belong $p(0,\Delta t_1),p(0,0;\Delta t_1,\Delta t_2),\ldots$, which in the limit of heterogeneous relaxation can all be expressed by the two-time correlation function $p(0;\Delta t_1)$; see Eq. (5).

Now the general question can be formulated as follows: What is the additional information content of correlation functions of the first class if all correlation functions of the second class are known? For the heterogeneous limit this question reduces to analyzing $p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)$ for given correlation function $p(0;t)$ known for all t.

III. SOLUTION FOR A BIMODAL REORIENTATION RATE DISTRIBUTION

A. Definition of the parameters

Here we analyze the simplest case of nonexponential relaxation where the rate distribution of reorientation rates is bimodal and the present state of the unit is fully described by its reorientation rate $k_i (i=1,2)$ (*two-state approximation*). For some specific limits results can be already found in [9,23]. In this section we neglect the possible presence of homogeneous contributions. We choose the reorientation rates such that $k_1<k_2$. The statistical weights of both states will be denoted as a_i. Since the dynamical state of a unit is fully characterized by its present reorientation rate, the time evolution of the system can be described as a Markov process [25].

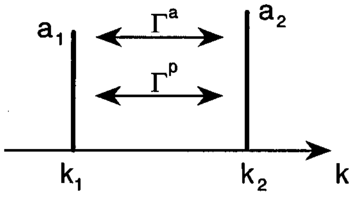

FIG. 2. Schematic representation of the reorientation and exchange rates used for the definition of the two-state system.

Before calculating the time evolution we have to specify the exchange processes between both states. In general the reorientation rate of a unit is sensitive to the local structure. Let us consider one selected unit. We may distinguish two cases. First, it is possible that due to reorientation processes of adjacent units the local structure and hence the reorientation rate of the selected unit change. We use the term *passive exchange*. Second, a reorientation process of the selected unit itself may trigger the change in local structure so that after the reorientation process the reorientation rate has changed. For obvious reasons we call this scenario *active exchange*.

We distinguish both exchange mechanisms by introducing individual exchange rates $\Gamma_{ij}^p=\Gamma^p/2a_i$ and $\Gamma_{ij}^a=\Gamma^a/2a_i$ for transitions from state i to state j, respectively. The choice of the denominators guarantees detailed balance. The total exchange rate Γ_{ij} is defined as $\Gamma_{ij}\equiv\Gamma_{ij}^p+\Gamma_{ij}^a$. The parameters entering the two-state approximation are sketched in Fig. 2. This approximation is analogous to the two-state model as described by Beckert and Pfeifer [22–24].

For given k_i and a_i the value of Γ^a is limited by the condition that an active exchange process has to be connected with a reorientation process. Hence $\Gamma_{ij}^a\leqslant k_i$, which yields $\Gamma^a\leqslant\Gamma^{a,\max}\equiv\min(2k_1a_1,2k_2a_2)$. In contrast to Γ^a, the value of Γ^p is not limited *a priori* (however, see also Sec. III B).

B. Rate equations and their solution

Now we want to determine how the populations $u_i(t)$ of both states change during a time interval, starting at $t=t_0$. We have to specify whether the index of the correlation functions for this time interval is 0 or ?. Hence we have to consider two different kinds of rate equations. Let us first assume that the experiment is sensitive to reorientations, corresponding to the index 0. Then the time evolution of $u_i(t)$ is described by

$$\frac{\partial}{\partial t}u_1=-k_1u_1+\Gamma^p\left(\frac{u_2}{2a_2}-\frac{u_1}{2a_1}\right), \tag{6}$$

$$\frac{\partial}{\partial t}u_2=-k_2u_2+\Gamma^p\left(\frac{u_1}{2a_1}-\frac{u_2}{2a_2}\right). \tag{7}$$

The terms proportional to k_i express that after one reorientation process a unit no longer contributes to the populations under consideration. Exchange processes between u_1 and u_2 can occur only via passive exchange since by definition the units belonging to u_i have not reoriented since $t=t_0$. The general solution may be written as $u_i(t_0+t)=X_{ij}(t)u_j(t_0)$, where we used the standard Einstein sum convention. The propagators $X_{ij}(t)$ can be obtained analytically from diagonalization of the two-dimensional matrix

$$\begin{pmatrix} -k_1-\Gamma^p/2a_1 & \Gamma^p/2a_2 \\ \Gamma^p/2a_1 & -k_2-\Gamma^p/2a_2 \end{pmatrix}. \tag{8}$$

Now we can calculate $p(0;t)$, which formally is given by $\Sigma_i u_i(t_0+t)$. On the basis of the X_{ij} this term can be written as $\Sigma_{i,j}X_{ij}(t)u_j(t_0)=\Sigma_{i,j}X_{ij}(t)a_j$. Here we used that at $t=t_0$ a fraction of $u_j(t_0)=a_j$ units are in state j.

The general solution reads

$$p(0;t)=\alpha_1\exp(-\kappa_1 t)+\alpha_2\exp(-\kappa_2 t). \tag{9}$$

For $\Gamma^p=0$ we trivially have $a_i=\alpha_i$ and $k_i=\kappa_i$. For $\Gamma^p>0$ diagonalization of the above matrix approximately yields $\kappa_i\approx k_i+\Gamma^p/2a_i$. The amplitudes α_i can be determined from the eigenvectors. The κ_i can be interpreted as effective reorientation rates. Typically, a unit that is slow at a given time reorients faster than expected from its rate k_1. The reason is that it may switch to the fast state very soon and then reorient much faster, yielding an effective $\kappa_1>k_1$. Note that $\kappa_1\approx k_1+\Gamma^p/2a_1$ implies $\Gamma^p/2a_1\leqslant\kappa_1$.

For the calculation of $p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)$ it is also necessary to determine the time evolution during a time interval that is not sensitive to reorientations (a waiting time). During this time interval the evolution is governed by the rate equations

$$\begin{aligned}\frac{\partial}{\partial t}u_1=\Gamma\left(\frac{u_2}{2a_2}-\frac{u_1}{2a_1}\right)\frac{\partial}{\partial t}u_2 \\ =\Gamma\left(\frac{u_1}{2a_1}-\frac{u_2}{2a_2}\right).\end{aligned} \tag{10}$$

Here the exchange is due to active as well as passive exchange processes. The solution can be written as $u_i(t_0+t)=Z_{ij}(t)u_j(t_0)$, with

$$Z_{11}(t)=a_1+a_2\exp[-(\Gamma_{12}+\Gamma_{21})t], \tag{11}$$

$$Z_{12}(t)=a_1-a_1\exp[-(\Gamma_{12}+\Gamma_{21})t]. \tag{12}$$

Analogous equations hold for $Z_{21}(t)$ and $Z_{22}(t)$. For finite Γ and large t we always obtain the equilibrium populations $u_i(t_0+t)\propto a_i$ independent of the initial values $u_i(t_0)$.

For an explicit calculation of $p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)$ the time evolution of the units during three subsequent time intervals has to be considered. During Δt_1 and Δt_3 reorientation as well as exchange processes have to be taken into account (expressed by the propagator X_{ij}), whereas during the second mixing time only exchange processes are relevant (expressed by Z_{ij}). Hence

$$\begin{aligned}p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)&=\sum_i u_i(t_3)\\ &=\sum_{i,j,k,l}X_{ij}(\Delta t_3)Z_{jk}(\Delta t_2)X_{kl}(\Delta t_1)a_l.\end{aligned} \tag{13}$$

From the structure of the general formula one can immediately conclude

$$\begin{aligned}p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)=c_\infty\{1-\exp[-(\Gamma_{12}+\Gamma_{21})\Delta t_2]\}\\ +c_0\exp[-(\Gamma_{12}+\Gamma_{21})\Delta t_2],\end{aligned} \tag{14}$$

with $c_0=p(0,?,0;\Delta t_1,\Delta t_2=0,\Delta t_3)$ and $c_\infty=p(0,?,0;\Delta t_1,\Delta t_2\to\infty,\Delta t_3)$. Direct calculation of c_0 and c_∞ is straightforward but very tedious. Fortunately, their values can be fixed by a simple argument. Due to Eq. (5) we can immediately write $c_0=p(0,0;\Delta t_1,\Delta t_3)=p(0;\Delta t_1+\Delta t_3)$. In the opposite limit $t_{m2}\to\infty$ we know that in the case of finite exchange rates the four-time correlation function can be factorized according to $p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)=p(0;\Delta t_1)p(0;\Delta t_3)$ so that

$$c_\infty=p(0;\Delta t_1)p(0;\Delta t_3). \tag{15}$$

In summary, we have shown that it is possible to express $p(0,?,0;\Delta t_1,\Delta t_2,\Delta t_3)$ in terms of $p(0;t)$ and $\Gamma_{12}+\Gamma_{21}$. In accordance with intuition, the four-time correlation function contains the information about the exchange processes and hence about the rate memory.

IV. GENERAL APPROACH TO THE RATE MEMORY

Our general task is to evaluate the information content of $p(0,?,0;t_{m0},t_{m2},t_{m0})$ as a typical member of the first class of correlation functions for the given set of correlation functions belonging to the second class of correlation functions (see Sec. II C). Here we use the notation t_{mi} instead of Δt_i in order to be consistent with the notation within the NMR literature. There the time intervals t_{mi} are also denoted *mixing times*.

We first consider the heterogeneous limit, expressed by Eq. (5). It is evident that from the application of Eqs. (1)–(3) and (5), $p(0,?,0;t_{m0},t_{m2},t_{m0})$ cannot be expressed in terms of $p(0;t)$. Intuitively this is clear since $p(0;t)$ does not contain direct information about possible exchange processes.

For reasons that will become clear further below we split the t_{mi} in small time intervals of length Δt. According to Eqs. (1)–(3) and (5), $p(0,?,0;t_{m0},t_{m2},t_{m0})$ may be rewritten as $p(0,\ldots,0,?,\ldots,?,0,\ldots,0;\Delta t,\ldots,\Delta t)$. In what follows Δt is chosen much smaller than any time scale involved in the reorientation and exchange processes. In order to be as general as possible we analyze the functions $p(i_1,\ldots,i_N;\Delta t,\ldots,\Delta t)$ with $i_n\in\{0,1,?\}$ from now on. Whenever the time intervals are of length Δt they will be omitted for simplicity, e.g., $p(1;\Delta t)=p(1)$.

A. Minimum and maximum rate memory

The first step of our general analysis is to define some reasonable physical limits for which multitime correlation functions can be directly expressed in terms of the two-time correlation function. We have already seen from the analysis of the two-state approximation that there exists a maximum exchange rate Γ that is of the order of the effective slow reorientation rate κ_1. Hence the time for which a slow unit ''remembers'' that it is slow is at least of the order of $1/\kappa_1$. We show that a limit of *minimum rate memory* can be strictly formulated in the general case.

Let us assume for a moment that it is possible to monitor the time evolution of the orientation of an individual unit. The question arises whether it is possible to predict the dynamical behavior of this unit during the next time step Δt on the basis of its previous behavior during the time of the experiment $t_{\rm expt}$ for given $p(0;t)$. The most simple case is that during $t_{\rm expt}$ no reorientation process has been observed. Then the probability p_r that the unit reorients during the next time step Δt is given by $p_r = [p(0;t_{\rm expt}) - p(0;t_{\rm expt} + \Delta t)]/p(0;t_{\rm expt})$, which for a Kohlrausch function $p(0;t) = \exp[-(t/\tau_0)^\beta]$ is given by

$$p_r(t_{\rm expt}) = \beta \Delta t (\tau_0/t_{\rm expt})^{1-\beta}. \tag{16}$$

We see that apart from the trivial case $\beta = 1$ the estimated future behavior depends on the experimental time $t_{\rm expt}$. Now let us assume that during the experimental time at least one reorientation process has occurred. Let the time since the last reorientation process be called t_r. If by chance $t_{\rm expt}$ is equal to t_r, the probability p_r depends on t_r as expressed by Eq. (16). The estimation of p_r becomes ambiguous if $t_{\rm expt} > t_r$. The additional information about the properties before the final reorientation process may influence the estimation of p_r in an *a apriori* unknown way. The condition that our estimation has to be consistent with $p(0;t)$ is not sufficient to remove this ambiguity, but only requires that p_r depends on t_r. This leads to define the limit of *minimum rate memory*. We require that the time correlations are as short as possible. In the special case mentioned above this simply means that no correlations to times before the final reorientation process exist. Stated differently, after a reorientation process no information about the dynamical history remains. This scenario is, for example, implemented in the well-known continuous time random-walk models. In these models the walker randomly chooses a new waiting time after a jump process [26].

This intuitive definition can be easily formalized. Let a reorientation process occur during the nth time interval for some given dynamical history $i_1, \ldots, i_{n-1}$. In the limit of minimum rate memory the probability that the dynamical future can be described by the sequence $i_{n+1}, \ldots, i_N$ is independent of the properties before the nth time interval. Formally this condition is expressed as

$$\frac{p(\ldots, i_{n-1}, i_n = 1, i_{n+1}, \ldots)}{p(\ldots, i_{n-1}, i_n = 1)} = \frac{p(i_n = 1, i_{n+1}, \ldots)}{p(i_n = 1)}, \tag{17}$$

which for future purposes is rewritten as

$$p(\ldots, i_{n-1}, i_n = 1, i_{n+1}, \ldots) = p(\ldots, i_{n-1}, i_n = 1)\, p(i_n = 1, i_{n+1}, \ldots)/p(i_n = 1). \tag{18}$$

In order to define the minimum rate memory it is necessary to localize the reorientation process, i.e., the value of t_r, as precisely as possible. This is the reason why the time axis has to be split in very short time intervals Δt.

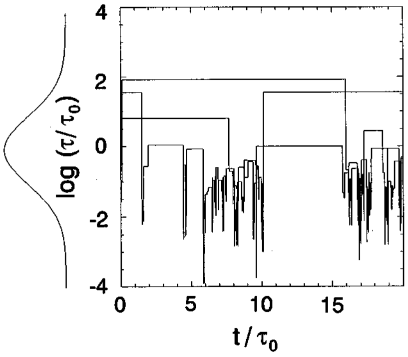

FIG. 3. Time evolution of the dynamical state of three randomly selected units with time in the limit of minimum rate memory. The equilibrium distribution of reorientation rates is chosen as a log-Gaussian distribution, centered around τ_0. It is sketched on the left-hand side. After every reorientation process the new reorientation rate is chosen randomly with appropriate probabilities in order to guarantee the equivalence of time and ensemble average.

As a simple example we analyze $p(0,?,0) = p(0,0,0) + p(0,1,0)$. From Eq. (18) we obtain $p(0,1,0) = p(0,1)p(1,0)/p(1)$. Since $p(0,1) = p(0,?) - p(0,0) = p(0) - p(0,0), p(1) = p(?) - p(0) = 1 - p(0)$ and using Eq. (5) we may finally write $p(0,?,0;\Delta t,\Delta t,\Delta t) = p(0;3\Delta t) + [(p(0;\Delta t) - p(0;2\Delta t)]^2/[1 - p(0;\Delta t)]$. Hence $p(0,?,0;\Delta t,\Delta t,\Delta t)$ can be expressed solely on the basis of $p(0;t)$. Analogous arguments hold for general probablity functions $p(i_1, \ldots, i_N)$, which can be evaluated by successive application of Eq. (18). Hence, in the limit of minimum rate memory $p(0,?,0;t_{m0},t_{m2},t_{m0})$ can be expressed in terms of $p(0;t)$ in a nontrivial way. The final expression contains terms $p(0;n\Delta t)$ for all values of $n \le N$. Hence, for $N \to \infty$ correlations of infinite length are involved. This feature is essential for taking into account the nonexponentiality of $p(0;t)$ as expressed by $\beta < 1$.

In order to visualize the limit of minimum rate memory we calculated the time evolution of individual units for which after all reorientation processes the new reorientation rate is selected *randomly* from the overall rate distribution. A random choice means that the probability after a reorientation process to have the rate k_i is proportional to $a_i k_i$, independent of the previous rate. The proportionality to the statistical weights a_i is obvious. The factor k_i takes into account that a unit in a fast state reorients more often so that a fast state has to be repopulated more frequently than a slow state in order to guarantee detailed balance. The time of the reorientation processes and the new reorientation rates have been determined via a random-number generator. For three different units the time evolution is shown in Fig. 3. One can clearly see that on average a slow unit is fast after a single reorientation process, whereas a fast unit remains fast during many reorientation processes. Note that, on average, half of the time the unit is slow ($\tau > \tau_0$), which simply means that the time average is identical to the ensemble average.

Next we discuss the limit of *maximum rate memory*. Intuitively one requires that a selected unit keeps its dynamical properties forever. In the above two-state approximation this corresponds to $\Gamma = 0$. Hence, in the limit of maximum rate memory $p(0,?,0;t_{m0},t_{m2},t_{m0})$ is independent of t_{m2} so that $p(0,?,0;t_{m0},t_{m2},t_{m0}) = p(0,?,0;t_{m0},0,t_{m0}) = p(0,0;t_{m0},t_{m0})$. More generally this reads

$$p(\ldots,i_{n-1},i_n=?,i_{n+1},\ldots) = p(\ldots,i_{n-1},i_{n+1},\ldots), \tag{19}$$

which may be reformulated as

$$\begin{aligned} p(\ldots,i_{n-1},i_n=1,i_{n+1},\ldots) &= p(\ldots,i_{n-1},i_{n+1},\ldots) \\ &\quad - p(\ldots,i_{n-1},i_n=0,i_{n+1},\ldots). \end{aligned} \tag{20}$$

Successive application of Eq. (20) again fully determines the value of $p(i_1,\ldots,i_N)$ for a given correlation function $p(0;t)$.

We would like to stress that both limits can be defined without referring to the special interpretation of the correlation functions as probability functions. From a formal point of view the limit of minimum rate memory corresponds to a maximum number of factorizations of the correlation function. The correlations are as short as possible, but are still consistent with the given non-exponential two-time correlation function. Any further factorization would automatically be inconsistent with the given $p(0;t)$. Also the introduction of the maximum rate memory is sufficiently general to hold beyond the idealized picture of reorientational dynamics.

B. Intermediate rate memory

For the definition of an intermediate rate memory one assumes that after a single reorientation process a unit with probability $p_{\min}$ randomly (see above for its precise meaning) selects a new reorientation rate (minimum rate memory) and with probability $p_{\max} = 1 - p_{\min}$ keeps its old reorientation rate (maximum rate memory). Of course, in general this is only an approximation of the real behavior. We introduce the dimensionless parameter $Q = 1/P_{\min}$. It denotes the average number of relaxation processes after which a unit has forgotten its initial dynamical state. From Eqs. (18) and (20) we can write

$$\begin{aligned} p(\ldots,i_{n-1},1,i_{n+1},\ldots) &= (1/Q)p(\ldots,i_{n-1},1)p(1,i_{n+1},\ldots)/p(1) \\ &\quad + (1-1/Q)[p(\ldots,i_{n-1},i_{n+1},\ldots) \\ &\quad - p(\ldots,i_{n-1},0,i_{n+1},\ldots)]. \end{aligned} \tag{21}$$

It will be clarified further below under which conditions the introduction of a single parameter is exact. After successive application of Eq. (21) $p(i_1,\ldots,i_N)$ can be expressed in terms of $p(0;n\Delta t)$ with $n \leq N$.

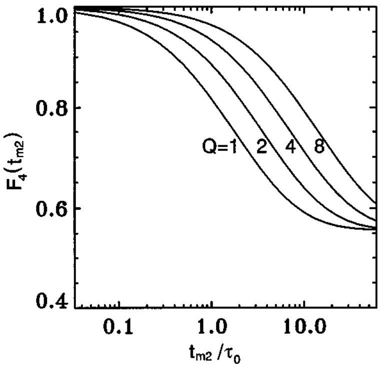

FIG. 4. Dependence of $F_4(t_{m2})$ on Q for $\beta = 0.5$. Note the approximate scaling of t_{m2} with Q.

Now we are in a position to calculate $p(0,?,0;t_{m0},t_{m2},t_{m0})$ for a given value of Q. As before we assume $p(0;t) = \exp[-(t/\tau_0)^\beta]$. In order to apply Eq. (21) for the calculation of $p(0,?,0;t_{m0},t_{m2},t_{m0})$ we discretize t_{m2} in R time intervals Δt much smaller than τ_0, yielding $p(0,?,\ldots,?,0;t_{m0},\Delta t,\ldots,\Delta t,t_{m0})$. This expression is an abbreviation for a sum of 2^R terms if all indices ? are written as a sum over 0 and 1. Therefore, the number of terms that have to be calculated exponentially increases with t_{m2} so that a direct numerical evaluation by successive application of Eq. (21) cannot be extended to large values of t_{m2}. However, it is possible to devise a recursive algorithm that allows one to calculate $p(0,?,0;t_{m0},t_{m2},t_{m0})$ also for large values of t_{m2}. The algorithm is presented in Appendix A. For the numerical calculations below we choose $t_{m0} = \tau_0$.

In Fig. 4 we present calculations of $F_4(t_{m2}) \equiv p(0,?,0;t_{m0},t_{m2},t_{m0})/p(0,0;t_{m0},t_{m0})$ for $\beta = 0.5$ and different values of Q. One can clearly see that the dependence on Q can be approximated by scaling t_{m2} with $1/Q$.

For practical purposes it is unsatisfactory that $p(0,?,0;t_{m0},t_{m2},t_{m0})$ is not given by a simple analytical expression. Let us first consider $Q = 1$. In the limit $t_{m2} \to 0$ it is no longer necessary to divide the waiting time in smaller subunits, hence one may choose $R = 1$ and application of Eq. (18) yields

$$\begin{aligned} p(0,?,0;t_{m0},t_{m2},t_{m0}) &\approx p(0;2t_{m0}+t_{m2}) \\ &\quad + p(0,1,0;t_{m0},t_{m2},t_{m0}), \end{aligned} \tag{22}$$

with

$$p(0,1,0;t_{m0},t_{m2},t_{m0}) \approx \frac{[p(0;t_{m0}) - p(0;t_{m0}+t_{m2})]^2}{1 - p(0;t_{m2})}. \tag{23}$$

It is easy to check that also the limit $t_{m2} \to \infty$ is correctly reproduced, yielding $p(0;t_{m0})^2$. Therefore, one may hope that for all values of t_{m2} the choice $R = 1$ yields a reasonable approximation to the true solution. For $Q \neq 1$ an analogous application of Eq. (21) does not yield the correct limit for $t_{m2} \to \infty$. However, having in mind the above scaling relations, the probability functions for $Q \neq 1$ can be simply obtained by scaling t_{m2} with $1/Q$. Hence we may approximate

$$\begin{aligned} p(0,?,0;\tau_0,t_{m2},\tau_0) &\approx p(0;2\tau_0 + t_{m2}/Q) \\ &\quad + p(0,1,0;\tau_0,t_{m2}/Q,\tau_0), \end{aligned} \tag{24}$$

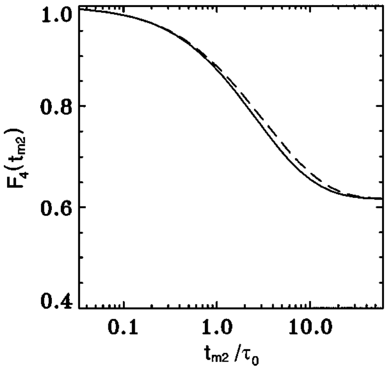

FIG. 5. Comparison of the exact result (solid line) for $F_4(t_{m2})$ with the approximate solution (dashed line) in Eq. (23) for $\beta=0.6$ and $Q=2$.

where the last term is approximated by Eq. (23). In Fig. 5 this approximate solution is plotted for $Q=2$ and $\beta=0.6$ together with the exact solution. Both curves agree within a few percent. Hence, for practical purposes it is sufficient to estimate $p(0,?,0;t_{m0},t_{m2},t_{m0})$ via Eqs. (23) and (24).

C. Generalization to the case of finite homogeneous contributions

We extensively used Eq. (5) in order to obtain the results presented above. For real systems and for arbitrary correlation functions this relation may be violated, because of a finite orientational memory. Then the correlation functions $p(0,0;\Delta t_1,\Delta t_2),p(0,0,0;\Delta t_1,\Delta t_2,\Delta t_3),\ldots$ can no longer be expressed via $p(0;\Delta t_1)$. For a strict calculation of $p(0,?,0;t_{m0},t_{m2},t_{m0})$ via successive application of Eq. (21) one has to know all $p(0,\ldots,0)$. In principle this strict calculation can be performed. However, two levels of approximation are possible. First Eq. (24) can be used in its generalized version

$$p(0,?,0;t_{m0},t_{m2},t_{m0})\approx p(0,0,0;t_{m0},t_{m2}/Q,t_{m0})+\frac{[p(0;t_{m0})-p(0,0;t_{m0},t_{m2}/Q)]^2}{1-p(0;t_{m2}/Q)}. \tag{25}$$

Here only the correlation functions $p(0;\Delta t_1)$, $p(0,0;\Delta t_1,\Delta t_2)$, and $p(0,0,0;\Delta t_1,\Delta t_2,\Delta t_3)$ are involved. Actually, this approximation has been used in the parallel work of Ref. [13], yielding very good agreement between simulated and estimated four-time correlation functions. A more drastic approximation is the direct use of Eq. (24) which for the analysis of experimental data may be the only feasible procedure.

V. RATE MEMORY DESCRIPTION VERSUS EXPLICIT SOLUTION OF RATE EQUATIONS

A. Two-state case

First we show that Eq. (21) can be reproduced on the basis of the rate equations of the two-state approximation. From this comparison Q can be expressed in terms of the parameters characterizing the two-state approximation (see Sec. III). *A priori* the equivalence of both approaches is not evident, mainly because two different exchange rates are included in the two-state model whereas the rate memory description only contains a single rate memory parameter Q.

Equation (21) describes the time evolution of the populations during the nth time interval. This may be compared with the explicit calculation on the basis of the two-state approximation. Since the time interval is infinitesimally small the calculation for the two-state approximation can be directly performed. The explicit calculation is deferred to Appendix B. It turns out that for the two-state approximation $p(0,?,0;t_{m0},t_{m2},t_{m0})$ is indeed fully characterized by a single parameter Q as introduced in Eq. (21). It is given by

$$Q=\frac{\Gamma^p+\gamma^a}{\Gamma^p+\Gamma^a}=\frac{\Gamma^p+\gamma^a}{\Gamma}, \tag{26}$$

with

$$(\gamma^a)^{-1}\equiv\frac{1}{2a_1k_1}+\frac{1}{2a_2k_2}. \tag{27}$$

Equation (26) connects the general description of the rate memory of Sec. IV with the strict calculation of the two-state approximation.

For $\Gamma^a=\gamma^a$ we get $Q=1$. Since this corresponds to the limit of minimum rate memory, for $\Gamma^a=\gamma^a$ a unit randomly selects a new reorientation rate after a reorientation process. This can be also shown explicitly. For a random choice of a new reorientation rate (see the discussion in Sec. III B) the probability p_i that the new reorientation rate is k_i must be proportional to a_ik_i, so that $p_1=a_1k_1/(a_1k_1+a_2k_2)$. Then the active exchange rate Γ_{21}^a from state 2 to state 1 is given by k_2p_1. From $\Gamma^a=2a_2\Gamma_{21}^a$ one directly obtains $\Gamma^a=\gamma^a$.

We briefly sketch a more intuitive derivation of Eq. (26). As already mentioned above, Eq. (21) expresses the fact that a fraction $1/Q$ of units that reorient during a given time interval forget their dynamical history, whereas the rest keeps its present rate. The exchange rate is given by $\Gamma=\Gamma^p+\Gamma^a$. This rate has to be smaller by a factor of Q as compared to the fictive value $\Gamma^p+\gamma^a$ of the total exchange rate for which every reorientation process would be connected with a loss of rate memory. Therefore, we expect $\Gamma^p+\gamma^a=Q\Gamma$, which is equivalent to Eq. (26).

Specializing to the limit $k_1\ll k_2$, Eq. (26) may be approximated as

$$Q=\frac{\Gamma^p+2a_1k_1}{\Gamma}\approx\frac{2a_1\kappa_1}{\Gamma}, \tag{28}$$

where we used $\Gamma^p/2a_1+k_1\approx\kappa_1$. Hence we obtain the interesting result that the relevant quantity that can be extracted from the four-time correlation function is the ratio of the *slow* effective reorientation rate and the exchange rate.

Surprisingly, Eq. (26) also shows that the minimum value of Q is smaller than one and is given by

$$Q_{\min}=\frac{\gamma^a}{\Gamma^{a,\max}}=\frac{1}{1+a_1k_1/k_2a_2}. \tag{29}$$

Here we assumed that $a_1k_1\leq a_2k_2$. If $\Gamma^a>\gamma^a$ the exchange among the two states as a consequence of a reorientation process is larger than in the case of a purely statistical redistribution. Hence we are in the regime of anti-correlations. From Eq. (29) one directly obtains $Q_{\min}>0.5$. It can be easily checked that a Kohlrausch law with $\beta=0.5$ can be very well approximated by a biexponential with $\alpha_1\approx\alpha_2$ and $\kappa_2/\kappa_1=13$. For $\alpha_1=\alpha_2$ one obtains $Q_{\min}\approx\kappa_2/(\kappa_2+\kappa_1)$, which for the example chosen above is 0.93 and hence very close to 1. Therefore in practice the relation $Q\geqslant1$ is approximately fulfilled and the regime of anticorrelation can be neglected. In any case, it is hard to think of a physical mechanism that should lead to such kinds of anticorrelations.

For the two-state approximation we may explicitly check the quality of the approximation (23) and (24). Choosing $\kappa_1\ll1/t_{m0}\ll\kappa_2$ and $\alpha_1=\alpha_2=1/2$, the exact solution can be written as $F_4(t_{m2})=(1/2)[1+\exp(-2\Gamma t_{m2})]$ [see Eq. (14)]. In contrast, after a short calculation the approximation (23) reads $F_4(t_{m2})=1/[2-\exp(-\kappa_s t_{m2}/Q)]=1/[2-\exp(-\Gamma t_{m2})]$. Both functions are very similar for all values of t_{m2}. However, this example also demonstrates that the exact solution of the two-state approximation can be obtained only if the time interval t_{m2} is split in many small time intervals and the four-time correlation function is calculated numerically along the lines described in Sec. IV.

B. General N-state case

First we clarify under which conditions our rate memory approach exactly describes a general N-state model. Performing a calculation in analogy to the calculation presented in Appendix B, it can be checked that exactly under the condition

$$\Gamma_{ij}^{a,p}\equiv\Gamma_c^{a,p}k_ia_jk_j/2, \tag{30}$$

with some constant Γ_c^a and Γ_c^p, the system can be described by a single rate memory parameter Q, which then is given by

$$Q=\frac{\Gamma_c^p+\gamma_c^a}{\Gamma_c^p+\Gamma_c^a}. \tag{31}$$

Here we defined

$$\gamma_c^a\equiv\frac{2}{\sum_i a_ik_i}. \tag{32}$$

Equation (30) simply means that units with longer reorientation rates keep their rates for a longer time. Note that for a two-state approximation one has to identify $\Gamma_c^{a,p}=\Gamma^{a,p}/a_1k_1a_2k_2$ and $(\gamma^a)^{-1}=(\gamma_c^a)^{-1}/a_1k_1a_2k_2$. It is easy to check that Eq. (31) then reduces to Eq. (26).

In the case that exchange processes are always connected with reorientation processes, i.e., in the limit of purely active exchange processes, the validity of Eq. (30) has the same simple interpretation as in the two-state case. On average a segment changes its rate after Q reorientation processes [Q given by Eq. (31)]. Here the limit of minimum rate memory simply means that every exchange process to an arbitrary new state comes together with a reorientation process. In real systems one might image that the new rate k_{new} after a reorientation process is still somewhat correlated with the old rate k_{old}. In this case the four-time correlation function F_4 may be approximated by some value $Q\geqslant1$, which now is a measure for the loss of dynamic memory by a single reorientation process. For $k_{\text{new}}\rightarrow k_{\text{old}}$ one would expect $Q\rightarrow\infty$, whereas the limit in which k_{new} is uncorrelated to k_{old} one recovers the minimum rate memory.

Even for the worst case, for which the exchange rates, passive as well as active, deviate from Eq. (30) in an arbitrary way, one can argue that the interpolation by a single parameter Q is still expected to be a good approximation. For a given value of t_{m0} the heterogeneous distribution can be formally split into two parts, defined by $k_i\leqslant1/t_{m0}$ and $k_i\geqslant1/t_{m0}$. The correlation function $p(0,?,0;t_{m0},t_{m2},t_{m0})$ is sensitive to exchange processes between the slow and the fast part and not to exchange processes within one part. Since the rate memory description is exact for a two-state case we expect that Eq. (24) is always a good approximation, independent of the validity of Eq. (30). This can be confirmed for a model system, for which Eq. (30) does not hold, but $p(0,?,0;t_{m0},t_{m2},t_{m0})$ can nevertheless be perfectly expressed via Eq. (24) [27]. Invalidation of Eq. (30) rather leads to a dependence of Q on the choice of t_{m0}. Experimentally, it turns out for ortho-terphenyl that this dependence is very small [10].

The arguments of the preceding paragraph might suggest that the crossover between both limiting regimes of the four-time correlation function can be described by a single rate; see Eq. (14). However, this is in disagreement with the actual calculation for a broad distribution of relaxation rates (see Fig. 4), showing significant nonexponential behavior. The reason is that in contrast to the two-state approximation, which was the basis for Eq. (14), the general approach takes into account that both regimes ($k_i\leqslant1/t_{m0}$ and $k_i\geqslant1/t_{m0}$) contain more than a single relaxation rate.

VI. DISCUSSION

It has been shown that the rate memory approach is appropriate to quantify the outcome of the four-time correlation function for a given two-time correlation function. The main advantages of this approach is that (i) the similarities of the mathematical structure of the two-time and multitime correlation functions are fully exploited, (ii) the analysis is free of any model assumptions and the value of Q has a simple physical interpretation, (iii) the role of the minimum rate memory $Q=1$ is clarified, (iv) there exist simple formulas that allow one to estimate the four-time correlation function for given two-time correlation function and rate memory parameter Q, and (v) homogeneous contributions can easily be taken into account. Alternatively, one can simultaneously analyze the two-time and the four-time correlation function by a special model involving reorientation rates k_i and exchange rates Γ_{ij} [10,23]. In order to keep the number of free parameters limited the exchange rates may be parametrized like, e.g., $\Gamma_{ij}=\Gamma_0(k_ik_j)^\alpha$ with some positive α. Using these rate equations, a simultaneous fit of the two-time and the four-time correlation function may be performed. However, all above-mentioned advantages of the Q-description get lost.

For example, the rate memory approach would predict that for a given two-time correlation function in the limit of large Γ_0 the numerical solution of the above model yields identical four-time correlation functions independent of the parameter α. This solution would be identical to the $Q=1$ curve. Without having analyzed the underlying structure of the present problem, this observation might come as a surprise. This also means that for $Q\approx 1$ a fit of the four-time correlation function does not discriminate between different choices for the Γ_{ij}. The situation changes for a situation where the rate memory parameter Q significantly depends on t_{m0}. Then the numerical solution of rate equations may indeed give some additional hints about the precise dependence of Γ_{ij} on k_i and k_j and hence about the nature of fluctuations within the heterogeneous distribution of relaxation rates.

The analysis of this work quantifies multitime correlation functions in the case of *dynamical* heterogeneities. The analysis breaks down for the case of *static* heterogeneities. A simple model is an ensemble of particles diffusing in a heterogeneous environment. For this example a description of the exchange in terms of constant rates is no longer possible. Rather the probability of an exchange process is related to the position of a particle. Hence the stochastic approach of this work inherent in Eq. (21) breaks down.

In order to link the formal analysis of this work with the physics of supercooled liquids we would like to give a tentative physical interpretation of Q. One expects that a strong interaction among different relaxation modes yields a large exchange rate and hence a small rate memory parameter. In contrast, for localized dynamics in fixed potentials one expects large values of Q. From NMR experiments on phenyl groups in polycarbonate it is known that the phenyl groups retain their individual flipping rate during a large number of flips [28]. Although a quantitative analysis of these experiments in terms of the Q parameter is not possible, one may estimate that the value of Q is at least of the order of 100. This clearly demonstrates that the value of Q is somewhat related to the locality of the dynamics. Whenever the dynamics is local, the dynamics occurs in a rather fixed potential that is constant for times much larger than the dynamical time scale. In contrast, the dynamics around the glass transition is very delocalized and is described by very small values of Q [9]. Hence we may tentatively say that Q is related to the cooperativity of the dynamics. As will be shown in elsewhere, this can be explicitly shown for a generalized Fredrickson model [27,29].

In summary, we have analyzed the information content of multitime correlation functions as compared to the standard two-time correlation function in the case of dynamic heterogeneities. The limits of minimum and maximum rate memory can be uniquely defined without any model assumptions. In these limits the multitime correlation functions such as $p(0,?,0;t_{m0},t_{m2},t_{m0})$ can be expressed in terms of $p(0;\Delta t_1), p(0,0;\Delta t_1,\Delta t_2),\ldots$. We have shown that it is possible to find a reasonable interpolation between both extreme limits, thereby introducing a rate memory parameter Q. The value of Q counts the number of relaxation processes after which a unit is uncorrelated to its initial dynamical state. We have formulated the problem such that the rate memory parameter can be directly extracted from the four-time correlation function for given two-time correlation function. The experimental relevance of this work is demonstated in the following paper [19]. For the two-state approximation the interpolation procedure is exact. Although the precise physical meaning of the rate memory still has to be clarified, one may already say that for glasses it is related to the cooperativity of the structural relaxation.

The next theoretical step is to elucidate the relation of the rate memory to microcopic properties of glasses and to check the predictions of theories of the glassy state with respect to the rate memory. We hope that this may be initiated by the present work.

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APPENDIX A

We want to show how to calculate $p(0,?,0;t_{m0},t_{m2},t_{m0})$ on the basis of Eq. (21) in a recursive way if the waiting time t_{m2} is divided into R and t_{m0} into S identical time intervals Δt. As mentioned in the text, the direct calculation of $p(0,?,0;t_{m0},t_{m2},t_{m0})$ requires the evaluation of 2^R terms, which is prohibitive in the limit of large waiting times t_{m2}. Let us define

$$A(m,n)\equiv p(i_0=0,i_1=?,\ldots,i_m=?,i_{m+1}=0,\ldots,\times i_{m+n}=0;t_{m0},\Delta t,\ldots,\Delta t). \tag{A1}$$

Our goal is to calculate $A(R,S)=p(0,?,0;t_{m0},t_{m2},t_{m0})$. Note that the $A(0,n)=p(0;n\Delta t+t_{m0})$ are given. Factorization of $A(m,n)$ around $i_m=1$ on the basis of Eq. (21) yields

$$A(m,n)=A(m-1,n+1)+(1/Q)\frac{[p(0;t_{m0})-A(m-1,1)][p(0;n\Delta t)-p(0;(n+1)\Delta t)]}{1-p(0;\Delta t)} +(1-1/Q)[A(m-1,n)-A(m-1,n+1)]. \tag{A2}$$

Hence $A(m,n)$ can be calculated just on the basis of $A(m-1,1),A(m-1,n)$, and $A(m-1,n+1)$. Starting from $A(0,0),\dots,A(0,R+S)$, one may first calculate $A(1,0),\dots,A(1,R+S-1)$. Continuing this procedure, one finally arrives at $A(R,S)$. The number of steps is of the order of $R(R+S)/2$ and hence depends only algebraically on R. Therefore, this algorithm allows the numerical determination of $p(0,?,0;t_{m0},t_{m2},t_{m0})$ for all relevant values of t_{m2}.

APPENDIX B

Our task is to calculate the different terms of Eq. (21) for the two-state approximation and finally to compare the left- and the right-hand side in order to check whether the rate memory can be expressed by a single parameter Q. The value of Δt is chosen such that $\Delta t\Gamma \ll 1$ and $\Delta t k_i \ll 1$. For given indices $i_1,\dots,i_{n-1}$ one might calculate step for step the population of the two states by direct integration of the rate equations. Note that for $\Delta t k_i \ll 1$ the integration over Δt can be directly performed. However, since Eq. (21) is supposed to hold for all $i_1,\dots,i_{n-1}$ and for all values of n_1 it has to be valid for arbitrary populations r_1 and r_2 of the two states after the (n-1)th time interval. Furthermore, no restrictions are imposed on the indices $i_{n+1},i_{n+2},\dots$. Therefore, the individual populations s_i after the nth time interval have to be identical on the left- and the right-hand side of Eq. (21). Here we check that for Q as given by Eq. (26) and for arbitrary populations r_i this condition can be fulfilled.

Two different kinds of terms have to be distinguished. The first kind of terms are of the form $p(\dots,i_{n+1},\dots,i_N)$. As discussed before, we have to calculate the populations s_i after the nth time step. For reasons of symmetry we can restrict ourselves to the calculation of s_1. As an example let us deal with the term $p(\dots,i_{n-1},1,i_{n+1},\dots)=p(\dots,i_{n-1},?,i_{n+1},\dots)-p(\dots,i_{n-1},0,i_{n+1},\dots)$. The populations before the nth time step are r_i. According to our analysis of Sec. III, we have $s_i=Z_{ij}(\Delta t)r_j-X_{ij}(\Delta t)r_j$, from which we obtain $s_1=\Delta t\{\Gamma(r_2/2a_2-r_1/2a_1)-[-k_1r_1+\Gamma^p(r_2/2a_2-r_1/2a_1)]\}=\Delta t[k_1r_1+\Gamma^a(r_2/2a_2-r_1/2a_1)]$. Analogous calculations can be performed for the other terms, yielding

$$s_1=\Delta t[k_1r_1+\Gamma^a(r_2/2a_2-r_1/2a_1)] \quad \text{for } p(\dots,i_{n-1},1,i_{n+1},\dots), \tag{B1}$$

$$s_1=\Delta t[k_1a_1] \quad \text{for } p(i_n=1,i_{n+1},\dots), \tag{B2}$$

$$s_1=r_1 \quad \text{for } p(\dots,i_{n-1},i_{n+1},\dots), \tag{B3}$$

$$s_1=r_1+\Delta t[-k_1r_1+\Gamma^p(r_2/2a_2-r_1/2a_1)] \quad \text{for } p(\dots,i_{n-1},i_n=0,i_{n+1},\dots). \tag{B4}$$

Note that for the calculation of $p(i_n=1,i_{n+1},\dots)$ the initial populations r_i are given by a_i. The second kind of terms $p(\dots,i_n=1)$ involve the total probability after the nth time step. Let us calculate $p(i_n=1)$. Integration yields $s_1=\Delta t[k_ia_i]$, hence $p(i_n=1)=s_1+s_2=\Delta t[a_1k_1+a_2k_2]$. In summary, one obtains

$$p(i_n=1)=\Delta t[a_1k_1+a_2k_2], \tag{B5}$$

$$p(\dots,i_{n-1},i_n=1)=\Delta t[r_1k_1+r_2k_2]. \tag{B6}$$

Summing up the terms of the right-hand side of Eq. (21) yields

$$s_{1,\text{right}}/\Delta t=(1/Q)\frac{a_1k_1(r_1k_1+r_2k_2)}{k_1a_1+k_2a_2}+(1-1/Q)\times\left[k_1r_1-\Gamma^p\left(\frac{r_2}{2a_2}-\frac{r_1}{2a_1}\right)\right]. \tag{B7}$$

The left-hand side of Eq. (21), hence $s_{1,\text{left}}$, is given by Eq. (B1).

Solving the relation $s_{1,\text{left}}=s_{1,\text{right}}$ for Q yields, after some lengthy but straightforward algebra, the expression given in Eq. (26). Since the value of Q does not depend on the r_i we have proved that it is indeed sufficient to introduce a single parameter Q in order to describe all possible probabilities $p(i_1,\dots,i_N)$ and hence the function F_4 for the two-state approximation.

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