Fluctuation-dissipation relations for a general class of master equations

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The fluctuation-dissipation relation is calculated for a class of stochastic models obeying a master equation. The transition rates are assumed to obey detailed balance also in the presence of a field. It is shown that in general the linear response cannot be expressed via time-derivatives of the correlation function alone, but an additional function $\xi(t, t_w)$, which has been rarely discussed before is required. This function depends on the two times also relevant for the response and the correlation and vanishes under equilibrium conditions. It can be expressed in terms of the propagators and the transition rates of the master equation but it is not related to any physical observable in an obvious way. Instead, it is determined by inhomogeneities in the temporal evolution of the distribution function of the stochastic variable under consideration. $\xi(t, t_w)$ is considered for some examples of stochastic models, some of which exhibit true non-equilibrium dynamics and others approach equilibrium in the long term. In particular, models in which a relevant variable, e.g. a magnetization, is related in a prescribed way to the states of the system are considered as projections from a composite Markov process. From these model calculations, it is conjectured that $\xi(t, t_w)$ vanishes when one is concerned with measurements of the analogue of a structure factor for large wave-vectors or if every transition among the states randomizes the value of the stochastic variable considered.

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I. Introduction

The out-of-equilibrium dynamics of stochastic models has gained intensive interest in the last decade. In particular, the deviations from the fluctuation dissipation theorem (FDT), relating the linear response to the two-time correlation function have been investigated in great detail, for a recent review see[1]. Starting with an investigation of the spherical $p$-spin-glas model[2], much attention has been paid to study the behavior of the response and the correlation for models of glassy dynamics. While in equilibrium the FDT relates the response to the correlation in a unique way, this does not hold in out-of-equilibrium situations. The violations of the FDT usually are parameterized via the introduction of a function $X(t, t_w)$, which is defined via:

$$R(t, t_w) = \frac{X(t, t_w)}{T} \frac{\partial C(t, t_w)}{\partial t_w}$$

(1)
Here, the correlation function of a quantity $M(t)$ is defined by $C(t, t_w) = \langle M(t)M(t_w) \rangle$ and the corresponding response to a field conjugate to $M(t)$ is $R(t, t_w) = \delta\langle M(t) \rangle / \delta H(t_w)|_{H=0}$ for $t \geq t_w$. In case that $M$ is a so called neutral variable,[3] $X(t, t_w)$ is independent of $M$ and the long time limit $X_\infty$ allows the definition of an effective temperature[4].

The value of $X_\infty$ has been calculated for a variety of models with different results. One class of models that have been considered are coarsening models[5], for which $X_\infty$ is known to vanish[6]. Examples of such models are the well known spherical model[7, 8] and the $O(N)$ model in the limit of large $N$[9], as well as the Ising models in one[10] or higher dimension[11]. In the context of models for glassy dynamics for some discontinuous mean field spin models a different behavior has been found[12]. In particular, a relation between the degree of replica symmetry breaking and $X_\infty$ has been established. In addition, in some time sectors, in which both, the response and the correlation obey some scaling relations, it has been found that $X(t, t_w)$ is a function of the correlation alone, $X(C)$. For disordered systems, a connection between the out-of-equilibrium dynamics and static properties has been established[13]. For coarsening systems, however, such a relation does not exist[14].

In addition to these analytical calculations, a number of molecular dynamics simulations have been performed on model glassforming liquids, for a recent review see ref.[15].

Some of the quoted models are soft-spin models in the sense that the stochastic dynamics is calculated from a Langevin equation. The classical treatment of FDT violations for unfrustrated stochastic models with Langevin dynamics has been given in ref.[16], where various examples, including a simple random walk have been considered. In addition to models obeying a Langevin equation, the out-of-equilibrium dynamics of models with a dynamics determined by a master equation[17] have been investigated, in particular in the context of the aging dynamics in spin glasses. In this context also the function $\xi(t, t_w)$, which will be the central topic of the present paper, has been discussed for the first time[18, 19]. A well known model in this context is Bouchaud's trap model[20] and a number of investigations of the FDT violations have been presented[21, 22, 23].

In the present paper, I consider models for which the probability distributions obey a master equation (ME) and I assume that the transition probabilities fulfill the conditions of detailed balance also in the presence of a perturbing field. The behavior of the function $\xi(t, t_w)$ will be discussed in detail for some specific models. I will mainly focus on models, in which the dynamics of some stochastic variable $M(t)$ is determined via transitions among the states of the system under consideration. Therefore, one has to assign values $M_k$ to the states $k$. This can be done in a variety of different ways. Here, I will discuss a class of models in which the stochastic process $M(t)$ is viewed as a projection from a two-dimensional composite Markov process (CMP)[17]. When the transition rates are chosen in an appropriate way, this procedure allows to treat several different models on the same footing, including random magnetic models. The outline of the paper is the following. In the next section the general formalism will be discussed. This includes a discussion of trap models because one generally finds that $\xi(t, t_w)$ vanishes for these models[21, 22, 23]. Section III is devoted to random magnetic models and a particular example of a kinetic random energy model is discussed in detail for illustrative purposes. Models for tagged
particle motion as they have been applied to the dynamics in supercooled liquids are considered in Section IV and the conclusions are presented in Section V.

II. Master equations and FDT violations

A. General formalism

Throughout this paper a stochastic dynamics according to a master equation (ME) is assumed. In a discrete notation let $G_{kl}(t)$ be the conditional probability to find the system in ’state’ $k$ at time $t$ provided it was in ’state’ $l$ at time $t=0$. At this point it is not necessary to specify the meaning of the term ’states’. Denoting the transition probabilities for a transition from state $k$ to state $l$ by $W_{kl}$, the ME reads as:

$$\dot{G}_{kl}(t) = -\sum_n W_{nk} G_{kl}(t) + \sum_n W_{kn} G_{nl}(t)$$

(2)

Of course, the same ME is obeyed by the populations of state $k$, $p_k(t) = \sum_l G_{kl}(t)p_l(0)$. In addition, I only consider transition probabilities that obey detailed balance

$$W_{kl} p_{eq}^l = W_{lk} p_{eq}^k$$

(3)

where the $p_{eq}^k$ are the populations in thermal equilibrium. These are invariant with respect to the master operator, i.e. $p_{eq}^k = \sum_l G_{kl}(t)p_{eq}^l$.

Throughout the present paper it is assumed that the system is prepared in some initial state described by a fixed set of populations, $p_k^0$. The populations then evolve according to $p_k(t) = \sum_l G_{kl}(t)p_l^0$. In the general case, of course, the $p_k^0$ are different from the $p_{eq}^k$, but they still fulfill the sum rule $\sum_k p_k^0 = 1$ as required for probabilities.

Central to the topic of the present paper is the two-time correlation function

$$C(t, t_w) = \langle M(t) M(t_w) \rangle = \sum_{k,l} M_k M_l G_{kl}(t-t_w)p_l(t_w)$$

(4)

where $M_k$ is the value of $M(t)$ in state ’$k$’. In this expression, $t_w$ denotes the time that has evolved after the initial preparation of the system in the populations $p_k^0$. In the following $t \geq t_w$ will always be assumed. In addition, the correlation function can always be decomposed according to

$$C(t, t_w) = C_{eq}(t-t_w) + \Delta C(t, t_w) \quad \text{with} \quad C_{eq}(t-t_w) = \sum_{k,l} M_k M_l G_{kl}(t-t_w)p_{eq}^l$$

(5)

because of the properties of $G_{kl}(t_w)$. Note that this property only holds if the $W_{kl}$ obey detailed balance, cf. eq. (3). From $G_{kl}(t_w \to \infty) = p_{eq}^k$ one sees that $\Delta C(t, t_w)$ vanishes for long waiting times, because exactly this long time limit has been subtracted from $\Delta C(t, t_w)$. Eq. (4) holds for all models considered in the present paper.

If $\langle M(t) \rangle \neq 0$, it is advantageous to consider $\dot{C}(t, t_w) = \langle M(t) M(t_w) \rangle - \langle M(t) \rangle \langle M(t_w) \rangle$, given by $\dot{C}(t, t_w) = \sum_{k,l} M_k M_l [G_{kl}(t-t_w) - p_k(t)]p_l(t_w)$.  


In order to calculate the linear response of the system,
\[ R(t, t_w) = \frac{\delta \langle M(t) \rangle}{\delta H(t_w)} \bigg|_{H=0} \]  
(6)
the dependence of the transition probabilities on a field \( H \) conjugate to \( M \) has to be fixed. In principle there is no restriction regarding this dependence. From equilibrium considerations one expects a Boltzmann-like dependence, \( e^{\beta H M} \). This, however, does not fix the dependence on the values of \( M_k \) in the initial or final state of a \( k \to l \) transition. In the present paper, I choose the following form, which assures that the system also in the presence of the field fulfills detailed balance:

\[ W_{kl}(H) = W_{kl} e^{\beta H X_{kl}} \quad \text{with} \quad X_{kl} = \alpha M_k - (1 - \alpha) M_l \]  
(7)

Here, \( \alpha \) is a parameter that can take on any value. The same dependence has also been used by Bouchaud and Dean\[21\] in a study of the aging properties of the trap model\[20\]. Very recently, Ritort has generalized this dependence in using \( X_{kl} = \gamma M_k - \mu M_l \) with arbitrary \( \gamma \) and \( \mu \) with the effect that the \( W_{kl}(H) \) do no longer obey detailed balance\[22\].

Even though \( \alpha \) in principle can take on any value, there often will be some guiding principle. For example, if the states ‘\( k \)’ denote the energies in a canonical ensemble, one expects that \( \alpha \) can be determined from the dependence of the unperturbed \( W_{kl} \) on \( k \) and \( l \). If the \( W_{kl} \) are of a form allowing a Kramers-Moyal expansion\[24\], and therefore the ME has a well defined Fokker-Planck equation as a limit one would naturally choose \( \alpha = 1/2 \). However, it has to be pointed out that usually the states \( k \) are understood as metastable states or components\[25\] in connection with glassy systems. Then the corresponding free energies are to be viewed as coarse-grained quantities\[1\] and one does no longer have a strict relation of \( \alpha \) to the unperturbed \( W_{kl} \).

Using eq.(7), the linear response \( R(t, t_w) \), eq.(6), can be calculated with the result

\[ R(t, t_w) = \beta \sum_{k,l,n} M_k \left[ G_{kn}(t - t_w) - G_{kl}(t - t_w) \right] W_{nl} X_{nl} p_l(t_w) \]  
(8)

After some algebra this can be related to the correlation function:

\[ R(t, t_w) = \beta \left[ \alpha \frac{\partial C(t, t_w)}{\partial t_w} - (1 - \alpha) \frac{\partial C(t, t_w)}{\partial t} + \alpha \xi(t, t_w) \right] \]  
(9)

where I defined the function

\[ \xi(t, t_w) = \sum_{k,l,n} M_k M_l G_{kn}(t - t_w) \left[ W_{nl} p_l(t_w) - W_{ln} p_n(t_w) \right] \]  
(10)

It is important to point out that eq.(9) holds for arbitrary Markov processes obeying detailed balance. Additionally, the function \( \xi(t, t_w) \) cannot be related to a time derivative of the correlation function and therefore the response is not determined by \( C(t, t_w) \) alone in the general case. \( \xi(t, t_w) \) plays a similar role as the asymmetry in the treatment of
the response derived from a Langevin equation. Of course, a relation between \( R(t, t_w) \) and \( \hat{C}(t, t_w) \) mentioned above is easily obtained from eq.\( \text{(9)} \) by noting that \( \partial \hat{C}(t, t_w)/\partial t = \partial C(t, t_w)/\partial t - \partial (\langle M(t) \rangle \langle M(t_w) \rangle)/\partial t \) and similarly for \( \partial \hat{C}(t, t_w)/\partial t_w \).

If the system is prepared in an equilibrium state initially, \( p_0^k = p_{eq}^k \), one has \( p_l(t_w) = p_{eq}^l \) and eq.\( \text{(3)} \) shows that \( \xi_{eq}(t, t_w) \equiv 0 \). Furthermore, the response and the correlation are functions of the time-difference only, i.e. \( C_{eq}(t, t_w) = C_{eq}(t - t_w) \) and \( R_{eq}(t, t_w) = R_{eq}(t - t_w) \) and thus

\[
R_{eq}(t) = -\beta \frac{dC_{eq}(t)}{dt}
\]

which is just the well known FDT.

To the best of the authors knowledge, eq.\( \text{(9)} \) has not been derived in this form before. However, equations similar to eq.\( \text{(9)} \) have been given for various models in the literature. Hoffmann and Sibani\[19\] have derived eq.\( \text{(9)} \) for the special case \( \alpha = 1 \). Later on Bouchaud and Dean\[21\] give a similar expression with, however, \( \xi(t, t_w) = 0 \). Furthermore, Fielding and Sollich\[3\] derived eq.\( \text{(9)} \) for the special case of \( \alpha = 0 \). In all these cases the authors considered model systems where the quantities \( M_k \) denote a magnetization which is attached to state \( k \) in some way. Such models will be treated as special cases in the following chapters. Before doing so it is instructive to have a somewhat closer look at the quantity \( \xi(t, t_w) \). As noted by Hoffmann and Sibani, \( \xi(t, t_w) \) vanishes if the relaxation to equilibrium is determined by distribution functions that are equilibrated with respect to the states \( k \) and depend on time only parametrically. In order to see this explicitly let us assume that the initial conditions are such that one can write \( p_k(t_w) = p_{eq}^k \delta_k(t_w) \) with unspecified functions \( \delta_k(t_w) \). In this case eq.\( \text{(10)} \) reads as

\[
\xi(t, t_w) = \sum_{k,l,n} M_k M_l G_{kn}(t - t_w) W_{nl} p_{eq}^l \left[ \delta_l(t_w) - \delta_n(t_w) \right]
\]

From this expression it is evident immediately that \( \xi(t, t_w) \) vanishes for \( \delta_k(t_w) = \delta(t_w) \) \( \forall k \).

In the following sections some specific choices of the states \( k \) and of the dynamic variables will be presented and eq.\( \text{(9)} \) will be discussed for these cases. In particular, I will concentrate on the function \( \xi(t, t_w) \) which according to the above discussion is a measure of inhomogeneities in the relaxation process under consideration.

**B. Trap models**

As already mentioned above, Bouchaud and Dean\[21\] derived eq.\( \text{(9)} \) for a trap model, although with \( \xi(t, t_w) = 0 \). In order to understand this, one has to consider the quantities of interest in the trap model in more detail. Instead of the correlation function given in eq.\( \text{(4)} \), Bouchaud and Dean consider a slightly different function:

\[
\hat{C}(t, t_w) = q_{EA} \Pi(t, t_w)
\]

where \( \Pi(t, t_w) \) denotes the probability that the system has not left the initial trap during \( t + t_w \) and \( q_{EA} \) is the Edwards-Anderson order parameter\[26\]. Note that \( \Pi(t, t_w) \) can be
interpreted as a structure factor for large wave-vectors, because every escape out of a given 
trap gives rise to a decorrelation and thus to a decay of $\Pi(t, t_w)$. If one now identifies the 
unspecified states $k$ of the last section with the traps and neglects any correlation between 
the values $M_k$ and the trap energies, only the $G_{kk}(t)$ are relevant$^{[23]}$. Assuming that the 
$M_k$ are distributed among the traps according to some fixed distribution $\rho(M)$, one finds 
for the correlation function

$$C(t, t_w) = \Pi(t, t_w) = \langle M^2 \rangle \sum_k G_{kk}(t - t_w)p_k(t_w)$$

with $q_{EA} = \langle M^2 \rangle$ and accordingly

$$\tilde{\xi}(t, t_w) = \langle M \rangle^2 \sum_{k,l} G_{kk}(t - t_w) [W_{kl}p_l(t_w) - W_{lk}p_k(t_w)]$$

From this last expression it is evident that for a symmetric distribution $\rho(-M) = \rho(M)$ 
$\tilde{\xi}(t, t_w)$ vanishes, $\tilde{\xi}(t, t_w) = 0$, and the relation between the response and the correlation 
reads as

$$\tilde{R}(t, t_w) = \beta \left[ \alpha \partial_{t_w} \tilde{\xi}(t, t_w) - (1 - \alpha) \partial_t \tilde{\xi}(t, t_w) \right]$$

For $\alpha = 0$, i.e. a dependence only on the initial trap, this expression reduces to the one 
given by Bertin and Bouchaud$^{[27]}$. Very recently, Sollich$^{[23]}$ has shown that the above 
expression holds for any trap model independent of the form of the transition rates. It 
will be shown later that $\xi(t, t_w) = 0$ is also found for other models in which any transition 
yields a complete decorrelation of the stochastic variable of interest.

C. Composite Markov processes

In this section I will consider the following class of models. In order to relate the quantities 
$M_k$ to the values of $k$, I now treat the states as configurations of the system, characterized by 
their (free) energies $\epsilon_k$ and consider the composite Markov process (CMP) \{\epsilon(t), m(t)\}$^{[17]}$. 
Typically, one is interested in the dynamics of the process $m(t)$ only. For example, when 
considering the relaxation properties in a (free) energy landscape determined by some 
model, often a random assignment of the $m_k$ to the states $k$ is used. The stochastic process 
m(t) is obtained from the CMP \{\epsilon(t), m(t)\} via the definition of marginal probabilities, 
i.e. by integrating out $\epsilon(t)$$^{[17]}$. Note, that usually the process $m(t)$ defined this way is no 
longer a Markov process. Generally, $m(t)$ can be related to the quantities $M_k$ in various 
ways. For instance, in the magnetic models to be treated in the following section one 
identifies the $M_k$ with ’magnetizations’ $m_k$. Another example is given by the case of the reorientation of a molecule in a liquid and the application of an electric field. In this case 
one chooses $M_k = \mu \cos(\Omega_k)$ with $\Omega_k$ denoting the orientation of the molecule and $\mu$ the 
value of the static dipole moment. Assuming that $\Omega$ is a random variable, one considers 
the CMP \{\epsilon(t), \Omega(t)\}. Similarly, one can treat the translational motion of tagged particles 
by identifying $M_k$ with $e^{iqr_k}$, where $r_k$ denotes the position and now the CMP \{\epsilon(t), r(t)\} 
is considered.
The CMP $\{\epsilon(t), m(t)\}$ is completely specified by the transition rates $W(\epsilon_k, m_k|\epsilon_i, m_l)$. Of course, there are many ways to choose these rates and in the present paper I will make the specific assumption:

$$W(\epsilon_k, m_k|\epsilon_i, m_l) = W(m_k|m_l) + \kappa_{kl}\Lambda_{(kl)}(m_k|m_l)$$ (12)

Here, the $W(m_k|m_l)$ denote transition rates for a $m_l \rightarrow m_k$ transition and the $\kappa_{kl}$ those for a $\epsilon_l \rightarrow \epsilon_k$ transition. Finally, the $\Lambda_{(kl)}(m_k|m_l)$ determine what kind of change takes place with the $m_k$ in case of a $\epsilon_l \rightarrow \epsilon_k$ transition. The choice made in eq.(12) is general enough to cover most situations of interest. Furthermore, it will be assumed throughout that no correlation between the $\epsilon_k$ and the $m_k$ exists initially and therefore the corresponding probabilities factorize:

$$p(\{\epsilon_k, m_k\}; t=0) = p(\epsilon_k; 0)p^eq_k(m_k) = p^0_kp^eq_k(m_k)$$ (13)

This means that additionally only the states $k$ are affected by the initial non-equilibrium situation. This choice is sufficient for all models considered in the present paper.

The two classes of models that will be considered in the present paper are completely determined by the choice of the $W(m_k|m_l)$ and the $\Lambda_{(kl)}(m_k|m_l)$. Random magnetic models can be obtained from eq.(12) with the choice

$$W(m_k|m_l) = 0 \quad \text{and} \quad \Lambda_{(kl)}(m_k|m_l) = \sigma_k(m_k)$$ (14)

where $\sigma(m_k)$ denotes the a priori distribution of the $m_k$ in state $k$, usually assumed to be independent of $k$, $\sigma_k(m_k) = \sigma(m_k) \ \forall k$. Note that $\Lambda_{(kl)}(m_k|m_l) = \sigma_k(m_k)$ means that this quantity solely depends on the destination state. The implications of eq.(14) will be worked out in the next section.

Another class of models concerns the models for dipole reorientation and translational noted already above. Here, one considers the CMP $\{\epsilon(t), a(t)\}$, with $a(t) = \Omega(t)$ or $a(t) = \mathbf{r}(t)$. In this example, eq.(12) reads as:

$$W(\epsilon_k, a|\epsilon_i, a') = W_k(a|a')\delta_{k,l} + \kappa_{kl}\Lambda(a|a')$$ (15)

where I have already neglected a possible dependence of $\Lambda$ on $k, l$. Two classes of models can be distinguished in the present context. One class is given by the so-called environmental fluctuation models and is defined by the choice of the on-site relaxation rates $W_k(a|a')$ and of $\Lambda(a|a')$. Usually, the latter quantity is either set to unity (no particle movement associated with an exchange) or one chooses $\Lambda(a|a') = p^eq(a)$ (complete randomization). In case of rotational motion the latter choice means that with any exchange process a random reorientation takes place.

The 'energy landscape model' is defined by assuming that there is no on-site relaxation at all, $W_k(a|a') = 0$, and the geometry of the molecular motion is determined by $\Lambda(a|a')$. Note that in this model the process $\epsilon(t)$ really defines the dynamics and $a(t)$ can be viewed as some kind of slave process. In its applications to the dynamics of supercooled liquids.
the assumption of angular jumps of a finite width $\Delta \Omega$ [32], i.e. $\Lambda(\Omega|\Omega') = \delta(\Omega - [\Omega' + \Delta \Omega])$, has proven successful [33], but also random rotational jumps, $\Lambda(\Omega|\Omega') = p^{eq}(\Omega)$, have been used for general considerations [31]. In case of translational motion of tagged particles, an isotropic model with $\Lambda(r|r') \propto \delta(r - [r' + \delta R])$ with a jump length $\delta R$ has been used to give a simple explanation of the apparent translational enhancement in supercooled liquids [33]. Before considering these kinds of models further, I will treat the random magnetic models in the following section.

III. Random magnetic models

In the usual treatment of magnetic models one simply assumes that a random magnetization $m_k$ is assigned to the states $'k'$ [9, 13]. Here, I will treat the CDP $\{\epsilon(t), m(t)\}$ as introduced in the preceding section with the transition rates determined by eq. (14), i.e.

$$W(\epsilon_k, m_k|\epsilon_l, m_l) = \sigma_k(m_k)\kappa_{kl}$$ \hspace{1cm} (16)

The initial condition, eq. (13), for these models reads as $p(\epsilon_k, m_k; 0) = p_0^k \sigma_k(m_k)$. Starting from the ME, eq. (2), where now $\sum_k$ has to be read as $\int dm_k$, one finds that the ansatz $G(\{\epsilon_k, m_k\}, t|\{\epsilon_l, m_l\}, 0) = \sigma_k(m_k)G_{kl}(t)$ with $G_{kl}(t) \equiv G(\epsilon_k, t|\epsilon_l, 0)$ solves the ME. The same applies for the time dependent probabilities, $P(\{\epsilon_k, m_k\}, t) = \sigma_k(m_k)P_k(t)$. In calculating the correlation, the response and $\xi(t, t_w)$ some care has to be taken in performing multiple summations. For instance, in an abbreviated form one has $\xi(t, t_w) = \sum_{k,l,n} f dm_k f dm_l f dm_n \sigma_k(m_k)\sigma_l(m_l)\sigma_n(m_n)m_k m_l A_{k,l,n}$ after all substitutions have been performed. In such an expression, one has to treat the terms $k = l$ and $k \neq l$ separately and then perform the integrations. This way all quantities of interest can be obtained from eqns. (14-16). In the most general case the results depend on the moments $\langle m_k^n \rangle = \int dm_k \sigma_k(m_k)m_k^n$. For example, the correlation is found to be given by:

$$C(t, t_w) = \sum_k \langle \Delta m_k^2 \rangle G_{kk}(t - t_w)p_k(t_w) + \sum_{k,l} \langle m_k \rangle G_{kl}(t - t_w)p_l(t_w)$$ \hspace{1cm} (17)

with $\langle \Delta m_k^2 \rangle = \langle (m_k - \langle m_k \rangle)^2 \rangle$. If even distribution functions, $\sigma_k(m_k) = \sigma_k(-m_k)$, for which $\langle m_k \rangle = 0$ are chosen, the second term in the above expression for the correlation function vanishes. For $\xi(t, t_w)$, one finds in this case:

$$\xi(t, t_w) = \sum_{k,l} \langle m_k^2 \rangle G_{kl}(t - t_w) \left[ \kappa_{lk}p_k(t_w) - \kappa_{kl}p_l(t_w) \right]$$ \hspace{1cm} (18)

These expressions can be analyzed for arbitrary random magnetic models. It has, however, to be pointed out that the simple choice, eq. (16) is meaningful only, if the magnetizations are randomly distributed among the energies, because this cannot account for any correlations between the $m_k$ and the $\epsilon_k$. In the following, I will illustrate the general formulae for the case of a simple model for which the master equation can be solved analytically.
**Example: kinetic random energy model**

As an example, I will treat the special case of a kinetic random energy model (REM) with a special choice of the transition rates $\kappa_{kl}$. I will follow the treatment of Koper and Hilhorst\[34\], who considered various forms of the transition rates. For the purpose of the present paper the simplest choice

$$\kappa_{kl} = \kappa_0 \exp (-\beta \epsilon_k)$$

(19)

is sufficient, where $\kappa_0$ is a rate constant, to be set to unity in the following, and $\beta = T^{-1}$. This means that the $\kappa_{kl}$ only depend on the destination state of the transition via the Boltzmann factors $B_k \equiv \exp (-\beta \epsilon_k)$. The corresponding ME can easily be solved giving $G_{ik}(t) = Z(\beta)^{-1} B_i + [\delta_{ik} - Z(\beta)^{-1} B_i] \exp (-Z(\beta)t)$ with the partition function $Z(\beta) = \sum_k B_k$ and $\delta_{ik}$ denotes the Kronecker symbol. The equilibrium populations are given by $p_i^{eq} = Z(\beta)^{-1} B_i$.

In principle one can choose the random variable to depend on the $\epsilon_k$, a possible choice being $\langle m_k^2 \rangle = B_k^n$ for arbitrary $n$, cf. the discussion given on this point by Fielding and Sollich\[3\]. Without showing explicit results here for the case $n \neq 0$, it is appropriate to mention that also for the simple model considered in this section, the FDT-violations depend on the value of $n$, meaning that the $m_k$ chosen this way do not represent neutral variables\[1, 3\]. In the following, I will choose $n = 0$, $\langle m_k \rangle = 0$ and $\langle m_k^2 \rangle = 1$. In addition, the initial populations $p_i^0$ will be chosen as $p_i^0 = N^{-1}$, appropriate for a quench from high temperatures in the beginning of the experimental protocol. For this case one finds, using the abbreviation $Z(\beta) = Z(2\beta)/Z(\beta)^2$:

$$C^{(B)}(t, t_w) = C^{(B)}_{eq}(t - t_w) + \Delta C^{(B)}(t, t_w)$$

$$C^{(B)}_{eq}(\tau) = Z(\beta) + [1 - Z(\beta)] \exp (-Z(\beta) \tau)$$

$$\Delta C^{(B)}(t, t_w) = Z(\beta) [\exp (-Z(\beta)t) - \exp (-Z(\beta)t_w)]$$

(20)

and

$$\xi^{(B)}(t, t_w) = Z(\beta) \Delta C^{(B)}(t, t_w)$$

(21)

For the response one has

$$R^{(B)}(t, t_w) = -\beta \left[ \frac{\partial C^{(B)}_{eq}(t - t_w)}{\partial t} - Z(\beta) Z(\beta) \exp (-Z(\beta)t) \right]$$

(22)

In these expressions, the explicit dependence on the Boltzmann factors $B_i$ has been denoted by the superscript $B$. Interestingly, the expression for the response is independent of $\alpha$. It should, however, be noted that in the more general case of a variable $\langle m_k^2 \rangle = B_k^n$, $n \neq 0$, $R^{(B)}(t, t_w)$ is found to depend on $\alpha$.

Below the transition temperature $T_c = J/(2\sqrt{\log 2})$ the random energies are exponentially distributed\[34\], where $J$ is related to the variance of the Gaussian distribution of the REM\[35\]. The corresponding distribution of Boltzmann factors $B_k$ is given by

$$p(B) = \frac{\nu}{N} x B^{-1-x} \quad \text{for} \quad \left( \frac{\nu}{N} \right)^{(1/x)} < B < \infty$$

(23)
and \( p(B) = 0 \) otherwise. Here, \( x = T/T_c \), \( \nu = 1/(2\sqrt{\pi \log 2}) \) and \( N \) denotes the number of random energies. All quantities of interest are obtained as averages over the distribution \( p(B) \), i.e.

\[
F(t) = \langle F^{(B)}(t) \rangle_B = \int dB p(B) F^{(B)}(t)
\]  

(24)

In order to perform the averages of the quantities given in eqns. (20,21,22), the only integrals required are:

\[
\Phi(t) = \langle e^{-Z(\beta)t} \rangle = \exp (-\tilde{v} t^x)
\]

\[
\Psi(t) = \langle Z(\beta)e^{-Z(\beta)t} \rangle = (1 - x) \left[ \Phi(t) - \tilde{v}^{-1/x} \Gamma(1 - 1/x; \tilde{v} t^x) \right]
\]

(25)

where \( \tilde{v} = v \Gamma(1 - x) \) with the Gamma function \( \Gamma(a) \). Furthermore, \( \Gamma(a, b) \) denotes the incomplete Gamma function. The calculation of the averages follows the lines of ref.[34] and poses no problem.

In particular, one finds:

\[
C_{eq}(\tau) = 1 - x + \Phi(\tau) - \Psi(\tau)
\]

\[
\Delta C(t, t_w) = \Psi(t) - \Psi(t_w)
\]

(26)

\[
R(t, t_w) = -\beta \partial_t [C_{eq}(t - t_w) + \Psi(t)]
\]

and

\[
\xi(t, t_w) = \partial_{t_w} \Psi(t_w) - \partial_t \Psi(t)
\]

(27)

Koper and Hilhorst[34] treated \( C_{eq}(\tau) \) in their investigation. Using the asymptotic behavior of \( \Gamma(a, b) \) it can be shown that this function behaves as \( C_{eq}(\tau) \sim \exp (-\tilde{v} t^x) \) at long times. For the integrated response \( \chi(t, t_w) = \int_{t_w}^t dt' R(t, t') \) one finds:

\[
\chi(t, t_w) = \beta \left[ C_{eq}(0) - C_{eq}(t - t_w) - (t - t_w) \partial_t \Psi(t) \right]
\]

(28)

where the first two terms correspond to the equilibrium response, \( \chi_{eq}(\tau) = \beta \left[ 1 - C_{eq}(\tau) \right] \), because \( C_{eq}(0) = 1 \) for \( n = 0 \). The limiting behavior of the integrated response can be summarized as follows:

\[
t_w \to \infty : \quad \chi(t_w + \tau, t_w) \to \chi_{eq}(\tau) \quad \forall \tau
\]

\[
\tau \to \infty : \quad \chi(t_w + \tau, t_w) \to \beta x \equiv T_c^{-1} \quad \forall t_w
\]

(29)

\[
t_w \to 0 : \quad \chi(t_w + \tau, t_w) \to \beta x \left[ 1 - \Phi(\tau) \right] \quad \forall \tau
\]

\[
\tau \to 0 : \quad \chi(t_w + \tau, t_w) \to 0 \quad \forall t_w
\]

This behavior is illustrated in Fig.1, which shows a typical FDT-plot[1], \( \tilde{y}^{-1}\chi(t_w + \tau, t_w) \) versus \( C(t_w + \tau, t_w) \), for \( x = 0.3 \). From this plot and eq.(20) it is evident that the limiting fluctuation-dissipation ratio[1] for this model is given by \( X_\infty = T_c^{-1} \). The dotted lines in Fig.1 represent a slope of \((-1)\) (ordinary FDT) and a slope of \((-x)\), the limiting behavior for long times \( \tau \). Therefore, in this simple model, the effective temperature coincides with the transition temperature \( T_c \).
The function $-\xi(t_w + \tau, t_w)$ is plotted versus $\tau$ in Fig. 2 for various values of the waiting time $t_w$ for $x = 0.3$. The behavior for other values of $x$ is very similar. For very short $\tau$ the function $\xi$ starts from zero and approaches a plateau value determined by $[\partial_{t_w} \Psi(t_w)]$ for long times $\tau$, cf. eq. (27). Only in the limit of long waiting one has $\xi(t_w + \tau, t_w) = 0$. The lower panel of Fig. 2 shows a logarithmic plot of $(-\xi)$, which demonstrates the linear behavior of $\xi$ and also that the cross-over to the plateau value happens around the waiting time, i.e. for $\tau \sim t_w$. For not too long waiting times, the approximate expression

$$\xi(t_w + \tau, t_w) \simeq (x\bar{v})t_w^{x-1}\left[\left(1 + \frac{\tau}{t_w}\right)^{x-1} - 1\right]$$

(30)

holds with high accuracy. This expression is shown in the lower panel of Fig. 2 as the thin dotted lines. For $t_w = 10^{-5}$, it cannot be distinguished from the exact expression, eq. (27).

From these considerations it becomes clear that even for this simple example the assumption that the distribution function determining the relaxation is equilibrated with respect to the $\epsilon_k$ is meaningless. On the contrary, the system gets stuck in a distribution characterized solely by the transition temperature $T_c$. In order to further discuss the properties of the function $\xi(t, t_w)$, in the next section I consider a different class of models.

### IV. Models for tagged particle motion

Models exhibiting truly non-equilibrium dynamics are often considered as models for glassy systems. However, when one is concerned with supercooled liquids, the usual situation is one in which the system can reach metastable equilibrium for long times. The glass transition temperature is merely a convenient way of classifying the time scale of the primary relaxation [36]. Nevertheless, investigating the out-of-equilibrium dynamics of simple models for molecular motion in supercooled liquids is capable of providing additional information about the mechanisms of the dynamics.

In this section, I consider models for tagged particle motion that have been used successfully to describe the translational and reorientational dynamics in supercooled liquids on a phenomenological level [29, 31, 33].

In case of the reorientational motion, the correlation function $C(t, t_w)$, eq. (4), is obtained by identifying $M(t)$ with orientation dependent static dipole moments $\mu(t)$. The time dependence has its origin in the temporal fluctuations of the direction of $\mu$ relative to a space fixed axis. It should be pointed out that $C(t, t_w)$ is directly related to the so called rotational correlation function $g_1(t, t_w)$, where the general definition is

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

(31)

Here, the angle $\theta$ is the polar angle of the axially symmetric principal axes system in the laboratory fixed coordinate system and $P_L(x)$ denotes the Legendre polynomial of rank $L$. For instance, in dielectric spectroscopy $\theta$ is the angle between the applied field and $\mu$ and $g_1(t, t_w)$ is measured. In NMR or light scattering $g_2(t, t_w)$ typically is observed.
If one is interested in translational motions of tagged particles, one choice is to identify $M(t)$ with $e^{iqr(t)}$, with $\mathbf{q}$ denoting the wave-vector and $\mathbf{r}(t)$ the position of the particle. This means, one has a close relation between $C(t, t_w)$ and the incoherent intermediate scattering function:

$$
C(q)(t, t_w) = \langle e^{iqr(t)} e^{-iqr(t_w)} \rangle
$$

where I have already assumed that the system is isotropic, $q = |\mathbf{q}|$.

In the following I consider the CMP $\{\epsilon(t), a(t)\}$, where the $a(t)$ either denotes the orientation $\Omega(t)$ or the position $\mathbf{r}(t)$.

**Energy landscape models**

I start the discussion with the CMP $\{\epsilon(t), a(t)\}$ in the context of the energy landscape model introduced in ref.[31]. In this model, one associates a (free) energy $\epsilon_k$ with each basin or metabasin of the potential energy landscape of the system[1, 38]. In the model of a random first order transition put forward by Wolynes et al., see e.g. ref.[39], the $\epsilon_k$ would be interpreted as the free energies of the metastable glassy states, characterized by an analogue of the Edwards-Anderson order parameter. The slow primary relaxation in such scenarios is determined by the transition among the various states. In the energy landscape model a tagged particle is allowed to reorient about an average jump angle $\Theta$ and also to hop a mean distance $\delta R$ whenever a $k \rightarrow l$ transition takes place[31, 33]. As already mentioned in Sect.IIC, the simplest choice for the transition rates given in eq.(15) is $W_k(a|a') = 0$ and $\Lambda(a|a') \propto \delta(a - [a' + \Delta a])$ with $\Delta a$ denoting $\Theta$ or $\delta R$. In the context of reorientational motions, sometimes it is sufficient to consider rotational random jumps, which just means that any $k \rightarrow l$ transition randomizes the molecular orientations completely. In this case one chooses $\Lambda(\Omega|\Omega') = 1/(8\pi^2)$.

In Appendix A the solution of the ME for this model is explained and the expressions for the quantities relevant in the present context are derived. The correlation function $C(t, t_w)$ is given in eq.(A.6) and $\xi(t, t_w)$ in eq.(A.7). From the latter expression it is obvious that $\xi$ is closely related to the non-equilibrium part of the correlation function, $\Delta C$. The response then follows from the general expression, eq.(9). For $\xi(t, t_w)$ it is found that it is given by

$$
\xi^{(1)}(t, t_w) \propto \cos (\Theta)
$$

in case of reorientations with an jump angle $\Theta$. If random reorientations are assumed instead, one has $\xi^{(1)}(t, t_w) \equiv 0$. For translational motion in an isotropic model one finds

$$
\xi^{(Q)}(t, t_w) \propto j_0(Q)
$$

where $j_0(x)$ is a Bessel function and $Q = (q \cdot \delta R)$ with the wave-vector $q$. The limiting behavior is found to be given by ($p \equiv Q \text{ or } L$):

$$
t_w \to \infty : \quad \xi^{(p)}(t_w + \tau, t_w) \to 0 \quad \forall \tau
$$

$$
\tau \to \infty : \quad \xi^{(p)}(t_w + \tau, t_w) \to 0 \quad \forall t_w
$$

$$
t_w \to 0 : \quad \xi^{(p)}(t_w + \tau, t_w) \to \xi^{(p)}(\tau, 0) \quad \forall \tau
$$

$$
\tau \to 0 : \quad \xi^{(p)}(t_w + \tau, t_w) \to 0 \quad \forall t_w
$$

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It is evident that in contrast to the simple kinetic REM considered in the previous section, \( \xi(t_w + \tau, t_w) \) vanishes in the limit of long \( \tau \). The reason for this difference is that in the present model the system reaches equilibrium in this limit.

Although the general expressions for \( \xi \) are not very instructive, two limits can be analyzed in simple terms and the relevant formulae are given in Appendix A. One limit is given by either random rotations or large wave-vectors. In both cases, one finds that \( \xi \) vanishes. This means that whenever a transition gives rise to a randomization of the relevant variable, \( \xi \) is expected to vanish. This is very similar to the case of the trap models discussed in Sect.IIB. Therefore, in this situation, the correlation function \( C(t, t_w) \) is essentially the same as the function \( \Pi(t, t_w) \), giving the probability for staying in the same orientation/position (as opposed to the same trap). This can also be seen from the direct comparison of the expression for \( C^{(1)}(t, t_w) \) and \( C^{(Q)}(t, t_w) \) given in eq.(A.9) with the one given for \( \Pi(t, t_w) \) in Sect.IIB, because only \( G_{kk}(t) = e^{-\kappa_k t} \) enters these expressions, cf. eq.(A.8). The correlation functions in this limit are independent of \( L \) or \( Q \) because every transition gives rise to a complete decorrelation. Thus, there is a close link between the simple model considered here and trap models concerning the vanishing of the function \( \xi(t, t_w) \). It should, however, be noticed that this correspondence relies only on the 'geometric' aspects and has nothing to do with the aging dynamics in the models considered. The important point regarding \( \xi(t, t_w) \) is the fact that due to the randomization of the relevant stochastic variable in each transition the distribution of orientations/positions is homogeneous. A very important difference between the model for translational model and the trap model, however, is that the wave-vector is a quantity that can be adjusted experimentally. Therefore, the limit of vanishing \( \xi^{(Q)} \) can be reached continuously in principle.

The other limit that can be investigated in detail is that of very small rotational jump angles \( \Theta \) (rotational diffusion) or small wave-vectors \( q \). In this case, one finds that the equilibrium correlation functions decay approximately exponentially in time with diffusion coefficients related to the averaged transition rate \( \langle \kappa \rangle = \sum_{k,l} \kappa_{kl} p_{eq}^k \), cf. eq.(A.11). In this limit, the prefactor of \( \xi \), \( \cos(\Theta) \) or \( j_0(Q) \), are approximately equal to unity.

Environmental fluctuation models for molecular reorientations

In order to show that the results obtained in the framework of the energy landscape model qualitatively are the same also for other models, I will now discuss the exchange models mentioned earlier. For simplicity it is assumed that there are two 'states', one in which molecular reorientation is fast, denoted by 'f' in the following, and one in which molecules reorient slowly, denoted by 's'[29]. The generalization to an arbitrary number of states poses no problem and has been used to describe several features of the reorientational relaxation in supercooled liquids, including dielectric relaxation[30] and four dimensional
NMR experiments. If the exchange rates, $\kappa_{sf}$ and $\kappa_{fs}$, vanish, one has a static heterogeneous dynamics in the sense that slow molecules remain slow forever. The solution of the corresponding ME and the relevant results are given in Appendix B, where it is shown that there are only slight differences to the case of the energy landscape model.

For the case of no changes in molecular orientation due to $k \rightarrow l$ transitions, orientational relaxation takes place solely due to on-site reorientations. From the expression for $\Delta C(t, t_w)$, eq. (B.2), it becomes evident that this function vanishes, if the reorientation rates in the two environments, $\Gamma_f$ and $\Gamma_s$, are equal, i.e. $\Delta C(t, t_w) = \xi(t, t_w) = 0$ for $\Gamma_s = \Gamma_f$. The same holds if one has $\kappa_{sf} = \kappa_{fs}$. Furthermore, it is evident that in this model the only relaxation during the waiting time is given by exchange. For vanishing exchange rates $\xi$ vanishes, but $\Delta C$ remains at its initial value for all waiting times. The latter fact is easily understood because in this case there is no way for equilibration of the $p^0_{s/f}$. As in the energy landscape model, $\xi(t_w + \tau, t_w)$ vanishes in the limits of small and large $\tau$ and has a maximum at intermediate $\tau$ determined by the effective decay rates.

So far, I have considered the two-state model in which an exchange process has no effect on the molecular orientation. However, the other extreme scenario, in which the molecular orientation randomizes completely in case of a $k \rightarrow l$ transition, can easily be treated in the same way. It turns out that the only relevant difference to the model considered above is that now $\xi(t, t_w) = 0$, cf. eq. (B.3). In this case the orientational distribution is homogeneous at each instant of time and the argument for a vanishing $\xi$ given in Sect. IIA applies.

V. Conclusions

I have considered the fluctuation-dissipation relation for a general class of stochastic models obeying a master equation. I have chosen transition rates which in the presence of a field are disturbed in a multiplicative way. Only cases for which detailed balance is obeyed with and without field were considered.

The main result of the present paper is given in eq. (9) and shows that in the general case the response cannot be related to time-derivatives of the correlation function alone. Instead, a function $\xi(t, t_w)$ occurs additionally in the expression for the response, which cannot be related to any physical quantity in a simple manner. An exception to this finding is provided by trap models, where it has been shown the $\xi(t, t_w)$ vanishes for even distributions. Hoffmann and Sibani were the first who considered the function $\xi(t, t_w)$ for the special case of $\alpha = 1$ in the general expression for the fluctuation dissipation relation, eq. (9). However, they did not further discuss the meaning of this function apart from the fact that it vanishes if the relaxation is determined by probability distributions that are homogeneous with respect to the states of the stochastic process under consideration.

In the present paper I have shown that this assumption is likely to be wrong even for very simple minded models. As one example I considered a kinetic random energy model with an extremely simple choice for the transition rates in Sect.III. The limiting effective temperature was found to coincide with the transition temperature of the REM, $T_{\text{eff}} = T_c$. 

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It was found that even for this model $\xi(t_w + \tau, t_w) \neq 0$ for $t_w < \infty$. Due to the fact that the system never reaches equilibrium in this model, one also has a non-vanishing long time limit $\xi(\infty, t_w)$.

Furthermore, I have shown that for some models in which any transition leads to a complete loss of correlation of the stochastic variable under study, one finds that the function $\xi(t, t_w)$ vanishes. This holds for trap models and also for models of molecular reorientations, provided these reorientations proceed via random rotational jumps. If the energy landscape model is applied to translational motions of tagged particles, one has $\xi^{(Q)}(t, t_w) \propto j_0(Q)$, if the intermediate scattering function $C^{(Q)}(t, t_w)$ is measured. If $Q \gg 1$, one therefore also finds that $\xi^{(Q)}$ vanishes. In this example, the fact that $\xi$ vanishes thus relies on an experimentally adjustable parameter and does not reflect a property of the transition rates. It is well known, that a stimulated NMR echo experiment is the ‘rotational analogue’ of the intermediate scattering function [41]. If this experiment is performed in a way that is analogous to $C^{(Q \gg 1)}(t, t_w)$, every single rotational jump leads to a decorrelation and the random rotational jump model applies. Also in case of the trap model any transition out of a trap leads to a loss of correlation. Thus, also $\Pi(t, t_w)$ corresponds to $C^{(Q \gg 1)}(t, t_w)$. Therefore, it is tempting to speculate that whenever an analogue of $C^{(Q)}(t, t_w)$ in the large $Q$-limit is considered for $C(t, t_w)$ in the sense that every transition gives rise to a complete decorrelation, the function $\xi^{(Q)}(t, t_w)$ is expected to vanish. This also means that whenever every transition among the states of a system obeying a ME randomizes the stochastic variable under consideration, I expect $\xi(t, t_w) = 0$.

For all models considered in the present paper, it turns out that $\xi(t, t_w)$ is related to the non-equilibrium part of the correlation function, $\Delta C(t, t_w)$. Furthermore, the main difference between the kinetic REM and the models considered for tagged particle motion consists in the fact that in the latter models the system reaches equilibrium for long times. It is found that $\xi(t_w + \tau, t_w)$ (if it is non-vanishing) for these models is of a transient nature and vanishes for short and long $\tau$, in contrast to the case of the kinetic REM, where $\lim_{\tau \to \infty} \xi(t_w + \tau, t_w) \neq 0$.

At the moment it is not clear, how the function $\xi(t, t_w)$ behaves for other types of models. A study of kinetic Ising chains is under way. Also, it would be interesting to investigate the behavior of $\xi(t, t_w)$ for varying initial conditions. In the present paper, eq.(13) was always assumed to hold.

To conclude, I have shown that for some general class of models the fluctuation dissipation relation is determined by time-derivatives of the correlation function and an additional function $\xi(t, t_w)$. As noted earlier[19], $\xi(t, t_w)$ is a measure for deviations from homogeneity in the distribution functions determining the relaxation. This function is expected to vanish in situations where transitions among the states considered lead to a randomization of the relevant stochastic variable, meaning that in such a case the relevant distributions are homogeneous.
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Appendix A: Energy landscape model

In this Appendix I will give the relevant formulae that are needed for the solution of the ME for the CMP \( \{ \epsilon(t), a(t) \} \), where \( a(t) \) has to be identified with the orientation \( \Omega \) or the position \( r \), depending on the situation. Because the solution of the ME proceeds in the same way for both cases, the treatment can be formulated quite generally. The transition rates are given by

\[ W(\epsilon_k, a|\epsilon_l, a') = \kappa_{kl}\Lambda(a|a') \]  

which follows from eq.(15) for \( W_k(a|a') = 0 \). Again, I neglected possible dependencies of \( \Lambda(a|a') \propto \delta(a - (a' + \Delta a)) \) on the initial and final states of the transition. To solve the corresponding ME, eq.(2), 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. \( \Lambda(p) = \int da da' U^{-1}(a, p)\Lambda(a|a')U(a, p) \).

Next, the conditional probability is expanded in terms of these eigenvectors,

\[ G(\{ \epsilon_k, a \}; t|\{ \epsilon_l, a_0 \}, 0) = \int dp U(a, p)G_k^{(p)}(t)U^{-1}(a_0, p) \]  

The Greens functions \( G_k^{(p)}(t) \) are then found from the solution of

\[ \dot{G}_k^{(p)}(t) = -\kappa_k G_k^{(p)}(t) + \Lambda(p) \sum_n \kappa_{kn} G_n^{(p)}(t) \]  

where the sum rule \( \kappa_k := \sum_{l \neq k} \kappa_{lk} \) was used for the diagonal element. The initial populations are chosen according to eq.(13), which in the present context reads as:

\[ p(\{ \epsilon_k, a \}; 0) = p^{eq}(a)p_k^0 \]  

If one considers isotropic rotational motions with a fixed mean jump angle \( \Theta \), one has to identify \( a \) with \( \Omega \). In this case one has \( p^{eq}(a) = \frac{1}{8\pi} \), \( U(a, p) = \sqrt{\frac{2L+1}{8\pi^2}}D_m^{(L)}(\Omega) \), \( \Lambda(p) = P_L(\cos(\Theta)) \) and the integration over \( p \) is now a sum over \( L \).

In case of translational jumps onto all postions 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 \( U(a, p) = \frac{1}{\sqrt{V}}e^{iqr} \) 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) reads as:

\[ \text{Rotation : } \dot{G}_k^{(L)}(t) = -\kappa_k G_k^{(L)}(t) + P_L(\cos(\Theta)) \sum_n \kappa_{kn} G_n^{(L)}(t) \]  
\[ \text{Translation : } \dot{G}_k^{(Q)}(t) = -\kappa_k G_k^{(Q)}(t) + j_0(Q) \sum_n \kappa_{kn} G_n^{(Q)}(t) \]  

(A.5)
Using $\Delta p$, from eq.(A.7) it is obvious that $\xi$.

In this limit, the general expression for the Greens function, eq.(A.3), approximately reads $\Lambda$ in perturbation theory, as outlined below.

Once the $G_{kl}^{(p)}(t)$ are obtained from the (numerical) solution of the equations (A.3), all quantities of interest can be calculated and one finds, cf. eq.(A.3):

$$C_{eq}^{(p)}(\tau) = \sum_{k,l} G_{kl}^{(p)}(\tau) p_{eq}^l ; \quad \Delta C^{(p)}(t_w + \tau, t_w) = \sum_{k,l} G_{kl}^{(p)}(\tau) [p_l(t_w) - p_{eq}^l]$$

(A.6)

and

$$\xi(t_w + \tau, t_w) = \Lambda(p) \frac{\partial}{\partial t_w} \left( \Delta C^{(p)}(t_w + \tau, t_w) \right)$$

(A.7)

In these expressions the $p_k(t_w) = \sum_l G_{kl}(t_w)p_{eq}^l$. 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, $t_w = 0$. Furthermore, in case of reorientational motions I have omitted a trivial factor $\frac{1}{\hbar^2}$. Note that for dipole reorientations, one is concerned with $C^{(1)}(t,t_w)$ and $\xi^{(1)}(t,t_w)$, i.e. one always has to use $L=1$ in the present context.

If in case of $a=\Omega$ it is assumed that the reorientations proceed via random jumps, one has to replace the factor $P_L(\cos(\Theta))$ in eq.(A.3) by $\delta_{L,0}$, meaning that for $L>0$ only the diagonal element is retained.

In general, the behavior of the function $\xi^{(p)}(t,t_w)$ and all other quantities is obtained from a numerical solution of the equations for the Greens functions, eq.(A.3) [31, 33]. For this purpose, the transition rates $\kappa_{kl}$ have to be chosen in a prescribed way. It is however, possible to give some general results valid in specific situations. Consider the case of rotational random jumps, for which one has $\Lambda(p > 0) = 0$. Similarly, if the incoherent scattering function is observed for large wave-vectors, $Q \gg 1$ (or $q \gg (\delta R)^{-1}$), one has $j_0(Q) \approx 0$. In both situations it is clear that $\xi^{(p)}(t,t_w)$ vanishes. In the other extreme, namely very small wave-vectors or rotational diffusion, one has $\Lambda(p) = 1 - \eta_p$ with $\eta_p = Q^2/6$ and $\eta_L = L(L+1)(\Theta/2)^2$. In both of these limiting situations, one can treat the problem in perturbation theory, as outlined below.

$\Lambda(p) \to 0$:

In this limit, the general expression for the Greens function, eq.(A.3), approximately reads as $G_{kl}^{(p)}(t) = -\kappa_{kl} G_{kl}^{(p)}(t)$ and therefore one has $(\kappa_k := \sum_{l \neq k} \kappa_{lk})$

$$G_{kl}^{(p)}(t) \simeq \delta_{kl} e^{-\kappa_k t}$$

(A.8)

Using $\Delta p_k(t_w) = p_k(t_w) - p_{eq}^k$, one easily finds from eq.(A.6):

$$C_{eq}^{(p)}(\tau) \simeq \sum_k e^{-\kappa_k \tau} p_{eq}^k$$

and

$$\Delta C^{(p)}(t_w + \tau, t_w) \simeq \sum_k e^{-\kappa_k \tau} \Delta p_k(t_w)$$

(A.9)

From eq.(A.7) it is obvious that $\xi^{(p)}(t,t_w) \to 0$ for $\Lambda(p) \to 0$. 


In this case one is in the diffusive limit and one has \( \eta = Q^2/6 \) and \( \eta = L(L+1)(\Theta/2)^2 \), as already noted above. Here, one can use the ME for \( p=0 \) as the unperturbed problem and consider perturbation theory with a perturbation given by matrix elements \( V_{kl} = -\eta_p \kappa_{kl} \). This can be seen directly from the ME, eq. (A.3) and using \( \Lambda(p) = 1 - \eta_p \) therein, cf. ref. [33]. The unperturbed Greens functions thus coincide with the Greens function matrix are explicitly given by

\[
G_{kl}(t) = \sum_{m,n} \int_0^t ds G_{km}(t-s) \kappa_{mn} G_{nl}(s)
\]

A straightforward calculation yields:

\[
C(p)(t_w + \tau, t_w) \simeq 1 - \eta_p \left( \langle \kappa \rangle \tau + \int_0^\tau ds \sum_k \kappa_k [p_k(s + t_w) - p_k^{eq}] \right)
\]

where the mean relaxation rate is defined by

\[
\langle \kappa \rangle = \sum_k \kappa_k p_k^{eq}
\]

Therefore, up to linear order in \( \eta_p \) one finds

\[
C_{eq}^{(p)}(\tau) \simeq e^{-\eta_p \langle \kappa \rangle \tau}
\]

and

\[
\Delta C^{(p)}(t_w + \tau, t_w) \simeq -\eta_p \int_0^\tau ds \sum_k \kappa_k [p_k(s + t_w) - p_k^{eq}] e^{-\eta_p \langle \kappa \rangle \tau}
\]

Therefore, in the limit of small wave-vectors the model predicts an exponentially decaying intermediate incoherent scattering function, \( C_{eq}^{(Q)}(\tau) \equiv S(q, \tau) \simeq \exp(-q^2 D_T \tau) \), 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 \( C_{eq}^{(L)}(\tau) \simeq \exp(-L(L+1)D_R \tau) \) with \( D_R = (\Theta/2)^2 \langle \kappa \rangle \). Remember, that in the present discussion only \( L = 1 \) is relevant. Again, \( \xi(t, t_w) \) is given by eq. (A.7).

**Two-state model**

In order to illustrate the results obtained above for the energy landscape model, I now consider only two states. This is sufficient in order to discuss the qualitative features of the general model. The elements of the Greens function matrix are explicitly given by

\[
G_{11}(t) = p_1^{eq} + p_2^{eq} e^{-\bar{\kappa}t}, \quad G_{22}(t) = p_2^{eq} + p_1^{eq} e^{-\bar{\kappa}t}, \quad G_{12}(t) = p_1^{eq}(1 - e^{-\bar{\kappa}t}) \quad \text{and} \quad G_{21}(t) = p_2^{eq}(1 - e^{-\bar{\kappa}t})
\]

Here, I defined \( \bar{\kappa} = \kappa_{12} + \kappa_{21} \). Furthermore, one has \( \Delta p_1(t_w) = \left( p_1^0 p_2^{eq} - p_2^0 p_1^{eq} \right) e^{-\bar{\kappa}t_w} \) and \( \Delta p_2(t_w) = -\Delta p_1(t_w) \). With these quantities one finds for the two limiting situations discussed above:

\[
\Lambda(p) \to 0: \quad C_{eq}^{(p)}(\tau) \simeq e^{-\kappa_{21} \tau} p_1^{eq} + e^{-\kappa_{12} \tau} p_2^{eq}
\]

\[
\Delta C^{(p)}(t_w + \tau, t_w) \simeq \left[ p_1^0 p_2^{eq} - p_2^0 p_1^{eq} \right] e^{-\bar{\kappa}t_w}
\]

Equation (A.13)
One therefore finds that $\xi^{(p)}$ vanishes in the limit of small and large measuring times $\tau$ as well as for long waiting times $t_w$. In addition $\xi^{(p)}$ has a maximum as a function of $\tau$ for $\tau_{\text{max}}=\ln(\kappa_{12}/\kappa_{21})/(\kappa_{12} - \kappa_{21})$.

$$\Lambda(p) = 1 - \eta_p : \quad C^{(p)}_{eq}(\tau) \simeq e^{-\eta_p(\kappa)\tau}$$

$$\Delta C^{(p)}(t_w + \tau, t_w) \simeq \eta_p \left( \frac{\kappa_{12} - \kappa_{21}}{\bar{\kappa}} \right) \left[ p_0^{eq}p_2 - p_2^{0eq}p_1^{eq} \right] \left[ 1 - e^{-\bar{\kappa}\tau} \right] e^{-\eta_p(\kappa)\tau} e^{-\bar{\kappa}t_w}$$

Here, the situation regarding $\xi^{(p)}$ is analogous, the difference being that the maximum of $\xi^{(p)}(t_w + \tau, t_w)$ now occurs at $\tau_{\text{max}} = \bar{\kappa}^{-1} \ln \left( 1 + \frac{\bar{\kappa}}{\eta_p(\kappa)} \right)$.

**Appendix B: Environmental fluctuation model**

Such models are defined by the transition rates given in eq.(15), where now the on-site reorientations are modelled via finite $W_k(\Omega|\Omega')$. For simplicity, it is assumed in the following, that the reorientations proceed via random rotational jumps, $W_k(\Omega|\Omega') = -\Gamma_k \delta(\Omega - \Omega') + \Gamma_k/(8\pi^2)$. In addition, it has to be quantified what happens to the molecular orientation in case of $k \rightarrow l$ transition. As in the original model of Beckert and Pfeifer[28], 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 Greens functions are obtained from:

$$\dot{G}^{(L)}_{kl}(t) = - (\Gamma_k + \kappa_k) G^{(L)}_{kl}(t) + c_L \sum_n \kappa_{kn} G^{(L)}_{nl}(t)$$

Here, I defined $c_L = 1$, if $\Lambda(\Omega|\Omega') = 1$ and $c_L = \delta_{L,0}$ if $\Lambda(\Omega|\Omega') = 1/(8\pi^2)$[29]. As in the case of the energy landscape model, the relevant quantities are given by eqns.(A.6) and (A.7) if again it is assumed that there is no correlation initially, $p(\{\epsilon_k, \Omega|0\}) = \frac{1}{\eta_p^{eq}}\epsilon_k^{eq}$.

In the following, the explicit expressions will be given for the simple two-state model discussed in Sect.IV. Here, I consider the case $c_L = 1$. As in the text, the states are denoted by $f$ and $s$. The equilibrium populations of the states are given by $p_f^{eq}$ and $p_s^{eq}$, the reorientation rates are $\Gamma_f$, $\Gamma_s$ and the exchange rates are denoted by $\kappa_{sf}$ and $\kappa_{fs}$. The solution of eq.(B.1) poses no problem and one finds, again omitting a factor $\mu^2/3$:

$$C^{(1)}_{eq}(\tau) = \frac{1}{2w} \left[ z_f e^{-\Lambda_f\tau} + z_s e^{-\Lambda_s\tau} \right]$$

$$\Delta C^{(1)}(t_w + \tau, t_w) = \frac{\gamma}{w} \left[ p_f^{0eq}p_s - p_s^{0eq}p_f^{eq} \right] \left[ e^{-\Lambda_f\tau} - e^{-\Lambda_s\tau} \right] e^{-2\bar{\kappa}t_w}$$

Using the abbreviations $\bar{\kappa} = (1/2)(\kappa_{sf} + \kappa_{fs})$, $\bar{\Gamma} = (1/2)(\Gamma_f + \Gamma_s)$, $\gamma = (1/2)(\Gamma_f - \Gamma_s)$ and $\Delta_u = (1/2)(\kappa_{fs} - \kappa_{sf})$ one has for the effective decay rates $\Lambda_{fs} = \bar{\Gamma} + \bar{\kappa} \pm \sqrt{(\Delta_u + \frac{\gamma}{\kappa_{fs}})^2 + \kappa_{fs}\kappa_{sf}}$. Furthermore, I used $w = \sqrt{\gamma^2 + 2\gamma\Delta_u + \bar{\kappa}^2}$ and $z_{fs} = w \mp \bar{\kappa} \pm \gamma(p_f^{eq} - p_s^{eq})$. Finally, for the function $\xi$ one finds:

$$\xi^{(1)}(t, t_w) = - (2\bar{\kappa}) \Delta C^{(1)}(t, t_w)$$
The most important thing that changes, if one assumes that a random reorientation is associated with every $k \to l$ transition, $c_L = \delta_{L,0}$, in eq. (B.1) is that one now finds:

$$\xi^{(1)}(t, t_w) = 0 \quad \text{for} \quad c_L = \delta_{L,0} \quad (B.4)$$

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Figure captions

Fig.1 : $\beta^{-1}\chi(t_w + \tau, t_w)$ versus $C(t_w + \tau, t_w)$, for $x = 0.3$ and for various waiting times $t_w$. The dotted lines represent the slopes expected for ordinary FDT (slope: $-1$) and an effective temperature of $T_{\text{eff}} = T_c$ (slope: $-x$).

Fig.2 : $[-\xi(t_w + \tau, t_w)]$ versus $\tau$, for $x = 0.3$ for various waiting times $t_w$. Upper panel: linear scale, lower panel: logarithmic scale. In the lower panel, the approximate expression, eq. (30), is shown as thin dotted lines.
\[ \beta^{-1} \chi(t_w + \tau, t_w) \]

\[ C(t_w + \tau, t_w) \]

G. Diezemann; Fig. 1
\begin{equation} \xi(t_w + \tau, t_w) = 0.3 \end{equation}

G. Diezemann; Fig 2