Stochastic models for heterogeneous relaxation: Application to inhomogeneous optical lineshapes

Gregor Diezemann, Gerald Hinze and Hans Sillescu

Institut für Physikalische Chemie, Universität Mainz, Welderweg 15, 55099 Mainz, FRG

Dynamic heterogeneity has often been modeled by assuming that a single-particle observable, fluctuating at a molecular scale, is influenced by its coupling to environmental variables fluctuating on a second, perhaps slower, time scale. Starting from the most simple Gaussian Markov process we model the exchange between 'slow' and 'fast' environments by treating the fluctuating single-particle variable as a projection from a higher-dimensional Markov process. The moments of the resulting stochastic process are calculated from the corresponding Master equations or Langevin equations, depending on the model. The calculations show the importance of the way to treat exchange processes. The resulting stochastic process is non-Markovian for all models. However, the deviations from a Gaussian behavior depend on the details of the models. A comparison of our results with other model treatments and experiments should provide further insight into the concept of dynamic heterogeneity.

I. Introduction

In spectroscopy inhomogeneous lineshapes are observed if individual molecules within a sample give rise to different spectral components. This can be observed even in isotropic systems if the relevant coupling depends on molecular variables, like orientations, that differ from each other. Another, more important source for inhomogeneous line broadening is provided by intermolecular couplings with the environment. These give rise to dynamic fluctuations and can thus be explored by lineshape studies. Classical examples are given by the motional or exchange narrowing of NMR spectra[1]. The Anderson-Weiss theory[2] of narrowing Gaussian lineshapes has been a model for many later treatments although it applies to homogeneous systems only. Furthermore, typical 'slow motion' lineshapes in NMR are far from being Gaussian. However, for our purposes, the Gaussian approximation provides a good starting point since it implies the well-known Ornstein-Uhlenbeck (OU) process[3]. This allows one to introduce non-Gaussian perturbations in a transparent way.

A shortcoming of the OU process is that the two-time correlation function (2t-CF) of this Gaussian Markov process decays exponentially[3]. In complex systems like supercooled liquids, however, typically a non-exponential decay of 2t-CFs is observed. This forces us to consider non-Markovian models for the molecular observables. There are other fields in chemical physics where, starting from Gaussian fluctuations, non-Markovian effects have been incorporated in order to account for a more complex dynamics. Prominent examples are the problem of escape through a fluctuating bottleneck[4, 5, 6], first order chemical reactions[7, 8] and single molecule spectroscopy[9].

In our treatment, we closely follow the theory of solvation dynamics in time-resolved optical spectroscopy[10, 11] that has also previously been applied to treat heterogeneity in
terms of observed deviations from Markovian and Gaussian behavior\textsuperscript{[12, 13, 14]. It should be noted that the average frequency, $\langle \omega(t) \rangle$, remains constant in essentially all dynamical NMR and ESR spectra but it changes due to time-dependent Stokes shifts in time-resolved optical spectra. This can result in time-dependent optical linewidths that have been related to dynamic heterogeneity\textsuperscript{[12, 15].}

In the following Section, we briefly review the theory of time-dependent optical lineshapes in the form that will be used in the calculations. In Section III we treat the optical transition frequency $\omega(t)$ as a non-Markovian stochastic process, defined as the projection from a composite Markov process. For simplicity, we allow for two values of an additional environmental variable, $\epsilon(t)$, to treat exchange between a 'slow' ($\epsilon_s$) and a 'fast' ($\epsilon_f$) environment. Exchange in two (or multiple) state models has been treated a long time ago in relation with rotational\textsuperscript{[16, 17, 18, 19]} and translational\textsuperscript{[20, 21]} diffusion in complex systems. Here, we concentrate on the question regarding deviations from both, Gaussian and Markovian, behavior. The paper closes with a discussion of our results and conclusions in Section IV.

II. Short survey of the theory of optical lineshapes

This section consists of a brief review of the theory of time-dependent optical lineshapes in the inhomogeneous limit. In case of triplet state solvation all effects related to internal conversion, intersystem crossing, and the following electronic relaxation are assumed to be much faster than the dynamical features monitored experimentally. We mainly follow the general theoretical framework of refs.\textsuperscript{[10, 11, 14]} in the following. There, it has been shown that the time-dependent signal for a single chromophore immersed in a bath of solvent molecules can be written as:

$$I(\omega, t) = \int_{-\infty}^{\infty} d\omega_0 P(\omega, t|\omega_0)p_0(\omega_0)$$

Here, the transition frequencies $\omega(t)$ depend on all relative distances and orientations between the chromophore and the solvent molecules, which in turn depend on time. In Eq.(1) $P(\omega, t|\omega_0)$ denotes the conditional probability of finding a transition frequency $\omega$ at time $t$, given it was $\omega_0$ at time $t = 0$. The initial probability $p_0(\omega)$ is given by the emission spectrum at time $t = 0$, $I(\omega, 0)$, because of $P(\omega, 0|\omega_0) = \delta(\omega - \omega_0)$. Thus, observation of $I(\omega, t)$, Eq.(1), as a function of time is interpreted as following the trace of the initial non-equilibrium emission spectrum towards the equilibrium steady-state emission spectrum $I(\omega, \infty) = p^{eq}(\omega) = P(\omega, \infty|\omega_0)$. Furthermore, it is assumed that the time-independent spectra are well approximated by Gaussians,

$$p_0(\omega) = \frac{1}{\sqrt{2\pi\sigma_0^2}} e^{-\frac{(\omega-\Delta)^2}{2\sigma_0^2}} \quad \text{and} \quad p^{eq}(\omega) = \frac{1}{\sqrt{2\pi\sigma_\infty^2}} e^{-\frac{\omega^2}{2\sigma_\infty^2}}$$

where $\Delta = \langle \omega(0) \rangle$, $\sigma_0^2 = \langle (\omega(0) - \Delta)^2 \rangle$ and $\sigma_\infty^2 = \langle \omega(\infty)^2 \rangle$. The mean value $\langle \omega(\infty) \rangle$ has been set to zero without loss of generality. Therefore, the overall red-shift is given by $\Delta$. A Gaussian approximation for the conditional probability,

$$P(\omega, t|\omega_0) = \frac{1}{\sqrt{2\pi\sigma_\infty^2(1-C(t)^2)}} \exp \left( -\frac{[\omega - \omega_0C(t)]^2}{2\sigma_\infty^2(1-C(t)^2)} \right)$$

(3)
follows from a second order cumulant expansion with the Stokes shift correlation function given by $C(t) = \langle \omega(t)\omega(0) \rangle / \sigma^2_\infty$. Using Eq.(3) in Eq.(1) for the time-dependent spectrum again gives a Gaussian for $I(\omega, t)$ with a time-dependent mean and a second moment

$$\langle \omega(t) \rangle = \Delta C(t) \quad \text{and} \quad \langle \omega^2(t) \rangle = \sigma^2_\infty + (\Delta^2 + \sigma^2_0 - \sigma^2_\infty)C(t)^2$$

yielding a time-dependent variance

$$\sigma^2(t) = \langle \omega^2(t) \rangle - \langle \omega(t) \rangle^2 = \sigma^2_\infty + (\sigma^2_0 - \sigma^2_\infty)C(t)^2$$

This variance shows a monotonic behavior as a function of time in that it changes monotonously from $\sigma^2(0) = \sigma^2_0$ to $\sigma^2(\infty) = \sigma^2_\infty$.

It is precisely the deviations from the simple relation (5) observed in the triplet state solvation studies on supercooled liquids that has led to the interpretations of the results in terms of heterogeneous dynamics. In supercooled liquids, the Stokes shift correlation function decays non-exponentially and may be written as

$$C(t) = \int d\lambda p(\lambda) e^{-\lambda t}$$

with relaxation rates $\lambda$ and a distribution function $p(\lambda)$. Performing a so-called inhomogeneous cumulant expansion of the conditional probability, one finds

$$P(\omega, t|\omega_0) = \int d\lambda p(\lambda) P(\lambda)(\omega, t|\omega_0)$$

$$P(\lambda)(\omega, t|\omega_0) = \frac{1}{\sqrt{2\pi\sigma^2_\infty(1-e^{-2\lambda t})}} \exp\left(-\frac{[\omega - \omega_0 e^{-\lambda t}]^2}{2\sigma^2_\infty(1-e^{-2\lambda t})}\right)$$

instead of Eq.(3). For the first moment, one again finds $\langle \omega(t) \rangle = \Delta C(t)$, cf. Eq.(4), whereas the variance is given by

$$\sigma^2(t) = \sigma^2_\infty + (\sigma^2_0 - \sigma^2_\infty)C(t)^2 + \Delta^2 [C(2t) - C(t)^2]$$

This expression was found to give excellent agreement with the experimentally observed linewidth.

It is seen that according to Eq.(7) the stochastic process $\omega(t)$ can be viewed as originating from a superposition of Gaussian processes. This means that $\omega(t)$ is modeled as a non-Markovian Gaussian stochastic process. In the next Section we discuss various exchange models, with particular emphasis on the deviations from Gaussian behavior.

III. Calculation of frequency moments in exchange models

The simplest stochastic model for a process like solvation is a Gaussian Markov process, i.e. the OU-process. If the transition frequency $\omega(t)$ is modeled as an OU-process, one may consider the Langevin equation (LE):

$$\dot{\omega}(t) = -\gamma \omega(t) + \xi(t)$$

where $\xi(t)$ is a delta-correlated white noise, $\langle \xi(t) \rangle = 0$, $\langle \xi(t)\xi(t') \rangle = 2\sigma^2_\infty \gamma \delta(t - t')$ and $\gamma$ denotes the damping rate. The LE, Eq.(9), approximates the spectral diffusion process
as occurring on harmonic potential-energy surfaces. The transition frequency spreads in a
restoring potential \( V = (\gamma/2)\omega^2 \). Alternatively, one can consider the corresponding Fokker-
Planck equation (FPE) for the conditional probability:

\[
\dot{P}(\omega, t|\omega_0) = \dot{\Pi}^{FP}(\omega) P(\omega, t|\omega_0) \quad \text{with} \quad \dot{\Pi}^{FP}(\omega) = \gamma \left[ \frac{\partial}{\partial \omega} \omega + \sigma^2 \frac{\partial^2}{\partial \omega^2} \right] \tag{10}
\]

The resulting expression for \( P(\omega, t|\omega_0) \) is given by Eq.(3) with \( C(t) = \exp(-\gamma t) \). Therefore,
in order to have a model which yields a Stokes shift correlation function decaying non-
exponentially according to Eq.(3), one has to consider \( \omega(t) \) as a non-Markovian stochastic
process. In the present paper, this is achieved by considering exchange models. As already
indicated in the introduction, we restrict ourselves to two-state models, because these allow
for analytic solutions. The idea underlying such models can most easily be summarized in the
following way. We consider the solute to experience various surroundings characterized by an
environmental variable \( \epsilon_i, i \in \{s, f\} \). Thus, in a given environment, the spectral diffusion of
the optical transition frequencies \( \omega(t) \) occurs with a decay constant \( \gamma_i = \gamma(\epsilon_i) \). However, the
environments are not viewed to be static, but rather fluctuate in the course of time. These
environmental fluctuations are characterized by exchange rates \( \kappa_{i,k} = \kappa(\epsilon_i|\epsilon_k) \). In order to
further simplify the calculation, we take the exchange rates to be equal, \( \kappa_{s,f} = \kappa_{f,s} = \gamma_x \),
implying \( p^{eq}_i = p^{eq}(\epsilon_i) = 1/2 \). The generalization to a larger number of states is trivial. Also
other models, like energy landscape models\[23\], can be considered\[14\].

Even though we restrict ourselves to simple two-state models, we have to face the am-
biguity concerning the way of how to incorporate the exchange between the fast and slow
environments into the model. In the following, we consider two different, but in some way
strongly related ways of treating the rate exchange.

A. Master equation models

One class of models allowing to treat rate exchange processes can be defined by supple-
menting the FPEs in the slow and fast environments with some terms representing the
exchange process. This way one obtains rate equations for the conditional probability
\( P_{i,k}(\omega, t|\omega_0) \equiv P(\omega, \epsilon_i, t|\omega_0, \epsilon_k) \) for finding the pair \( \{\omega, \epsilon_i\} \) at time \( t \), given it had values
\( \{\omega_0, \epsilon_k\} \) at \( t=0 \). Still, we have to make some additional assumptions about what happens
with the value of \( \omega \) during the exchange process. Two limiting choices for this are the
following\[17, 19\]. Either one assumes that \( \omega \) does not change at all during a \( \epsilon_i \rightarrow \epsilon_k \) transition.
Alternatively, one allows \( \omega \) to randomize completely during such a transition, meaning
that after the transition \( \omega \) can take any value according to its statistical weight \( p^{eq}(\omega) \). Let
us start with the first choice. This is the same assumption that has often been used in
context of models for rotational and translational motions in supercooled liquids\[19, 21\] and
also in treatments of spectral diffusion\[13\].

We abbreviate the FP-operators in the fast and in the slow environments by \( \dot{\Pi}^{FP}_i(\omega) \). These operators are defined in Eq.(10), but with \( \gamma_i \) replacing \( \gamma \). We have to solve the coupled
FPEs:

\[
\dot{P}_{i,i}(\omega, t|\omega_0) = \dot{\Pi}_i^{FP}(\omega) P_{i,i}(\omega, t|\omega_0) - \gamma_x \left[ P_{i,i}(\omega, t|\omega_0) - P_{k,i}(\omega, t|\omega_0) \right] \quad ; \quad i \neq k \tag{11}
\]

Due to the coupling of the FPEs, the resulting \( P_{i,i}(\omega, t|\omega_0) \) are not Gaussians. Furthermore,
an analytical solution of Eq.(11) is not feasible. In order to calculate the spectral moments
or any other observable, an expansion in terms of the eigenfunctions of the FP operator \([24]\) is utilized, \(P_{i,k}(\omega, t|\omega_0) = e^{-\bar{\omega}^2 \sum_{n=0}^{\infty} N_n H_n(\bar{\omega}) H_n(\bar{\omega}_0) G_{i,k}^{(n)}(t)}\), where \(H_n(z)\) are Hermite polynomials, \(\bar{\omega}^2 = \omega^2/2\sigma^2\) and \(N_n^{-1} = 2^n n! (2\pi\sigma^2)^{1/2}\). Using this expression in the FPEs, Eq.(I), results in the following equations for the Green’s functions:

\[
\frac{\partial}{\partial t} G_{i,l}^{(n)}(t) = -(n\gamma_i) G_{i,l}^{(n)}(t) - \gamma_x \left[ G_{i,l}^{(n)}(t) - G_{k,l}^{(n)}(t) \right] \quad \text{where} \quad k \neq i
\]

which can be solved easily. In the following, we assume \(\sigma_0 = \sigma_\infty\) for simplicity. For the lowest-order spectral moments one finds, after performing the \(\omega\)-integrations:

\[
\begin{align*}
\langle \omega(t) \rangle &= \Delta C_1(t) \\
\langle \omega^2(t) \rangle &= \sigma^2_\infty + \Delta^2 C_2(t)
\end{align*}
\]

Furthermore, one has \(\langle \omega^3(t) \rangle = 3\Delta \sigma^2_\infty C_1(t) + \Delta^3 C_3(t)\) and \(\langle \omega^4(t) \rangle = 3\sigma^2_\infty + 6\sigma^2_\infty \Delta^2 C_2(t) + \Delta^4 C_4(t)\). In principle, all moments are accessible this way, although the calculations become rather tedious. It is important to notice at this point that the \(n\)th moment \(\langle \omega^n(t) \rangle\) is determined by the functions

\[
C_n(t) = \frac{1}{2} \sum_{i,k} G_{i,k}^{(n)}(t) = p_s^{(n)} \exp[-\gamma_s^{(n)} t] + p_f^{(n)} \exp[-\gamma_f^{(n)} t]
\]

Here, the \(p_s^{(n)}\) and \(\gamma_i^{(n)}\) are determined by the solution of Eq.(12):

\[
p_s^{(n)} = \frac{1}{2} \left( 1 \pm \frac{2\gamma_x}{Z_n} \right) \quad \gamma_s^{(n)} = \frac{1}{2} \left( 2\gamma_x + n(\gamma_f + \gamma_s) \mp Z_n \right)
\]

with \(Z_n = \sqrt{(n^2(\gamma_f - \gamma_s)^2 + 4\gamma_x^2)}\)

In Fig.1a we plotted the Stokes shift correlation function \(C_1(t) \equiv C(t)\) versus time. For the parameters chosen it is clearly seen that mainly the long time decay is affected by a finite exchange rate \(\gamma_x\). Fig.1b shows the time-dependent part of the variance, \(\sigma^2_{sc.}(t) = \frac{1}{2} \left( \sigma^2(t) - \sigma^2_\infty \right) / \Delta^2\) versus time for the same parameters. Additionally shown is the result of the Gaussian approximation, \(C_1(2t) - C_1(t)^2\), cf. Eq.(8). Remember, that this expression is in excellent agreement with the available experimental data\([13]\). It is clearly seen that \(\sigma^2_{sc.}(t)\) exceeds this expression, in particular in the time range, where both functions exhibit their maximum. It is exactly this excess observed for this particular model that previously led to the incorrect conclusion that the experimental data are only compatible with a long-lived dynamic heterogeneity\([13]\). In the present model the differences between \(\sigma^2_{sc.}(t)\) and \(C_1(2t) - C_1(t)^2\) originate solely from the fact, that the stochastic process \(\omega(t)\) is not only non-Markovian, but also non-Gaussian.

From the expressions given in Eq.(13) for \(n \gg 1\) one approximately has \(\gamma_s^{(n)} \approx \gamma_x + n\gamma_s/f\) and \(p_s^{(n)} \approx 1/2 \pm \gamma_x / (n(\gamma_f - \gamma_s))\). Therefore, using the parameters of Fig.1, one finds that even for \(n=100\) the exchange rate \(\gamma_x\) still contributes on the order of 30\% to \(\gamma_s^{(100)}\). In Fig.2 we show the quantities \(\zeta_n(t) = C_n(t) - C_1(nt)\). These give a measure for the deviations from a Gaussian behavior because in that case one has \(\zeta_n(t) \equiv 0\) for all \(n > 0\). This plot nicely illustrates the fact just discussed. With increasing \(n\) the maximum \(\zeta_n(t)\) is shifted towards
shorter times $t_{\text{max}, n}$, Fig.2a. However, one can see that the maximum of $\zeta_n(t)$ roughly occurs at $n \times t_{\text{max}, n} \sim \gamma_x^{-1}$, as shown in Fig.2b. This shows that not only the first few moments are affected by the deviations from Gaussian behavior in this model, but that these deviations even increase with $n$.

In the above treatment we considered the case in which the transition frequencies $\omega(t)$ do not change during a $\epsilon_i \rightarrow \epsilon_k$ transition. We already discussed that another extreme scenario would be defined by allowing $\omega(t)$ to randomize during such a transition. We just mention that for this model the eigenvalues for $n=0$ remain the same as in the case considered above. For finite $n$, however, one has $p^{(n)}_{i/f} = 1/2$ and $\gamma^{(n)}_{i/f} = \gamma_x + n\gamma_{s/f}$. Thus, the qualitative features are not very different in this case. In particular, in these exchange models the stochastic process $\omega(t)$ is non-Markovian and non-Gaussian.

**B. Langevin equation models**

Instead of starting from the coupled FPEs, Eq.(11), one can also define an exchange model by considering coupled Langevin equations. In such models one associates a value $\omega_i(t)$ with either of the states $i = s, f$ and introduces an additional exchange term, cf. Eq.(9):

$$\dot{\omega}_i(t) = - (\gamma_i + \gamma_x) \omega_i(t) + \gamma_x \omega_k(t) + \xi_i(t)$$

(16)

where again $i \neq k$ and $\xi_i(t)$ is a delta-correlated white noise, meaning that $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t) \xi_k(t') \rangle = \Gamma_{i,k} \delta(t - t')$. Note, that here we do not have different choices for the incorporation of exchange effects, since by definition the LE model involves diffusive motions only. Therefore, in such a model $\omega$ changes by an infinitesimal amount during an $\epsilon_i \rightarrow \epsilon_k$ transition. The solution of Eq.(16) results in two-dimensional Gaussians for the conditional probabilities. In order to show how the results are related to the ones obtained for the FPEs, we proceed in the following way. We introduce the eigenvalues $\lambda_\alpha$ and the corresponding eigenvectors $|\alpha\rangle$ of the matrix $W$ defined in Eq.(11). In such a notation we have $W_{i,k} = \langle i|W|k\rangle$, $W_{s,s} = -\gamma_s - \gamma_x$, $W_{f,f} = -\gamma_f - \gamma_x$, $W_{s,f} = W_{f,s} = \gamma_x$ and $\omega_i(t) = \langle i|\omega(t)\rangle$. Correspondingly, using $\sum_{\alpha} |i\rangle \langle i| = \sum_{\alpha} |\alpha\rangle \langle \alpha| = 1$ and the orthonormality of the vectors, we have $\omega_i(t) = \sum_{\alpha} \langle i|\alpha\rangle \omega_\alpha(t)$ and $W_{i,k} = \sum_{\alpha} \langle i|\alpha\rangle \lambda_\alpha \langle \alpha|k\rangle$. This yields the decoupled LEs:

$$\dot{\omega}_\alpha(t) = \lambda_\alpha \omega_\alpha(t) + \xi_\alpha(t)$$

(17)

from which it is immediately evident that the solutions for the corresponding $P_{\alpha}(\omega, t|\omega_0)$ are Gaussians determined by the correlation functions $C_{\alpha}(t) = \langle \omega_\alpha(t)\omega_\alpha(0)\rangle$. In Eq.(17), the projections of the noise give $\langle \xi_\alpha(t) \xi_\alpha(t') \rangle = \Gamma_{\alpha} \delta(t - t')$. Choosing $\Gamma_{i,k} = -2\sigma_{\infty} W_{i,k}$ yields $\Gamma_{\alpha} = -2\lambda_\alpha$. For the moments one finds:

$$\langle \omega_\alpha(t) \rangle = \langle \omega_\alpha(0) \rangle e^{\lambda_\alpha t} \quad \text{and} \quad \langle \omega_\alpha^2(t) \rangle = \langle \omega_\alpha^2(0) \rangle e^{2\lambda_\alpha t} + \sigma_{\infty}^2 \left( 1 - e^{2\lambda_\alpha t} \right)$$

(18)

and the correlation function is given by $C_{\alpha}(t) = \langle \omega_\alpha^2(0) \rangle e^{\lambda_\alpha t}$. For an arbitrary observable the expectation value is given by $\langle A(t) \rangle = (1/2) \sum_{\alpha} \langle A_\alpha(t) \rangle$, and thus

$$\langle \omega(t) \rangle = \Delta C_1(t) \quad \text{and} \quad \langle \omega^2(t) \rangle = \sigma_{\infty}^2 + \Delta^2 C_1(2t)$$

(19)

where the $C_{\alpha}(t)$ are defined in Eq.(14). Therefore, the time-dependent variance in this model is given by $\sigma_{\alpha}^2(t) = \sigma_{\infty}^2 + \Delta^2[C_1(2t) - C_1(t)^2]$, cf. Eq.(8). In Fig.1b, $C_1(2t) - C_1(t)^2$ is shown.
as the dashed line. The mathematical reason for the behavior of the moments, Eq. (19), lies in the fact that the matrix $W$ defined in Eq. (16) is identical to the one for $G^{(1)}_{i,k}(t)$ defined in Eq. (12). This means that the eigenvalues $\lambda_a$ are just given by $\lambda_{s/f} = -\gamma^{(1)}_{s/f}$ according to Eq. (15). The conclusion from this observation is that the Langevin model considered here is nothing but the Gaussian version of the master equation model studied above. A simple calculation shows that the LEs, Eq. (16), considered here corresponds to the coupled FPEs $\dot{P}_{i,l}(\omega, t|\omega_0) = \sum_k \hat{\Pi}^{FP}_{ik}(\omega)P_{k,l}(\omega, t|\omega_0)$. Here, $\hat{\Pi}^{FP}_{ik}(\omega)$ is obtained from Eq. (10) by the replacement $\gamma \rightarrow (-W_{i,k})$. The important point is that in this model $\omega(t)$ is a non-Markovian Gaussian process.

IV. Discussion and Conclusions

In the preceding section we have analyzed simple exchange models that allow one to account for fluctuations in dynamic heterogeneous systems. In the particular example of solvation dynamics we have focussed on the calculation of the lowest-order moments of the transition frequency distributions. Despite its simplicity this example allows to discuss various aspects of dynamic heterogeneity. In particular, without exchange the transition frequency $\omega(t)$ constitutes a Gaussian Markov process, the OU process. This is among the simplest stochastic processes one can study.

We have investigated different variants of the models to incorporate the way in which exchange processes change the temporal evolution of the conditional probability. These exchange processes are modeled as transitions between different environments, characterized by different values of an additional stochastic process $\epsilon(t)$. In the master equation models one has to make specific assumptions about the effect of exchange on the stochastic process $\omega(t)$. We discussed only two extreme choices. One choice, which also has been used in many earlier investigations, corresponds to the assumption that the processes $\omega(t)$ and $\epsilon(t)$ are uncorrelated. This means that $\omega(t)$ is not at all affected by a change in $\epsilon(t)$, i.e. by exchange. We have shown that the equations determining the moments $\langle \omega^n(t) \rangle$ can then be solved analytically. This allows to discuss their behavior in some detail. A very important finding is that in this case the process $\omega(t)$ is neither Gaussian nor Markovian for finite exchange rates $\gamma_x$. In contrast, when studying a Langevin model, we found that in that case $\omega(t)$ also is non-Markovian but Gaussian. Therefore, using this model yields excellent agreement with the experimental data for arbitrary choices of the exchange rates. This, however, is not astonishing because according to Eq. (7) any model that yields a description of $\omega(t)$ in terms of a non-Markovian Gaussian stochastic process will give results compatible with the experimental data.

The most important point in the discussion of the lifetime of the dynamic heterogeneities appears to be the question as to how to quantify this lifetime. It has been stressed earlier that this cannot be achieved by any two-time correlation function. This fact stimulated the development of NMR techniques to study higher-order time correlation functions. A comparison of the conditional probabilities $P(\omega, t|\omega_0)$ with two-dimensional NMR spectra shows that these are identically the same if $\omega$ is reinterpreted as the spin-precession frequency. The mentioned time dependence of $\langle \omega(t) \rangle$ that is absent in NMR does not enter the discussion here, because this time dependence does not alter $P(\omega, t|\omega_0)$. Thus, even if the full conditional probability would be known, one could not obtain information about
the heterogeneity lifetime. However, knowledge of higher moments would allow to better specify the detailed 'geometric' properties of the spectral diffusion process. In particular, one could get information about possible deviations from diffusive behavior, which was our starting point in this paper. It is exactly this issue which can be treated very efficiently by 2d-NMR methods. One can clearly distinguish between rotational diffusion and rotational jump models[27].

The comparison between the spectral diffusion process and the reorientational motion of molecules in supercooled liquids further shows the different impact of exchange on various models. Rotational diffusion (or also rotations by finite jumps) represents a Markov process. This process, however, is not Gaussian. Therefore, in this example it hardly matters in which way exchange processes are incorporated. By contrast, in the example of spectral diffusion, different ways of treating exchange give different results concerning the properties of the resulting stochastic process. As discussed above, using master equation models usually will destroy the Gaussian properties of $\omega(t)$. Therefore, in this case one has a larger variety of modifications that can be achieved by considering various exchange models.

In conclusion, we have investigated different scenarios for exchange processes in dynamically heterogeneous systems. Starting from a Gaussian Markov process, we have shown that different assumptions concerning the coupling of $\omega(t)$ to the exchange processes yield different results. In particular, if the values of $\omega$ change continuously during an exchange process the resulting stochastic process is non-Markovian but still Gaussian. Such a 'diffusive' change of $\omega(t)$ during exchange of course means that the effect of 'exchange' ($\gamma_x$) is very similar to the one of 'relaxation' ($\gamma_{s/f}$). In contrast, if exchange does not at all affect the values of $\omega$ or if it causes them to change discontinuously also the Gaussian properties of the resulting stochastic process is lost. In any case, deviations from a Gaussian behavior are not good candidates for the determination of heterogeneity lifetimes. Still, they may be helpful in discriminating among various variants of exchange models.

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Figure captions

Fig.1 : The first and second moments versus time for the master equation model.
   a: The Stokes shift correlation function $C_1(t)$ according to Eq.(14) versus time for
      $\gamma_s=0.1s^{-1}$, $\gamma_f=10.0s^{-1}$, $\gamma_x=0.33s^{-1}$ (full line) and $\gamma_x=0$ (dotted line).
   b: The time-dependent part of variance, $\sigma_n^2(t) = [\sigma^2(t) - \sigma^2_\infty]/\Delta^2$, versus time (full
      line) for $\gamma_x=0.33s^{-1}$. Also shown is $C_1(2t) - C_1(t)^2$ as dashed line. This corresponds
      to the time-dependent part of the variance in the Langevin equation model. The $\gamma_s$ and $\gamma_f$
      are the same as in (a).

Fig.2 : The quantities $\zeta_n(t) = C_n(t) - C_1(nt)$ versus time for the same parameters as in
   Fig.1 ($\gamma_x=0.33s^{-1}$). a: $\zeta_2(t)$: full line, $\zeta_{10}(t)$: dashed line, $\zeta_{20}(t)$: dot-dashed line and
   $\zeta_{100}(t)$: dotted line.
   b: The same $\zeta_n(t)$ as in (a) are plotted versus the scaled time ($nt$). The arrow indicates
      $\gamma_x^{-1}=3.0s$. 

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Diezemann et al., Fig. 1

(a) $\gamma_s = 0.1 \, \text{s}^{-1}$

$\gamma_f = 10.0 \, \text{s}^{-1}$

$\gamma_x = 0.33 \, \text{s}^{-1}$

$\gamma_x = 0$

(b) $\gamma_x = 0.33 \, \text{s}^{-1}$
Diezemann et al., Fig. 2