

Dynamic heterogeneity, spatially distributed stretched-exponential patterns, and transient dispersions in solvation dynamics

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In the context of determining the extent of dynamical heterogeneity of relaxation processes, it has proven useful to represent the ensemble-averaged autocorrelation function $\phi(t)$ in the general form $\phi(t) = \int g(\tau)\chi(t/\tau)d\tau$, instead of focusing on the usual special case in which the basis functions $\chi(t/\tau)$ are exponentials. In practice, $\phi(t)$ is often fit by a stretched exponential, $\phi(t) = \exp[-(t/\tau)^\beta]$. Here we analyze the properties of the probability density $g(\tau)$ for the case in which $\phi(t)$ is a superposition of stretched exponentials, and is itself a stretched exponential, with a stretching exponent greater than or equal to those of the basis functions, $\chi(t/\tau)$. Various degrees of nonexponentiality intrinsic in each basis function translate into different values for the time-dependent variance $\sigma^2(t)$ of the stochastic quantity $\chi(t/\tau)$, in which τ is considered to be a spatially varying characteristic time scale. We state a simple but exact solution for $\sigma^2(t)$, and assess its relation to experimental data on the inhomogeneous optical linewidth $\sigma_{\text{inh}}(t)$, measured in the course of solvation processes in a supercooled liquid.

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I. INTRODUCTION

The primary relaxation in most glass-forming materials deviates strongly from a single exponential response pattern, especially near the glass-transition temperature T_g [1,2]. The experimental approach to the relaxation behavior is usually given in terms of the decay of a (normalized) autocorrelation function $\phi(t) = \langle \mu(t)\mu(0) \rangle / \langle \mu(0)\mu(0) \rangle$, in which $\mu(t)$ (e.g., a dipole moment) is measured following a perturbation at $t=0$. Typically, an experiment probes the ensemble average, in the sense that only the net effect of a large number of contributions from different sites within a sample is measured. Regarding this statistical average over all relaxors (relaxing entities) in the sample volume, one usually observes a nonexponential decay of the autocorrelation function $\phi(t)$. Because the individual contributions are not necessarily identical, we express $\phi(t)$ as a superposition of site-specific responses, $\phi(t) = \sum c_i \chi_i(t)$, without presuming the $\chi_i(t)$ to be themselves exponential. Such an ensemble-averaged dispersive relaxation pattern can be rationalized in two ways [3]. In the dynamically heterogeneous picture, the individual contributions are assumed to be purely exponential, $\chi_i(t) \propto \exp[-t/\tau_i]$, but subject to a (spatial) distribution of time scales τ_i . In the other extreme, the homogeneous picture, the contributions to $\phi(t)$ are not site specific, i.e., $\phi(t) \propto \chi_i(t)$.

For an experimental assessment of the nature of relaxation dynamics, one is confronted with the fact that a typical experiment has access only to the ensemble-averaged response of the material, whereas the individual contributions are not necessarily identical. In fact, recent experiments [4–8] and

simulations [9,10] aimed at discriminating between heterogeneous and homogeneous models of the dynamics indicate clearly that the relaxation time scale is a spatially varying quantity. However, the observation of heterogeneity or dynamical selectivity is not necessarily associated with purely exponential response functions for the individual relaxors [11,12]. On a gradual scale ranging from the heterogeneous to the homogeneous limit, one has to allow for the case of a certain degree of intrinsic nonexponentiality (or homogeneity) combined with site-specific time scales.

The following two heuristic expressions are commonly used to model $\phi(t)$. In many cases, the stretched exponential or Kohlrausch-Williams-Watts [13] (KWW) decay function

$$\phi(t) = \exp[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}], \quad 0 < \beta_{\text{KWW}} \leq 1 \quad (1)$$

captures the characteristic features of such (normalized) relaxation processes [1–3,14]. A common alternative analysis of decay patterns is in terms of a probability density $g(\tau)$ for finding a site related to the single time constant τ , such that the ensemble-averaged decay reads

$$\phi(t) = \int_0^\infty g(\tau) e^{-t/\tau} d\tau. \quad (2)$$

Equation (2) is usually associated with the idea of dynamic heterogeneity, i.e., that the characteristic time scale τ is a stochastic quantity, and that each site contributes exponentially to the overall decay [15–18]. Finding an appropriate $g(\tau)$ for a given set of $\phi(t)$ data is not decisive regarding the nature of the underlying processes, because any decay can be cast into the form of Eq. (2), even if the assumption of an exponential integral kernel, $\exp[-t/\tau]$, is conceptually inappropriate.

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A more general approach to a response pattern can be obtained by relaxing the condition of an exponential integral kernel in Eq. (2), i.e., expressing $\phi(t)$ as [3]

$$\phi(t) = \int_0^\infty g(\tau) \chi(t, \tau) d\tau. \quad (3)$$

Equation (3) is meant to describe the situation of uncoupled relaxors associated with a common nonexponentiality of decay patterns $\chi(t, \tau)$, but subject to a distribution of characteristic relaxation times τ [11,12]. The function $g(\tau)$ represents the probability density for finding a site with a time constant τ , and possible temporal fluctuations of the τ 's are ignored. Two special cases of Eq. (3), $g(\tau) = \delta(\tau - \tau_0)$ and $\chi(t) = \exp[-t/\tau]$, correspond to the purely homogeneous and heterogeneous pictures, respectively. Note, however, that various degrees of heterogeneity can be introduced by gradually changing the extent of non-exponentiality of $\chi(t)$ and adjusting $g(\tau)$ accordingly, so that a large number of equally adequate fits are obtained for a given data set of $\phi(t)$, but each associated with very different natures regarding the underlying molecular mechanisms of the relaxation process.

Because of their practical importance to experimental results, we focus on KWW-type decay functions, $\phi(t) = \exp[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}]$ and $\chi(t) = \exp[-(t/\tau)^{\beta_{\text{intr}}}]$, with only one parameter β which governs the deviation from exponential behavior. The degree of nonexponentiality *intrinsic* in each relaxor is measured by β_{intr} . Therefore, we confine the problem to the more specialized but practically relevant equation

$$\phi(t) = \exp[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}] = \int_0^\infty g(\tau) \exp[-(t/\tau)^{\beta_{\text{intr}}}] d\tau. \quad (4)$$

The scope of this work is to outline the necessary properties of the probability density $g(\tau)$ in order to satisfy Eq. (4) as a function of β_{KWW} and β_{intr} . In a second step, we demonstrate that different degrees of dynamical heterogeneity translate into a β_{intr} -dependent variance $\sigma^2(t)$ regarding the intrinsic responses $\exp[-(t/\tau)^{\beta_{\text{intr}}}]$. We state an exact expression for $\rho(t) = \sigma^2(t)$ for an arbitrary ensemble-averaged decay $\phi(t)$, and address its properties in Sec. II. A brief summary of previous experimental results on the time-dependent optical linewidth $\sigma_{\text{inh}}(t)$ derived from a solvation dynamics study is given in Sec. III. Section IV then establishes the link between the analytical result for $\rho(t)$ and the experimental quantity $\sigma_{\text{inh}}(t)$ and the implications regarding the nature of relaxation processes.

II. RESULTS

In what follows, $g(\tau)$ is understood as being the probability density which satisfies Eq. (4) for an arbitrary $\tau_{\text{KWW}} > 0$, and for any exponents β within the limits $0 < \beta_{\text{KWW}} < \beta_{\text{intr}} \leq 1$, whereas $\beta_{\text{KWW}} = \beta_{\text{intr}}$ leads to $g(\tau) = \delta(\tau - \tau_{\text{KWW}})$. We denote the n th moment of $g(\tau)$ by α_n , and the n th central moment of $g(\tau)$ by μ_n :

$$\alpha_n = \langle \tau^n \rangle = \int_0^\infty \tau^n g(\tau) d\tau,$$

$$\mu_n = \langle (\tau - \langle \tau \rangle)^n \rangle = \int_0^\infty (\tau - \langle \tau \rangle)^n g(\tau) d\tau. \quad (5)$$

We will refer only to normalized decays $\phi(0) = 1$, such that $\alpha_0 = \int g(\tau) d\tau = 1$ is demanded. We have calculated all moments α_n of $g(\tau)$, with the result

$$\begin{aligned} \alpha_n = \langle \tau^n \rangle &= \tau_{\text{KWW}}^n \frac{\beta_{\text{intr}} \Gamma(n/\beta_{\text{KWW}})}{\beta_{\text{KWW}} \Gamma(n/\beta_{\text{intr}})} \\ &= \tau_{\text{KWW}}^n \frac{\Gamma(1+n/\beta_{\text{KWW}})}{\Gamma(1+n/\beta_{\text{intr}})}, \end{aligned} \quad (6)$$

where $\Gamma(z)$ denotes Euler's gamma function. The function $g(\tau)$ can thus be represented by the inverse Fourier transform of the above results:

$$\begin{aligned} \tau g(\tau) &= g^*(\ln \tau) \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} (\tau/\tau_{\text{KWW}})^{i\sigma} \frac{\Gamma(1-i\sigma/\beta_{\text{KWW}})}{\Gamma(1-i\sigma/\beta_{\text{intr}})} d\sigma. \end{aligned} \quad (7)$$

By a simple transformation, solving Eq. (7) can be reduced to solving the special case $\beta_{\text{intr}} = 1$, for which a series expansion has been obtained earlier [19]. As result for all cases $0 < \beta_{\text{KWW}} < \beta_{\text{intr}} \leq 1$, we obtain

$$\tau g(\tau) = g^*(\ln \tau) = \beta_{\text{intr}} \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{(\tau/\tau_{\text{KWW}})^{n\beta_{\text{KWW}}}}{\Gamma(-n\beta_{\text{KWW}}/\beta_{\text{intr}})}. \quad (8)$$

For practical purposes, it is often desirable to have the logarithmic moments $\alpha_n^* = \langle \xi^n \rangle$ and central moments $\mu_n^* = \langle (\xi - \langle \xi \rangle)^n \rangle$ for $\xi \equiv \ln(\tau)$, and with respect to the probability density $g^*(\xi)$, which is related to $g(\tau)$ via $g^*(\xi) d\xi = g(\tau) d\tau$ or $g^*(\xi) = \tau g(\tau)$. The results for the mean α_1^* , the variances μ_2^* , and μ_3^* (related to the skewness defined either by $\mu_3^* \mu_2^{*-3/2}$ or by $\mu_3^{*2} \mu_2^{*-3}$) are

$$\begin{aligned} \alpha_1^* = \langle \xi \rangle &= \ln(\tau_{\text{KWW}}) + \psi(1) [\beta_{\text{KWW}}^{-1} - \beta_{\text{intr}}^{-1}], \\ \mu_2^* = \langle (\xi - \langle \xi \rangle)^2 \rangle &= \psi'(1) [\beta_{\text{KWW}}^{-2} - \beta_{\text{intr}}^{-2}], \\ \mu_3^* = \langle (\xi - \langle \xi \rangle)^3 \rangle &= \psi''(1) [\beta_{\text{KWW}}^{-3} - \beta_{\text{intr}}^{-3}]. \end{aligned} \quad (9)$$

In Eq. (9), $\psi^{(n)}(z) = d^n \ln \Gamma(z) / dz^n$ denotes the polygamma functions with $\psi(1) = -\gamma$ (Euler's constant, $\gamma \approx 0.577\dots$), $\psi'(1) = \pi^2/6$, and $\psi''(1) = -2\zeta(3)$, $\zeta(z)$ being Riemann's zeta function. Note that in general $\mu_n^* \neq \psi^{(n-1)}(1) [\beta_{\text{KWW}}^{-n} - \beta_{\text{intr}}^{-n}]$ for $n > 3$. Some details on calculating the linear and logarithmic moments of $g(\tau)$ and $g^*(\ln \tau)$ without invoking integral transforms are outlined in the Appendix.

The function $\chi(t)$, the integral kernel in Eq. (4), has been introduced as the individual relaxation contribution of a site with characteristic time scale τ . Since the value of τ varies from site to site whenever $\beta_{\text{intr}} > \beta_{\text{KWW}}$, it can be considered a random variable. Obviously, variations in τ lead to variations regarding the site-specific decay functions $\chi(t) = \exp[-(t/\tau)^{\beta_{\text{intr}}}]$, such that $\chi(t)$ is a function which varies statistically from site to site. For reasons which will be explained below, we calculate the mean and variance of $\chi(t)$

for a given ensemble-averaged decay $\phi(t)$, i.e., for a given probability density $g(\tau)$. The mean, $\langle\chi(t)\rangle$, is directly given by Eq. (3), $\langle\chi(t)\rangle = \phi(t)$. The dispersion or variance of $\chi(t)$, $\rho(t)$, can be obtained accordingly using Eq. (4),

$$\rho(t) = \langle[\chi(t) - \langle\chi(t)\rangle]^2\rangle = \phi(2^{1/\beta_{\text{intr}}t}) - [\phi(t)]^2, \quad (10a)$$

with $\rho(t=0) = \rho(t \rightarrow \infty) = 0$.

For the case of current interest, $\phi(t) = \exp[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}]$, we have

$$\rho(t) = \langle[\chi(t) - \langle\chi(t)\rangle]^2\rangle = \phi(2^{1/\beta_{\text{intr}}t}) - \phi(2^{1/\beta_{\text{KWW}}t}), \quad (10b)$$

with $\rho(t) = 0$ if $\beta_{\text{intr}} = \beta_{\text{KWW}}$, and with $\rho(t)$ attaining a maximum whenever $\beta_{\text{intr}} > \beta_{\text{KWW}}$. The position t_{max} at which (for finite values of t) the slope of $\rho(t)$ vanishes, $d\rho(t)/dt = 0$, is

$$t_{\text{max}} = \tau_{\text{KWW}} \theta^{1/\beta_{\text{KWW}}}, \quad \theta = \ln(2)[1 - \lambda]/[2 - 2^\lambda], \quad \lambda = \beta_{\text{KWW}}/\beta_{\text{intr}}. \quad (11)$$

The amplitude at the peak position, $\rho_{\text{max}} = \rho(t_{\text{max}})$, can be written as $\rho_{\text{max}} = \exp[-2^\lambda \theta] - \exp[-2\theta]$, which is bounded to $\rho_{\text{max}} \leq \frac{1}{4}$. Finally, we define the standard deviation of $\chi(t)$, $\sigma(t) = \sqrt{\rho(t)}$, and its peak value $\sigma_{\text{max}} = \sigma(t_{\text{max}})$, with $\sigma_{\text{max}} \leq \frac{1}{2}$. It is worth noting that the values of ρ_{max} and σ_{max} depend only on the key parameters β_{intr} and β_{KWW} in the form of the ratio $\lambda = \beta_{\text{KWW}}/\beta_{\text{intr}}$.

III. SOLVATION DYNAMICS

A brief summary of the experimental technique referred to, phosphorescence solvation dynamics, appears in order. The technique of phosphorescence solvation dynamics involves the time-resolved emission spectra of probe molecules dissolved at low concentration in a polar material. At time $t=0$, the chromophores are electronically excited from their ground state S_0 to their excited state T_1 , thereby inducing a change $\Delta\mu = \mu_E - \mu_G$ in the permanent dipole moment of the probes [20]. The effect of this transition is to initiate a dielectric relaxation process within the solvent [21], such that the emission energy $\nu_i(t)$ of each probe molecule i decreases with time, whenever orientational polarization is active within the excited state lifetime. The mean emission energy $\nu(t) = \langle\nu_i(t)\rangle$ reflects the average dynamics of the Stokes shift, which closely follows the macroscopic dielectric modulus $M(t)$ of the solvent, as has been demonstrated quantitatively [22]. The total Stokes shift on the energy scale is given by $\Delta\nu = \nu(0) - \nu(\infty)$, and the normalized decay can be represented by $C(t) = [\nu(t) - \nu(\infty)]/\Delta\nu$. At time $t=0$, the emission spectrum resembles a Gaussian profile characterized by its mean $\nu(0)$ and standard deviation $\sigma_{\text{inh}}(0)$. In the equilibrium state $t \rightarrow \infty$, the spectrum is again of Gaussian shape with $\sigma_{\text{inh}}(\infty) = \sigma_{\text{inh}}(0) = \sigma_0$. Therefore, this optical experiment not only observes the approach of the average energy $\nu(t)$ toward equilibrium, but also the distribution of site-specific solvation free energies in terms of the entire emission profile or in terms of its second central moment quantified by $\sigma_{\text{inh}}^2(t)$. It is important to realize that σ_{inh} refers to the *inhomogeneous* linewidth, where the energetic disper-

sion stems from a distribution of site-specific free energies and where the *homogeneous* linewidth of an individual emitter, σ_{hom} , remains negligible. The contributions of σ_{hom} to the observed optical linewidth remain small only at sufficiently low temperatures, where the dephasing times are accordingly large. For this reason, fluorescent probes are inappropriate for measuring $\sigma_{\text{inh}}(t)$. Note that the issue of inhomogeneous versus homogeneous optical broadening bears no direct relation to the problem of dynamic heterogeneity versus dynamic homogeneity.

For a system in thermodynamic equilibrium, the theory states that inhomogeneously broadened optical lines are of Gaussian shape, and that their variance σ_0^2 and response amplitude $\Delta\nu$ are related by [23,24]

$$\frac{\sigma_0^2}{\Delta\nu} = \frac{(\mu_G - \mu_E)kT}{ch\mu_E}, \quad (12)$$

i.e., this ratio no longer depends on the thermodynamic state of the solvent under steady state conditions. Therefore, the values of $\Delta\nu$ and σ_0 cannot be tailored independently by experimental conditions.

Similar to a dielectric relaxation experiment yielding the time-dependent susceptibility $\varepsilon(t)$, phosphorescence solvation dynamics probe the relaxation process due to orientational molecular motion in terms of $C(t)$. In the present context, the important feature of the solvation results is their additional information, $\sigma_{\text{inh}}(t)$, regarding the possible spatial variation of site-specific contributions to $C(t)$. Although such $\sigma_{\text{inh}}(t)$ data have recently been analyzed in terms of dynamic heterogeneity [8,12] by approximate simulation procedures, no analytical expression has been advanced so far which rationalizes the time-dependent width $\sigma_{\text{inh}}(t)$ of inhomogeneously broadened optical emission profiles. As we will show below, the function $\rho(t)$ in Eq. (10) is the key ingredient for modeling the time dependence of $\sigma_{\text{inh}}(t)$.

IV. DISCUSSION

Casting the possible spatial variation of response patterns in disordered materials into a probability density $g(\tau)$ of relaxation times is common practice. However, the ensemble-averaged relaxation function $\phi(t)$ is usually represented by a superposition of purely exponential contributions, which corresponds to our limiting case of heterogeneity with $\beta_{\text{intr}} = 1$. Only recently, it has been recognized that Eq. (4) is a practical approach for assessing the intermediate situations between the homogeneous and heterogeneous extremes [11,12]. Since solving Eq. (4) is more general than seeking for the $g(\tau)$ which results in a KWW type $\phi(t)$ in Eq. (2), we do not expect to find an expression for $g(\tau)$ much simpler than Eq. (8) for arbitrary values of the intrinsic dispersion measured by β_{intr} . The special case $\beta_{\text{intr}} = 1$ and $n = 1$ in Eq. (6) leads to the well known expression for the average KWW time scale, $\langle\tau\rangle_{\text{KWW}} = \tau_{\text{KWW}}\Gamma(1/\beta_{\text{KWW}})/\beta_{\text{KWW}}$ [19]. Also, the formulas for the mean α_1^* , variance μ_2^* , and skewness μ_3^* as regards $\xi = \ln(\tau)$ represent generalizations of former results [25] for the special case $\beta_{\text{intr}} = 1$. The above exact expressions for the moments of $g(\tau)$ and $g^*(\ln \tau)$ for arbitrary parameters within the limits $0 < \beta_{\text{KWW}} < \beta_{\text{intr}} \leq 1$ are especially of interest when approxi-

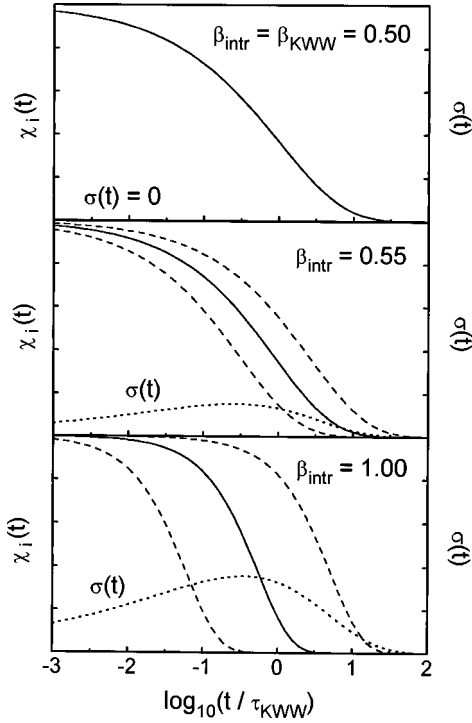


FIG. 1. Individual relaxation patterns $\chi_i(t)$ for an ensemble-averaged decay $\phi(t) = \langle \chi_i(t) \rangle$ of the KWW type with $\tau_{\text{KWW}} = 1$ and $\beta_{\text{KWW}} = 0.5$ and for various values of $\beta_{\text{intr}} = 0.50, 0.55,$ and 1.00 . The decays $\chi_i(t)$ in each panel are traces of $\exp[-(t/\tau_i)^{\beta_{\text{intr}}}]$ with $\ln(\tau_i) = \alpha_1^* - \sqrt{\mu_2^*}$ (left dashed line), α_1^* (solid line), and $\alpha_1^* + \sqrt{\mu_2^*}$ (right dashed line), i.e., at $\ln(\tau_i) = \langle \ln(\tau_i) \rangle \pm$ the standard deviation of $\ln(\tau_i)$. The dotted $\sigma(t)$ curves represent the standard deviations of the site specific decays, $(\langle \chi_i(t)^2 \rangle - \langle \chi_i(t) \rangle^2)^{1/2}$. The ensemble averaged decay $\phi(t)$ is identical for all three situations, and therefore reflects only partial information on the relaxation process.

mate expressions for $g(\tau)$ are required, which are easier to handle than the form of Eq. (8).

In the following, we will focus on the variance or dispersion of the intrinsic decay function $\chi(t) = \exp[-(t/\tau)^{\beta_{\text{intr}}}]$ as a function of β_{intr} . The average $\langle \chi(t) \rangle$ is directly given by Eq. (4), $\langle \chi(t) \rangle = \phi(t)$. For the variance $\rho(t)$ we have $\rho(t) = \langle [\chi(t) - \langle \chi(t) \rangle]^2 \rangle = \phi(2^{1/\beta_{\text{intr}}}) - [\phi(t)]^2$ from Eq. (10a), without having to specify a particular function for $\phi(t)$. The interpretation of $\rho(t)$ is as follows. If it were possible to detect the normalized responses $\chi_i(t)$ of the individual relaxors ($i = 1, \dots, N$) within the material under study, then the variance of amplitudes at time t is given by $\rho(t)$. Figure 1 outlines different situations for the example $\phi(t) = \exp[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}]$ with $\beta_{\text{KWW}} = 0.5$ and $\tau_{\text{KWW}} = 1$. For $\beta_{\text{intr}} = \beta_{\text{KWW}}$, there is no dispersion in $\chi(t)$, whereas $\sigma(t) = \sqrt{\rho(t)}$ (dotted lines) displays an increasingly pronounced peak as β_{intr} increases toward the purely heterogeneous limit at $\beta_{\text{intr}} = 1$. The different decays $\chi_i(t)$ in Fig. 1 are traces of $\exp[-(t/\tau_i)^{\beta_{\text{intr}}}]$ with $\ln(\tau_i) = \alpha_1^* - \sqrt{\mu_2^*}$, α_1^* , and $\alpha_1^* + \sqrt{\mu_2^*}$, in order from left to right curves, i.e., at $\ln(\tau_i) = \langle \ln(\tau) \rangle$ plus or minus the standard deviation of $\ln(\tau)$.

If $\sigma(t)$ or $\rho(t)$ were employed for establishing a scale for the degree of heterogeneity, one would encounter the fact that these quantities are time dependent whenever $\beta_{\text{KWW}} \neq \beta_{\text{intr}}$, i.e., for all cases except the purely homogeneous

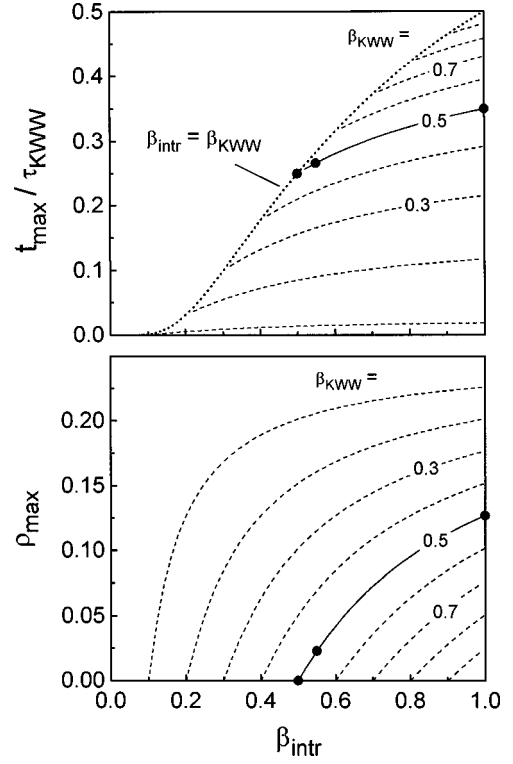


FIG. 2. Graphs of position t_{max} (in units of τ_{KWW}) and amplitude ρ_{max} regarding the peak of the time dependent variance $\rho(t) = \langle \chi_i(t)^2 \rangle - \langle \chi_i(t) \rangle^2$ as a function of β_{intr} . The curves are parametric in β_{KWW} , ranging from 0.1 to 0.9 in steps of 0.1. The dots for $\beta_{\text{KWW}} = 0.5$ mark the three situations outlined in Fig. 1.

limit. More sensible in this context are the peak values, either $\rho_{\text{max}} = \rho(t_{\text{max}})$ or $\sigma_{\text{max}} = \sigma(t_{\text{max}})$, with the positions of t_{max} given by Eq. (11). The dependences of t_{max} and ρ_{max} on β_{intr} and parametric in β_{KWW} are presented graphically in Fig. 2. The bounds for arbitrary exponents $0 < \beta_{\text{KWW}} \leq \beta_{\text{intr}} \leq 1$ are $0 \leq \rho_{\text{max}} \leq \frac{1}{4}$ and $0 \leq \sigma_{\text{max}} \leq \frac{1}{2}$. A further useful time-independent scale of the dispersion is the area under $\rho(t)$ normalized to its upper limit $\langle \tau \rangle_{\text{KWW}}/2$, where $\langle \tau \rangle_{\text{KWW}} = \tau_{\text{KWW}} \beta_{\text{KWW}}^{-1} \Gamma(\beta_{\text{KWW}}^{-1})$,

$$P(\beta_{\text{intr}}, \beta_{\text{KWW}}) = \frac{2}{\langle \tau \rangle_{\text{KWW}}} \int_0^\infty \rho(t) dt = 2 \times [2^{-1/\beta_{\text{intr}}} - 2^{-1/\beta_{\text{KWW}}}], \quad (13)$$

with $P(\beta, \beta) = 0$ and $P(1, 0) = 1$.

Up to this point, we have refrained from relating the results to experimental observables, except for identifying $\phi(t)$ with typical relaxation data. Numerous experimental techniques are available for measuring this ensemble-averaged response $\phi(t)$. However, an infinite number of values for β_{intr} can rationalize a dispersive $\phi(t)$ data set, such that $\phi(t)$ alone is bound to remain indecisive regarding the degree of heterogeneity of dynamical processes. In what follows, we argue that the standard deviation $\sigma(t) = \sqrt{\rho(t)}$, associated with the distribution of site-specific decays $\chi_i(t)$, can be measured directly in terms of the time dependent inhomogeneous optical line width $\sigma_{\text{inh}}(t)$, thereby fixing the value of β_{intr} .

For rationalizing $\sigma_{\text{inh}}(t)$, measured in the course of a solvation process, we assume a Gaussian distribution $n[\nu_i(\infty)]$ of equilibrated free energies centered at $\nu(\infty)$,

$$n[\nu_i(\infty)] = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp\left[-\frac{[\nu_i(\infty) - \nu(\infty)]^2}{2\sigma_0^2}\right], \quad (14)$$

and an independent distribution of time scales τ , such that the single site $\nu_i(t)$ can be written as

$$\nu_i(t) = \nu_i(\infty) + \Delta\nu \exp[-(t/\tau_i)^{\beta_{\text{intr}}}] = \nu_i(\infty) + \Delta\nu \chi_i(x). \quad (15)$$

Since the quantities $\nu_i(\infty)$ and $\chi_i(t)$ are independent random variables, the expectation value $\nu(t)$ and variance $\sigma_{\text{inh}}^2(t)$ of $\nu_i(t)$ can be obtained by adding the individual corresponding moments, which yields

$$\nu(t) = \langle \nu_i(t) \rangle = \nu(\infty) + \Delta\nu C(t) = \nu(\infty) + \Delta\nu \phi(t), \quad (16)$$

where $\phi(t) = C(t)$ is again the normalized ensemble-averaged response, and

$$\sigma_{\text{inh}}^2(t) = \langle [\nu_i(t) - \nu(t)]^2 \rangle = \sigma_0^2 + \Delta\nu^2 \rho(t), \quad (17)$$

with $\rho(t) = [C(2^{1/\beta_{\text{intr}}t}) - C(2^{1/\beta_{\text{KWW}}t})]$ from Eq. (10b). For the time-dependent relative changes in the Gaussian width, we finally arrive at

$$\frac{\sigma_{\text{inh}}(t)}{\sigma_0} = \left[1 + \frac{\Delta\nu^2}{\sigma_0^2} [C(2^{1/\beta_{\text{intr}}t}) - C(2^{1/\beta_{\text{KWW}}t})] \right]^{1/2}, \quad (18)$$

now demonstrating the impact of β_{intr} on the observable $\sigma_{\text{inh}}(t)$, whereas $C(t)$ expectedly remains independent of β_{intr} . The bounds of the time-dependent width $\sigma_{\text{inh}}(t)$ are $\sigma_{\text{inh}}(t) = \sigma_0$ for the case of $\beta_{\text{intr}} = \beta_{\text{KWW}}$ and $\sigma_{\text{inh}}(t) \leq [\sigma_0^2 + \Delta\nu^2/4]^{1/2}$ for other values of $0 < \beta_{\text{KWW}} < \beta_{\text{intr}} \leq 1$. Equation (18) now provides a straightforward link between the normalized Stokes shift response function $C(t)$ and the transient increase in the inhomogeneous linewidth $\sigma_{\text{inh}}(t)$. It predicts that an excess linewidth appears in the course of a solvation process if (and only if) the underlying dynamical processes exhibit a spatial variation of time scales. Conversely, one could conclude on homogeneous dynamics from an observation of a time-independent linewidth, i.e., if $\sigma_{\text{inh}}(t) \equiv \sigma_0$.

Finally, we address experimental data obtained for $\sigma_{\text{inh}}(t)$ in order to assess their use for delineating the value of β_{intr} and thereby the degree of heterogeneity in a real system. The experimental details on solvation data for quinoxaline (QX) as a chromophore dissolved in the glass-former 2-methyltetrahydrofuran (MTHF) have been reported elsewhere [8,12,21]. For this system just above the glass transition temperature $T_g = 91$ K, it has been found that $\Delta\nu = 246 \text{ cm}^{-1}$, $\sigma_{\text{inh}}(\infty) = \sigma_{\text{inh}}(0) = \sigma_0 = 160 \text{ cm}^{-1}$, and $C(t) = \exp[-(t/\tau_{\text{KWW}})^{0.5}]$, in favorable agreement with the dielectric properties $\varepsilon^*(\omega) = 1/M^*(\omega)$ of MTHF [21]. The upper panel of Fig. 3 shows the $C(t)$ decay recorded at $T = 95.1$ K together with a KWW fit with $\tau_{\text{KWW}} = 25$ ms and $\beta_{\text{KWW}} = 0.5$. This $C(t)$ and $\sigma_{\text{inh}}(t)$ data set has been ana-

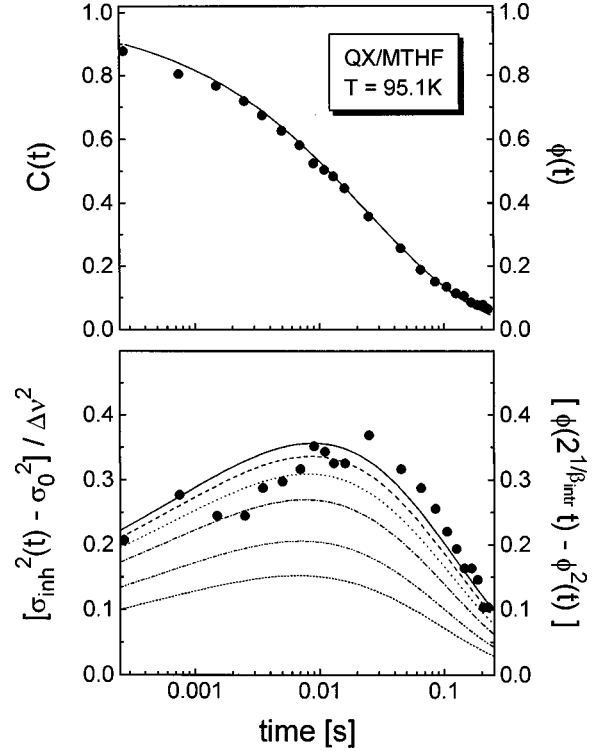


FIG. 3. Experimental solvation dynamics results (dots) for the system QX/MTHF at $T = 95.1$ K in terms of the normalized Stokes shift $C(t)$ and the inhomogeneous linewidth $\sigma_{\text{inh}}(t)$ scaled as $\rho(t)$. The solid line in the upper frame is a fit to the $C(t)$ data using $\phi(t) = \exp[-(t/25 \text{ ms})^{0.5}]$. The lines in the lower frame refer to $\rho(t)$ based on $\phi(t) = \exp[-(t/25 \text{ ms})^{0.5}]$ for various values of $\beta_{\text{intr}} = 1.00, 0.90, 0.80, 0.70, 0.60,$ and 0.55 , in the order from top to bottom curve. The case $\beta_{\text{intr}} = \beta_{\text{KWW}} = 0.5$ leads to $\rho(t) \equiv 0$.

lyzed recently by invoking numerical approximations to the function $g(\tau)$ and using simulations in order to estimate the impact of β_{intr} on the time-dependent emission spectra [8,12]. The advantage of the present result is to have simple but exact formulas for $\sigma_{\text{inh}}(t)$ in Eq. (18) or for $\sigma_{\text{inh}}^2(t)$ in Eq. (17), which are applicable to KWW-type overall dynamics. The results imply that we can interpret the variance of inhomogeneously broadened emission spectra as the sum of a spectral contribution σ_0 and a dynamic contribution $\rho(t)$. Conversely to Eq. (17), we now infer experimental values for $\rho_{\text{expt}}(t)$ from the $\sigma_{\text{inh}}(t)$ data using the expression $\rho_{\text{expt}}(t) = [\sigma_{\text{inh}}^2(t) - \sigma_0^2] / \Delta\nu^2$, for which there is no unknown parameter on the right hand side. The experimental results for $\rho_{\text{expt}}(t)$ are shown as dots in the lower panel of Fig. 3. The lines in this plot are calculated $\rho(t)$ curves using Eq. (10b) with $\phi(t) = C(t) = \exp[-(t/25 \text{ ms})^{0.5}]$ for various values of β_{intr} . A comparison between experiment and calculation indicates that the relaxation dynamics are consistent only with $0.8 \leq \beta_{\text{intr}} \leq 1$. In other words, the highest possible nonexponentiality inherent in the response of each relaxor corresponds to a decay of the type $\exp[-(t/\tau)^{0.8}]$, i.e., the predominant (if not the entire) contribution to the ensemble-averaged nonexponentiality associated with $\beta_{\text{KWW}} = 0.5$ stems from the time scale τ being a spatially varying quantity. Therefore, a parallel relaxation scheme is made responsible for the overall KWW-like dispersion, in contrast to a previous hierarchical model for rationalizing stretched-exponential behavior [26].

V. CONCLUSIONS

We have assessed the method of analyzing dispersive relaxation patterns $\phi(t)$ in terms of a distribution of KWW decays $\chi(t)$, instead of confining the integral kernel to the exponential case. This defines implicitly a probability density $g(\tau)$ or $g^*(\ln \tau)$ whose most relevant moments can be calculated. We find that the variance $\rho(t)$ of the stochastic quantity $\chi(t)$ bears interesting features, because it is sensitive to the relaxation dispersion inherent in each relaxor as quantified by β_{intr} . More importantly, $\rho(t)$ or $\sigma(t) = \sqrt{\rho(t)}$ is measurable by means of phosphorescence solvation dynamics, which allows one to derive β_{intr} from experimental data, whereas an ensemble-averaged decay $\phi(t)$ is bound to remain indecisive in this respect. The parameter β_{intr} establishes a continuous scale ranging from purely heterogeneous to homogeneous dynamics, with only a pronounced extent of heterogeneity ($0.8 \leq \beta_{\text{intr}} \leq 1$) being compatible with the mechanism of structural relaxation in real systems.

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APPENDIX

A brief outline of how the moments α_n of $g(\tau)$ and α_1^* , μ_2^* , and μ_3^* of $g^*(\ln \tau)$ are calculated is given below. The probability density $g(\tau)$ is defined implicitly in Eq. (4), and depends on the parameters $\tau_{\text{KWW}} > 0$, $\beta_{\text{KWW}} > 0$, and $\beta_{\text{intr}} > \beta_{\text{KWW}}$. Multiplying Eq. (4) by t^b with $\text{Re } b > -1$, and integrating over t within the limits $0, \dots, \infty$, yields

$$\int_0^\infty t^b \exp[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}] dt = \int_0^\infty g(\tau) \int_0^\infty t^b \exp[-(t/\tau)^{\beta_{\text{intr}}}] dt d\tau. \quad (\text{A1})$$

Substituting $w = (t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}$ and $v = (t/\tau)^{\beta_{\text{intr}}}$ defining $\rho = b + 1$ ($\text{Re } \rho > 0$), and using the definition of the gamma function $\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt$ ($\text{Re } z > 0$) leads to

$$\int_0^\infty \tau^\rho g(\tau) d\tau = \langle \tau^\rho \rangle = \tau_{\text{KWW}}^\rho \frac{\Gamma(1 + \rho/\beta_{\text{KWW}})}{\Gamma(1 + \rho/\beta_{\text{intr}})}, \quad (\text{A2})$$

which states the moments $\alpha_n = \langle \tau^n \rangle$ with respect to $g(\tau)$.

For obtaining the logarithmic moments α_1^* and $\mu_{n \geq 2}^*$ of $g^*(\ln \tau)$, we recall the above definitions $\xi = \ln(\tau)$ and $g^*(\xi) d\xi = g(\tau) d\tau$, and define $L(\rho)$ and $K(n)$:

$$L(\rho) = \int_{-\infty}^\infty e^{\rho \xi} g^*(\xi) d\xi = \langle \tau^\rho \rangle = \tau_{\text{KWW}}^\rho \frac{\Gamma(1 + \rho/\beta_{\text{KWW}})}{\Gamma(1 + \rho/\beta_{\text{intr}})} \quad (\text{Re } \rho > 0), \quad (\text{A3})$$

$$K(n) = \lim_{\rho \rightarrow 0^+} \frac{d^n \ln L(\rho)}{d\rho^n}, \quad (\text{A4})$$

where $K(n)$ now has the following properties: $\alpha_1^* = K(1)$, $\mu_2^* = K(2)$, and $\mu_3^* = K(3)$. The final evaluations of $K(n)$ generate the results stated in Eq. (9). Note again that $\mu_n^* = K(n)$ is not warranted for $n > 3$.

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