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Generating functional approach to multichannel parallel relaxation with application to the problem of direct energy transfer in fractal systems with dynamic disorder

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A model for multichannel parallel relaxation is suggested based on the following assumptions: (a) an individual channel is characterized by a set of continuous state variables; the corresponding relaxation rate is a function of the state variables as well as of the time interval for which the channel is open; (b) the number of channels is a random variable described by a correlated point process defined in the space of state parameters of an individual channel. Analytical expressions for the generating functional of the overall relaxation rate and for the average survival function are derived in terms of the generating functional of the point process. The general formalism is applied to the problem of direct energy transfer from excited donors to acceptors in fractal systems with dynamic disorder. It is assumed that the number of acceptors obeys a Poissonian distribution law with a constant average density in a d_f-dimensional fractal structure embedded in a d_s-dimensional Euclidean space ($d_s=1,2,3$) and that an individual relaxation rate is an inverse power function of the distance between the acceptor and the donor molecules. The dynamic disorder is described in terms of three different functions: the rate $\omega(t)$ of opening of a channel at time t, the attenuation function $\varphi(t)$ of the reactivity of an individual channel at time t, and the probability density $\psi(t)$ of the time interval within which a channel is open. Several particular cases corresponding to different functions $\omega(t)$, $\varphi(t)$, and $\psi(t)$ are investigated. The static disorder corresponds to a survival function of the stretched exponential type $\exp[-(\Omega t)^{\beta}]$ with $1>\beta>0$. For very strong dynamic disorder there is no attenuation of reactivity, the opening time is infinite and the survival function is given by a compressed exponential $\exp[-\text{const}.t^{1+\beta}]$, $1>\beta>0$. The other cases analyzed correspond to a slowly decreasing attenuation function and to an exponential distribution of the opening time, respectively; for them the efficiency of relaxation is between the ones corresponding to the two extreme cases of static and very strong dynamic disorder. The general conclusion is that the passage from static to the dynamic disorder results in an increase of the efficiency of the relaxation process. © *1995 American Institute of Physics.*

I. INTRODUCTION

The study of exotic (i.e., nonexponential) relaxation is a problem of topical interest in nonequilibrium statistical physics; it is of importance in the study of a variety of problems from condensed matter physics,[1-9] nuclear physics,[10] spectroscopy,[11-17] rheology,[18,19] seismology,[20] physical chemistry,[21] radiochemistry,[22-24] molecular biophysics,[25-28] cell and population dynamics,[29-31] etc. Among the different relaxation functions suggested in the literature the Kohlrausch–Williams–Watts modified exponential[1-6,8,9,16,17,30,31] plays a central role

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$$\langle \mathscr{S}(t)\rangle=\exp[-(\Omega t)^{\beta}], \tag{1}$$

where $\langle \mathscr{S}(t)\rangle$ is the average survival function characteristic to the relaxation process, t is the time, Ω is a characteristic frequency, and β is a dimensionless positive parameter. Most cases considered in the literature[1–9,16,31] correspond to $1>\beta>0$, a situation in which Eq. (1) is a stretched exponential. For $\beta>1$ Eq. (1) is a compressed exponential; although less common than the stretched exponential the compressed exponential has been used in spectroscopy[17] and in population dynamics.[30,31]

It is commonly assumed that the stretched exponential corresponds to a kind of universal behavior which is independent of the details of individual processes; this idea has stimulated the proposal of several "universal" mechanisms based either on parallel relaxation[1–6] or on hierarchically constrained dynamics.[2,8] In contrast much less attention has been paid to the theoretical interpretation of the compressed exponential.

The purpose of this article is to suggest a model which may generate both the stretched and compressed exponentials and to study its main properties. In our opinion the derivation of a universal model applicable to all situations in which the Kohlrausch–Williams–Watts law (1) occurs is rather illusory. This is the reason why our starting point is a particular problem, the extinction of fluorescence due to the direct energy transfer from a donor (an excited molecule) to an acceptor (either a molecule or a quasiparticle) in fractal disordered systems.[2] The study of this type of problem started with the work of Förster;[32] his model has been continually improved in the last fifty years.[2–6] We shall try to improve the Klafter–Shlesinger generalization[2] of the Förster model for fractal disordered systems by incorporating the dynamic disorder into the model; the importance of dynamic disorder in the context of nonexponential relaxation has been recently emphasized by many researchers.[26,27,33] We shall describe the dynamic disorder by combining the use of a random point process with the method of generating functionals. This technique has been recently introduced by the authors in other physical contexts, the study of fractal random processes,[34] of random spiral motions,[35] the analysis of stochastic gravitational fluctuations,[36] and the description of space and time dependent colored noise.[37]

Although the main motivation of our research is a concrete problem, in order to facilitate the application of the theory to other systems, we shall try first to give a general formulation of our approach and then to apply it to the problem of direct energy transfer. The plan of the article is as follows. In Sec. II we present the mathematical formalism of the theory. In Sec. III the theory is applied to the study of direct energy transfer in fractal systems with dynamic disorder. In Sec. IV a comparison between the systems with static and dynamic disorder is performed. Section V deals with the case when only the fastest process contributes to relaxation. In Sec. VI an alternative approach is suggested based on the use of a formal functional generalization of the theory of random point processes. Finally in Sec. VII some open questions and possible applications of our approach are analyzed.

II. GENERATING FUNCTIONAL APPROACH TO DYNAMIC DISORDER

We assume that a random number N of channels is involved in relaxation. Each individual channel is characterized by a set of continuous random state variables and by the random time interval for which the channel is open. The stochastic behavior of the number and states of the channels is described by a random point process.[38] For a given realization of the process the survival function $\mathscr{S}(t)$ is related to the relaxation rate $W(t)$ by the differential equation

$$d\mathscr{S}(t)/dt=-W(t)\mathscr{S}(t), \quad \text{with} \quad \mathscr{S}(0)=1 \tag{2}$$

or, after integration

$$\ell(t)=\exp\left[-\int_0^t W(t')dt'\right]. \tag{3}$$

In these equations due to the dynamical disorder the relaxation rate $W(t)$ is a random function of time. We suppose that each individual channel is characterized by a set of state variables

$$\mathbf{r}=(r_1,r_2,\ldots); \tag{4}$$

the contribution w_α of a given channel to the relaxation rate is a function of the state vector $\mathbf{r}_\alpha$ of the channel as well as of the time interval Δt_α that elapsed from the moment at which the channel was opened

$$w_\alpha=w(\mathbf{r}_\alpha,\Delta t_\alpha); \tag{5}$$

the total relaxation is the sum of the contributions of all channels

$$W(t)=\sum_{\alpha=1}^{N} w(\mathbf{r}_\alpha,t-t_\alpha)h(\ell_\alpha-t+t_\alpha), \tag{6}$$

where t is the current time, t_α is the time at which the αth channel was opened, $h(x)$ is the Heaviside function, and ℓ_α is the life time of the open state.

The stochastic properties of the total number N of channels and of the values of the corresponding state vectors $(\mathbf{r}_1,t_1),\ldots,(\mathbf{r}_N,t_N)$ can be described by using the formalism of random point processes.[38] We introduce the Janossy densities[38]

$$Q_0;Q_N(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_N,t_N)d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_N\,dt_N; \tag{7}$$

$Q_N(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_N,t_N)d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_N\,dt_N$ is the probability that there are N channels involved in the relaxation process and that the first channel has a state vector between $\mathbf{r}_1$ and $\mathbf{r}_1+d\mathbf{r}_1$ and it is opened at a time between t_1 and $t_1+dt_1\cdots$ and that the Nth channel has a state vector between $\mathbf{r}_N$ and $\mathbf{r}_N+d\mathbf{r}_N$ and it is opened at a time between t_N and t_N+dt_N.

We follow the usual convention according to which there are no restrictions concerning the values of the vectors $(\mathbf{r}_\alpha,t_\alpha)$ and thus a $1/N!$ Gibbs factor should be introduced in the normalization condition for the Janossy densities[38]

$$Q_0+\sum_{N=1}^{\infty}\frac{1}{N!}\int\int\cdots\int\int Q_N(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_N;t_N)d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_N\,dt_N=1. \tag{8}$$

In terms of the Janossy densities we introduce the joint (product) densities[38]

$$\begin{aligned}\eta_0&=1,\\ \eta_N(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_N,t_N)&d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_N\,dt_N\\ &=\left(\sum_{S=0}^{\infty}\frac{1}{S!}\int\int\cdots\int\int Q_{N+S}(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_{N+S},t_{N+S})d\mathbf{r}_{N+1}\,dt_{N+1}\cdots d\mathbf{r}_{N+S}\,dt_{N+S}\right)\\ &\quad\times d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_N\,dt_N.\end{aligned} \tag{9}$$

$\eta_1(\mathbf{r},t)$ is the average density of channels in the $(\mathbf{r},t)$ space and the other product densities describe the fluctuations of the number and state of channels. The Janossy densities can be expressed in terms of the product densities as[38]

$$Q_N(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_N,t_N)d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_N\,dt_N = \left(\sum_{S=0}^{\infty}\frac{(-1)^S}{S!}\int\int\cdots\int\int \eta_{N+S}(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_{N+S},t_{N+S})d\mathbf{r}_{N+1}\,dt_{N+1}\cdots d\mathbf{r}_{N+S}\,dt_{N+S}\right) \times d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_N\,dt_N. \tag{10}$$

The main advantage of the joint densities is that they allow to evaluate the moments of the number of channels in a simple way. In particular, given a region Σ in the $(\mathbf{r},t)$ space, the factorial moments of the number of channels are given by[38]

$$\mathcal{F}_m=\langle N(N-1)\cdots(N-m+1)\rangle=\int_\Sigma\int\cdots\int_\Sigma\int \eta_m(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_m,t_m)d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_m\,dt_m. \tag{11}$$

η_N are product densities rather than probability densities and thus they do not obey a normalization condition similar to Eq. (8).

In terms of Q_N and η_N we can define two different types of generating functionals: for the Jannosy densities

$$\Lambda[Z(\mathbf{r},t)]=\sum_{N=1}^{\infty}\frac{1}{N!}\int\int\cdots\int\int Z(\mathbf{r}_1,t_1)\cdots Z(\mathbf{r}_N,t_N)Q_N(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_N,t_N)d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_N\,dt_N + Q_0 \tag{12}$$

and for the product densities

$$\Xi[Z(\mathbf{r},t)]=1+\sum_{N=1}^{\infty}\frac{1}{N!}\int\int\cdots\int\int Z(\mathbf{r}_1,t_1)\cdots Z(\mathbf{r}_N,t_N) \times \eta_N(\mathbf{r}_1,t_1;\ldots;\mathbf{r}_N,t_N)d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_N\,dt_N, \tag{13}$$

respectively, where $Z(\mathbf{r},t)$ is a suitable test function. It is easy to check that these two generating functionals are related to each other through the relationship[38]

$$\Lambda[Z(\mathbf{r},t)]=\Xi[Z(\mathbf{r},t)-1]. \tag{14}$$

Now we introduce the probability density

$$\psi(\ell|\mathbf{r})d\ell, \quad \int_0^\infty \psi(\ell|\mathbf{r})d\ell=1 \tag{15}$$

of the life time of the open state of a channel characterized by the state vector $\mathbf{r}$.

The relaxation dynamics is determined by the stochastic properties of the overall relaxation rate $W(t)$ which can be formally described in terms of a probability density functional

$$\mathscr{P}[W(t), t \leq T]D[W(t)], \quad \iint \mathscr{P}[W(t)]D[W(t)] = 1, \tag{16}$$

where T is a cutoff value of the current time, $\iint$ stands for the operation of functional integration, and $D[W(t)]$ is an integration measure defined over the space of functions $W(t)$. The main difficulty related to the use of the probability density functional (16) is due to the fact that we do not have a suitable definition for the integration measure $D[W(t)]$. This difficulty can be circumvented by making use of the generating functional

$$G[K(t);T] = \iint \exp\left(-\int_0^T K(t)W(t)dt\right)\mathscr{P}[W(t)]D[W(t)], \tag{17}$$

where $K(t)$ is a suitable test function. We shall see later that the generating functional $G[K(t);T]$ does not depend on the integration measure $D[W(t)]$. The probability density functional $\mathscr{P}[W(t)]$ $D[W(t)]$ is an average of a Dirac-delta functional symbol

$$\delta\left[W(t) - \sum_{\alpha=1}^{N} w(\mathbf{r}_\alpha, t - t_\alpha)h(\ell_\alpha - t + t_\alpha)\right]D[W(t)] \tag{18}$$

corresponding to the superposition of the contributions of the individual channels given by Eq. (6), over the number N of channels, over the state vectors $\mathbf{r}_1,...\mathbf{r}_N$, over the times $t_1,...,t_N$ and over the life times $\ell_1,...,\ell_N$ of the open states of the channels

$$\mathscr{P}[W(t)]D[W(t)] = \sum_{N=0}^{\infty} \frac{1}{N!} \int\int\cdots\int\int\int\cdots\int Q_N(\mathbf{r}_1, t_1; ...; \mathbf{r}_N, t_N)$$
$$\times \psi(\ell_1|\mathbf{r}_1)\cdots\psi(\ell_N|\mathbf{r}_N)\,\delta\left[W(t) - \sum_{\alpha=1}^{N} w(\mathbf{r}_\alpha, t - t_\alpha)h(\ell_\alpha - t + t_\alpha)\right]$$
$$\times D[W(t)]d\mathbf{r}_1\, dt_1\cdots d\mathbf{r}_N\, dt_N d\ell_1\cdots d\ell_N, \tag{19}$$

where the average is evaluated in terms of the Janossy densities Q_N and of the probability density $\psi(\ell|\mathbf{r})$ of the life time of the open state of a given channel. By inserting Eq. (19) into Eq. (17) and making use of the expressions (12)–(14) for the generating functionals of the point process we get a closed expression for the generating functional of the overall relaxation rate

$$G[K(t);T] = \Xi\left[Z(\mathbf{r}, t') = \int_0^\infty d\ell\,\psi(\ell|\mathbf{r})\left[\exp\left(-\int_{t'}^{\min(T, \ell + t')} w(\mathbf{r}, t - t')K(t)dt\right) - 1\right]\right]. \tag{20}$$

As expected the expression (20) for the generating functional $G[K(t)]$ is independent of the integration measure $D[W(t)]$.

From Eqs. (3) and (20) we notice that the average survival function

$$\langle \mathscr{S}(t)\rangle = \iint \exp\left(-\int_0^t W(t')dt'\right)\mathscr{P}[W(t)]D[W(t)] \tag{21}$$

can be expressed in terms of the generating functional $G[K(t)]$. From Eqs. (17), (20), and (21) we obtain

$$\langle \ell(t) \rangle = G[K(t)=1,\ T=t]$$
$$= \Xi\left[Z(\mathbf{r},t') = \int_0^\infty d\ell\, \psi(\ell|\mathbf{r}) \left[\exp\left(- \int_{t'}^{\min(t,\ell+t')} w(\mathbf{r},t''-t')dt'' \right) - 1 \right] \right]. \quad (22)$$

Equation (22) is the main result of this article; it allows us to evaluate the average survival function $\langle \ell(t) \rangle$ in terms of the stochastic properties of the individual channels involved in the relaxation process.

III. DIRECT ENERGY TRANSFER IN FRACTAL SYSTEMS WITH DYNAMIC DISORDER

Following Klafter and Shlesinger[2] we consider an initially prepared excited donor at the origin of a coordinate system surrounded by a random number of acceptors placed at different distances from the donor. Each acceptor corresponds to a relaxation channel; the corresponding state vector **r** is given by the position of the acceptor with respect to the origin. Klafter and Shlesinger[2] assume that the relaxation rate corresponding to a given acceptor is inversely proportional to a positive power of the distance $r=|\mathbf{r}|$ from the acceptor to the donor

$$w(\mathbf{r}) \sim \mathscr{M} |\mathbf{r}|^{-\sigma}, \quad (23)$$

where $\mathscr{M}$ is a proportionality constant with dimension $[\text{time}]^{-1}$ $[\text{length}]^{\sigma}$ and σ is a dimensionless positive coefficient depending on the nature of the interaction ($\sigma=6$ for dipole–dipole interactions, $\sigma=8$ for dipole–quadrupole interactions, etc.). In this article we assume that due to dynamic disorder the right hand side (rhs) of Eq. (23) should be multiplied by a positive attenuation factor φ ($\varphi>0$) which is a function of the time interval Δt for which the channel is open. We have

$$w(\mathbf{r},\Delta t) = \mathscr{M} |\mathbf{r}|^{-\sigma} \varphi(\Delta t). \quad (24)$$

Another assumption made in this article is related to the probability density $\psi(\ell|\mathbf{r})$ of the life time of the open state of a channel. As all acceptors have the same behavior irrespective of their position $\psi(\ell|\mathbf{r})$ should be independent of **r**

$$\psi(\ell|\mathbf{r}) = \psi(\ell) \quad \text{independent of} \quad \mathbf{r}. \quad (25)$$

We consider that the acceptors do not interact with each other and thus the different reaction channels are independent; such a situation can be described by an independent random point process in space–time continuum for which all Janossy densities Q_N are determined by the first product density $\eta_1(\mathbf{r},t)$. We have[37,38]

$$Q_0 = \exp\left(- \int \int \eta_1(\mathbf{r},t) d\mathbf{r}\, dt \right),$$
$$Q_N(\mathbf{r}_1,t_1;...;\mathbf{r}_N,t_N) = \exp\left(- \int \int \eta_1(\mathbf{r},t) d\mathbf{r}\, dt \right) \eta_1(\mathbf{r}_1,t_1) \cdots \eta_1(\mathbf{r}_N,t_N). \quad (26)$$

Equation (26) is crucial for the further development of the theory. It shows that for independent processes only the average density of acceptors $\eta_1(\mathbf{r},t)$ in the space–time continuum determines the relaxation law. Here we consider[2] an average homogeneous distribution of acceptors in a d_f-dimensional fractal structure embedded in a d_s-dimensional Euclidean space and suppose that the acceptors are enclosed in a d_s-dimensional hypersphere with a very large radius $r_0 \to \infty$ surrounding the origin. We follow a commonly used heuristic approach and assume that the fractal hypervolume of a hypersphere with radius $\mathbf{r}$ is[37,39–40]

$$V^*(r) = [\Gamma(1+d_f/2)]^{-1} \pi^{d_f/2} r^{d_f}. \tag{27}$$

The average space–time density of acceptors $\eta_1(\mathbf{r},t)$ is given by

$$\eta_1(\mathbf{r},t) d\mathbf{r}\, dt = \rho (d\mathbf{r})_{\text{fractal}} \omega(t) dt, \tag{28}$$

where

$$\rho = dN/(d\mathbf{r})_{\text{fractal}} \quad \text{const} \tag{29}$$

is the average space fractal density of acceptors and

$$(d\mathbf{r})_{\text{fractal}} = \frac{\pi^{(d_f-d_s)/2}}{d_s \Gamma(1+d_f/2)} \Gamma(1+d_s/2) d_f r^{d_f-d_s}\, d\mathbf{r} \tag{30}$$

is a fractal analog[39,40] of the Euclidean differential element of volume $d\mathbf{r}$, and $\omega(t)$ is the rate of generation of acceptors.

By combining Eqs. (12)–(14) and (26)–(30) we get the following expression for the generating functional $\Xi[Z(\mathbf{r},t)]$ of the random point process:

$$\Xi[Z(\mathbf{r},t)] = \exp\left\{ \frac{\pi^{(d_f-d_s)/2}}{d_s \Gamma(1+d_f/2)} \rho d_f \Gamma(1+d_s/2) \int_0^{\mathrm{T}} dt\, \omega(t) \int_{|\mathbf{r}| \le r_0} Z(\mathbf{r},t) r^{d_f-d_s}\, d\mathbf{r} \right\}. \tag{31}$$

From Eqs. (20) and (31) we can compute the generating functional of the overall relaxation rate

$$G[K(t);T] = \exp\left\{ -\frac{\pi^{(d_f-d_s)/2}}{d_s \Gamma(1+d_f/2)} \rho d_f \Gamma(1+d_s/2) \int_0^\infty d\ell \psi(\ell) \int_0^{\mathrm{T}} dt'\, \omega(t') \int r^{d_f-d_s} \times \left[1 - \exp\left(-\mathscr{M} r^{-\sigma} \int_{t'}^{\min(\mathrm{T},\ell+t')} \varphi(t-t') K(t) dt \right) \right] d\mathbf{r} \right\}. \tag{32}$$

Now we express the space integrals in Eq. (32) in polar coordinates in d_s-dimensional Euclidean space and integrate over the angular variables. We obtain

$$G[K(t);T] = \exp\left\{ -\frac{\pi^{d_f} \rho}{\Gamma(1+d_f/2)} d_f \int_0^\infty d\ell \psi(\ell) \int_0^{\mathrm{T}} \omega(t') dt' \int_0^{r_0} r^{d_f-1} \times \left[1 - \exp\left(-\mathscr{M} r^{-\sigma} \int_{t'}^{\min(\mathrm{T},\ell+t')} \varphi(t-t') K(t) dt \right) dr \right] \right\}. \tag{33}$$

In Eq. (33) the integral over r can be evaluated in the limit $r_0 \to \infty$ by means of the substitution

$$y = \mathscr{M} r^{-\sigma} \int_{t'}^{\min(\mathrm{T},\ell+t')} \varphi(t-t') K(t) dt. \tag{34}$$

The result of the integration over y is

$$G[K(t);T] = \exp\left\{ -\Omega^\beta \int_0^\infty d\ell \psi(\ell) \int_0^{\mathrm{T}} dt'\, \omega(t') \left[\int_{t'}^{\min(\mathrm{T},\ell+t')} \varphi(t-t') K(t) dt \right]^\beta \right\}, \tag{35}$$

where

$$\Omega=\left(\frac{\rho\Gamma(1-d_f/\sigma)}{\Gamma(1+d_f/2)}\right)^{\sigma/d_f}\mathscr{M}\pi^{\sigma/2} \tag{36}$$

is a characteristic frequency and

$$\beta=d_f/\sigma \tag{37}$$

is a dimensionless fractal exponent. As for the problem of direct energy transfer we have $d_f\leqslant 3$ and from $\sigma\geqslant 6$ it follows that $1>\beta>0$.

By using Eq. (35) the expression (22) of the average survival function becomes

$$\langle\mathscr{E}(t)\rangle=\exp\left\{-\Omega^\beta\int_0^\infty d\ell\psi(\ell)\int_0^t dt'\,\omega(t')\left[\int_{t'}^{\min(t,\ell+t')}\varphi(t''-t')dt''\right]^\beta\right\}. \tag{38}$$

Now we apply the general relaxation equation (38) to several particular cases. The model with static disorder of Klafter and Shlesinger[2] is recovered as a particular case of our approach if all acceptors are generated before or at $t=0$

$$\omega(t)=\delta(t), \tag{39}$$

there is no attenuation

$$\varphi(t-t')=1, \tag{40}$$

and all acceptors have an infinite life time

$$\psi(\ell)=\delta(\ell-\ell_0),\quad \ell_0\to\infty. \tag{41}$$

In this case Eq. (38) leads to the well-known stretched exponential relaxation law (1) where the parameters Ω and β are given by Eqs. (36) and (37), respectively.

The other extreme corresponds to the case of very strong dynamic disorder for which the acceptors are generated with a constant rate

$$\omega(t)=\omega\quad \text{const}, \tag{42}$$

there is no attenuation [Eq. (40)] and all acceptors have an infinite life time [Eq. (41)]. In this case we get a compressed exponential

$$\langle\mathscr{E}(t)\rangle=\exp[-\Omega^\beta\omega t^{1+\beta}]. \tag{43}$$

Between these two extremes we can consider other cases of interest. A third case corresponds to a constant generation rate [Eq. (42)], an infinite life time [Eq. (41)], and to a slowly decreasing attenuation function

$$\varphi(t-t')=A(t-t')^{H-1},\quad 1>H>0, \tag{44}$$

where A is a positive constant with dimension $[\text{time}]^{1-H}$ and H is a positive fractal exponent smaller than unity. In this case the average survival function is also given by a compressed exponential of the type (43)

$$\langle\mathscr{E}(t)\rangle=\exp\left\{-\frac{(\Omega A/H)^\beta}{1+H\beta}\,\omega t^{1+H\beta}\right\}=\exp[-\text{const.}\,t^{1+\beta'}] \tag{45}$$

but the corresponding exponent

$$\beta' = H\beta < \beta \tag{45'}$$

is smaller than the exponent β characteristic for very strong dynamic disorder.

A fourth case corresponds to a constant generation rate [Eq. (42)], no attenuation [Eq. (40)], and to an exponential distribution of the life time

$$\psi(\Lambda) = \langle \Lambda \rangle^{-1} \exp(-\Lambda/\langle \Lambda \rangle), \tag{46}$$

where $\langle \Lambda \rangle$ is the average life time of an acceptor. The average survival function is

$$\langle \mathscr{S}(t) \rangle = \exp\{-\Omega^\beta \omega \langle \Lambda \rangle^{1+\beta}[((t/\langle \Lambda \rangle) - \beta)\gamma(\beta+1, t/\langle \Lambda \rangle) + (t/\langle \Lambda \rangle)^{\beta+1} \exp(-t/\langle \Lambda \rangle)]\}, \tag{47}$$

where

$$\gamma(a,t) = \int_0^t e^{-t} t^{a-1}\, dt \tag{48}$$

is the incomplete gamma function. As $t \to \infty$ the survival function (47) tends to an exponential

$$\langle \mathscr{S}(t) \rangle = \exp\{-(\Omega \langle \Lambda \rangle)^\beta \omega \Gamma(1+\beta) t\}, \quad \text{as} \quad t \to \infty, \tag{49}$$

where $\Gamma(a) = \gamma(a,\infty)$ is the complete gamma function.

IV. STATIC VERSUS DYNAMIC DISORDER

For a system with dynamic disorder the relaxation rate $W(t)$ is a random function of time and the average survival function $\langle \mathscr{S}(t) \rangle$ is given by the path integral (21). In contrast for a system with static disorder the relaxation rate W is a random number rather than a random function and the static average of the survival function $\mathscr{S}(t)$ is simply a superposition of exponential relaxation laws $\int P(W) \exp(-Wt)\, dW$ which expresses the contributions of the different relaxation rates selected from a given probability density $P(W)dW$.

In order to make a comparison between static and dynamic disorder we compute the one-time probability density

$$P(W;t)dW; \quad \text{with} \quad \int_0^\infty P(W;t)dW = 1 \tag{50}$$

of the overall transfer rate at time t. From Eq. (17) we note that the Laplace transform of $P(W,t)$

$$\mathscr{L}P(W;t) = \int_0^\infty \exp(-KW) P(W;t) dW \tag{51}$$

is given by

$$\mathscr{L}P(W;t) = G[K(t') = K\delta(t-t')]. \tag{52}$$

By inserting Eq. (35) into Eq. (52) we get

$$\mathscr{L}P(W;t) = \exp[-(b(t)K)^\beta], \tag{53}$$

with

$$b(t)=\Omega\left[\int_0^\infty d\ell\psi(\ell)\int_0^t dt'\,\omega(t')[\varphi(t-t')h(\ell+t'-t)]^\beta\right]^{1/\beta}. \tag{54}$$

From Eq. (53) it follows that the one-time probability density of the overall relaxation rate can be expressed in terms of the Lévy type probability densities for positive variables[1,41]

$$\Psi_\beta(x)=\mathscr{L}^{-1}\exp(-K^\beta),\quad \text{with}\quad \int_0^\infty \Psi_\beta(x)dx=1, \tag{55}$$

where $\mathscr{L}^{-1}$ is the inverse Laplace transformation. From Eqs. (53) and (55) we get

$$P(W,t)dW=\Psi_\beta(W/b(t))dW/b(t). \tag{56}$$

The functions $\Psi_\beta(x)$ have been extensively studied in the literature.[1,41] For large values of $x, \Psi_\beta(x)$ can be expanded in the following asymptotic series:[41]

$$\Psi_\beta(x)=\frac{1}{\pi}\sum_{k=0}^\infty \frac{1}{k!}(-1)^{k+1}x^{-(1+k\beta)}\Gamma(1+k\beta)\sin(\pi k\beta),\quad x\gg 0 \tag{57}$$

and thus for $W\to\infty$ $P(W;t)$ is given by

$$P(W,t)\sim\pi^{-1}\sin(\pi\beta)(b(t))^\beta\Gamma(1+\beta)W^{-(1+\beta)}$$
$$=\frac{\pi^{d_f/2}\rho d_f\int_0^\infty d\ell\psi(\ell)\int_0^t dt'\;\omega(t')[\varphi(t-t')h(\ell+t'-t)]^{d_f/\sigma}}{\sigma\mathscr{M}^{-d_f/\sigma}\Gamma(1+d_f/2)W^{1+d_f/\sigma}},\quad W\to\infty. \tag{58}$$

As $1>\beta>0$ from Eq. (58) it follows that all positive integer moments of the overall relaxation rate $\langle W(t)\rangle,\langle W^2(t)\rangle,\cdots$, are infinite, a behavior which is typical for a statistical fractal probability density.

Now we can proceed to make a comparison between the static and dynamic disorder. For systems with static disorder the average survival function is simply given by[42]

$$\langle\mathscr{E}(t)\rangle_{\text{static}}=\int_0^\infty P(W;t)\exp(-Wt)dW. \tag{59}$$

For systems with dynamic disorder Eq. (59) is obviously incorrect; in this case the average value of the survival functions is given by Eqs. (21), (22) and (38). For evaluating the dynamic average (21) the information contained in the one-time probability density of the overall relaxation rate $P(W;t)$ is not enough; we need to know the probability density functional $\mathscr{P}[W(t)]D[W(t)]$ or the generating functional $G[K(t)]$. However, Eq. (59) can be considered as an approximation of the exact ensemble averages (21), (22) and (38). For establishing the validity range of such an approximation we insert the expression (55) for $P(W;t)$ into Eq. (59) and evaluate the integral over W. We get

$$\langle\mathscr{E}(t)\rangle_{\text{static}}=\exp\left\{-(\Omega t)^\beta\int_0^\infty d\ell\psi(\ell)\int_0^t dt'\,\omega(t')[\varphi(t-t')h(\ell+t'-t)]^\beta\right\}. \tag{60}$$

As expected, the static and dynamic averages (60) and (38) are generally different. We notice however that they are identical if the restrictions (39)–(41) are fulfilled, a situation which corresponds to the Klafter–Shlesinger generalization[2] of the Förster model; in this case we have

$$\langle\mathscr{E}(t)\rangle_{\text{static}}=\langle\mathscr{E}(t)\rangle_{\text{dynamic}}=\exp[-(\Omega t)^\beta]. \tag{61}$$

V. RELAXATION DYNAMICS OF THE FASTEST CHANNEL

A common approximation for the problem of direct energy transfer is based on the assumption that only the fastest channel contributes to relaxation dynamics;[2,6] in other words one assumes that the transfer is restricted only to the nearest neighbor acceptor. For investigating the relaxation dynamics of the fastest channel we should evaluate the generating functional of the transfer rate; paradoxically for a single channel this is a more complicated problem than in the case of multichannel dynamics considered before. For simplicity we restrict ourselves to the evaluation of the one-time probability density

$$\mathscr{T}(W;t)dW, \quad \text{with} \quad \int_0^\infty \mathscr{T}(W;t)dW=1. \tag{62}$$

This probability density can be expressed in terms of the probability density

$$\mathscr{p}(r,t')dr\,dt', \quad \text{with} \quad \int_0^\infty \int_0^\infty \mathscr{p}(r,t')dr\,dt'=1 \tag{63}$$

of the distance r from the excited donor to the nearest acceptor and of the time t' at which the acceptor was generated. For given values of the distance r, of the initial time t', and of the life time ℓ the value of the relaxation rate is given by

$$W(t)=\mathscr{M}r^{-\sigma}\varphi(t-t')h(\ell-t+t'). \tag{64}$$

It follows that the probability density $\mathscr{T}(W;t)$ can be expressed as an average of a delta function corresponding to Eq. (64)

$$\mathscr{T}(W;t)=\int_0^\infty d\ell\psi(\ell)\int\int_0^t dt'\mathscr{p}(r,t')\delta(W-\mathscr{M}r^{-\sigma}\varphi(t-t')h(\ell-t+t'))dr. \tag{65}$$

The donor is surrounded by a hypersphere of radius r in which no acceptors exist; the corresponding fractal hypervolume $V^*(r)$ is given by Eq. (27). In the space–time continuum we define a space–time hypervolume (Ref. 37) $\nu^*(r,t')$ which is empty, that is, for which no acceptors exist. $\nu^*(r,t')$ is simply equal to

$$\nu^*(r,t')=V^*(r)t'. \tag{66}$$

The probability density $\mathscr{p}(r,t')$ can be expressed as

$$\mathscr{p}(r,t')dr\,dt'=\mathscr{E}(\nu^*(r,t'))\rho\omega(t')\,\frac{\partial V^*(r)}{\partial r}\,dr\,dt', \tag{67}$$

where $\mathscr{E}(\nu^*)$ is the probability that the space–time hypervolume $\nu^*(r,t')$ is empty. $\mathscr{E}(\nu^*)$ obeys the balance equation

$$\mathscr{E}(\nu^*+\Delta\nu^*)=\mathscr{E}(\nu^*)(1-\rho\omega(t')\Delta\nu^*), \tag{68}$$

which, for $\Delta\nu^*\rightarrow 0$, leads to a differential equation in $\mathscr{E}(\nu^*)$. By integrating this equation with the initial condition $\mathscr{E}(0)=1$ we get

$$\mathscr{E}(\nu^*)=\exp\left\{-\rho V^*(r)\int_0^{t'}\omega(t'')dt''\right\}. \tag{69}$$

By combining Eqs. (27), (66), (67), and (69) we get the following equation for the probability density $\not\varphi(r,t')$:

$$\not\varphi(r,t')dr\,dt' = \exp\left\{-\rho\,\frac{\pi^{d_f/2}r^{d_f}}{\Gamma(1+d_f/2)}\int_0^{t'}\omega(t'')dt''\right\}\frac{d_f\pi^{d_f/2}r^{d_f-1}}{\Gamma(1+d_f/2)}\,\rho\omega(t')dr\,dt'. \quad (70)$$

By inserting Eq. (70) into Eq. (65) and integrating over r we can get rid of the delta function, resulting in

$$\mathcal{T}(W;t) = \frac{\pi^{d_f/2}d_f\rho}{\sigma\mathcal{M}^{-d_f/\sigma}\Gamma(1+d_f/2)}\,W^{-(1+d_f/\sigma)}\int_0^\infty d\ell\psi(\ell)\int_0^t dt'\omega(t')[\varphi(t-t')h(\ell-t+t')]^{d_f/\sigma}\exp\left\{-\frac{\pi^{d_f/2}\rho}{\Gamma(1+d_f/2)}\left(\frac{\mathcal{M}}{W}\,\varphi(t-t')h(\ell-t+t')\right)^{d_f/\sigma}\int_0^{t'}\omega(t'')dt''\right\}. \quad (71)$$

The asymptotic behavior of the probability density $\mathcal{T}(W;t)$ as $W\to\infty$ can be easily evaluated from Eq. (71). As $W\to\infty$ the exponential tends to unity and Eq. (71) becomes

$$\mathcal{T}(W;t) \sim \frac{\pi^{d_f/2}\rho d_f\int_0^\infty d\ell\psi(\ell)\int_0^t dt'\omega(t')[\varphi(t-t')h(\ell+t'-t)]^{d_f/\sigma}}{\sigma\mathcal{M}^{-d_f/\sigma}\Gamma(1+d_f/2)W^{1+d_f/\sigma}}, \quad W\to\infty. \quad (72)$$

By comparing Eqs. (58) and (72) we note that as $W\to\infty$ the behavior of the probability densities $P(W;t)$ and $\mathcal{T}(W;t)$ are exactly the same. The physical explanation of this result is simple: the very large rates are generated by acceptors which are very close to the donor. For the closest acceptor the corresponding rate is the largest and its contribution to the total relaxation rate outweighs the contributions of remote acceptors. For not very large values of W, however, all acceptors contribute to relaxation and the probability density $\mathcal{T}(W;t)$ of the transfer rate of the fastest channel is a poor approximation for the probability density $P(W;t)$ of the total relaxation rate. This explanation for the same type of asymptotic behavior is similar to the one given to the Holstmark theorem from spectroscopy[43] and astrophysics;[44] a similar interpretation was suggested by the authors in the case of time and space dependent colored noise.[37]

The probability density $\mathcal{T}(W;t)$ does not describe the correlations among the fluctuations of the relaxation rate $W(t)$ at different times and thus it cannot be used for the evaluation of the average survival function in the case of dynamic disorder. For static disorder, i.e., if the conditions (39)–(41) are fulfilled, we have

$$\langle\mathcal{S}(t)\rangle_{\text{static}}^{\text{n.n.}} = \int_0^\infty \exp(-Wt)\mathcal{T}(W;t)dW, \quad (73)$$

where the superscript n.n. stands for the nearest neighbor approximation. The probability density $\mathcal{T}(W;t)$ can be computed from Eqs. (39)–(41) and (71)

$$\mathcal{T}(W) = \frac{d_f\pi^{d_f/2}\rho W^{-(1+d_f/\sigma)}}{\sigma\mathcal{M}^{-d_f/\sigma}\Gamma(1+d_f/2)}\exp\left\{-\frac{\pi^{d_f/2}\rho}{\Gamma(1+d_f/2)}\left(\frac{\mathcal{M}}{W}\right)^{d_f/\sigma}\right\} \quad \text{independent of} \quad t. \quad (74)$$

The integral over W in Eq. (73) cannot be computed exactly; we evaluate it by means of the method of steepest descent

$$\langle\mathcal{S}(t)\rangle_{\text{static}}^{\text{n.n.}} \sim \exp[-(\Omega' t)^\alpha], \quad (75)$$

where

$$\Omega' = \left(\frac{d_f+\sigma}{\sigma}\right)^{(d_f+\sigma)/d_f} \left(\frac{\pi^{d_f/2}\rho_{\cdot}\mathscr{M}^{d_f/\sigma}}{\Gamma(1+d_f/2)}\right)^{\sigma/d_f} \tag{76}$$

and

$$\alpha = d_f/(d_f+\sigma) = \beta/(1+\beta) < \beta. \tag{77}$$

Equation (75) is again a stretched exponential but with a smaller exponent $\alpha<\beta$ because of the truncating influence of more distant acceptors. In particular for $d_f=1$ Eqs. (75)–(77) reduce to the relationships derived by Klafter and Shlesinger[2] for one-dimensional relaxation.

VI. AN ALTERNATIVE APPROACH

In this section we suggest a different approach for describing the multichannel relaxation in terms of the theory of random point processes. We start out with the simplest case of static disorder. We classify the channels with respect to their contributions $w_1, w_2,\ldots$ to the total relaxation rate. For a set of N channels with individual rates $w_1,\ldots,w_N$ the total relaxation rate W is equal to

$$W = w_1 + \cdots + w_N. \tag{78}$$

By making an analogy with the formalism developed in Sec. II we describe the stochastic properties of the number N of channels and of the individual rates $w_1,\ldots,w_N$ in terms of a random point process in the w space defined by a set of Janossy densities

$$Q_0, Q_N(\mathbf{w}_N)d\mathbf{w}_N, \quad \text{with} \quad \mathbf{w}_N = (w_1,\ldots,w_N), \tag{79}$$

which obey the normalization condition

$$Q_0 + \sum_{N=1}^{\infty} \frac{1}{N!} \int Q_N(\mathbf{w}_N)d\mathbf{w}_N = 1. \tag{80}$$

In terms of the Janossy densities Q_N we define the product densities

$$\eta_N(\mathbf{w}_N)d\mathbf{w}_N = d\mathbf{w}_N \sum_{S=0}^{\infty} \frac{1}{S!} \int Q_{N+S}(\mathbf{w}_N,\mathbf{w}_S)d\mathbf{w}_S, \tag{81}$$

with

$$Q_N(\mathbf{w}_N)d\mathbf{w}_N = d\mathbf{w}_N \sum_{S=0}^{\infty} \frac{(-1)^S}{S!} \int \eta_{N+S}(\mathbf{w}_N,\mathbf{w}_S)d\mathbf{w}_S \tag{82}$$

and the generating functionals

$$\Lambda[Z(w)] = Q_0 + \sum_{N=1}^{\infty} \frac{1}{N!} \int Q_N(\mathbf{w}_N)Z(w_1)\cdots Z(w_N)d\mathbf{w}_{N'}, \tag{83}$$

$$\Xi[Z(w)]=1+\sum_{N=1}^{\infty}\frac{1}{N!}\int\eta_N(\mathbf{w}_N)Z(w_1)\cdots Z(w_N)d\mathbf{w}_N, \tag{84}$$

with

$$\Lambda[Z(w)]=\Xi[Z(w)-1]. \tag{85}$$

The probability density of the total relaxation rate $P(W)$ can be expressed as an average of a delta function corresponding to the superposition law (78)

$$P(W)dW=dW\sum\frac{1}{N!}\int Q_N(\mathbf{w}_N)\delta(W-\Sigma w_u)d\mathbf{w}_N. \tag{86}$$

By applying in Eq. (86) the Laplace transform with respect to the total relaxation rate W we can make a connection with the generating functional $\Xi[Z(w)]$

$$\mathscr{L}P(W)=\int_0^{\infty}\exp(-KW)P(W)dW=\Xi[Z(W)=\exp(-KW)-1]. \tag{87}$$

As for static disorder the average survival function can be expressed in terms of the Laplace transform of $P(W)$; we have [see also Eq. (59)]

$$\langle\mathscr{E}(t)\rangle_{\text{static}}=\mathscr{L}P(W)|_{K=t}=\Xi[Z(W)=\exp(-tW)-1]. \tag{88}$$

In particular if all channels are independent the point process is Poissonian,[37,38] and all Janossy densities can be expressed in terms of the first product density $\eta_1(w)$

$$Q_0=\exp\left(-\int\eta_1(w)dw\right),$$

$$Q_N(\mathbf{w}_N)=\exp\left(-\int\eta_1(w)dw\right)\eta_1(w_1)\cdots\eta_1(w_N) \tag{89}$$

and the generating functional $\Xi[Z(w)]$ is given by an exponential

$$\Xi[Z(w)]=\exp\left[\int\eta_1(w)Z(w)dw\right]. \tag{90}$$

By combining Eqs. (87) and (90) we obtain

$$\langle\mathscr{E}(t)\rangle_{\text{static}}=\exp\left\{-\int_0^{\infty}\eta_1(w)[1-\exp(-wt)]dw\right\}. \tag{91}$$

Equation (91) was first derived by Huber[4] by means of a succession of approximations without a straightforward significance. Our analysis shows that Eq. (91) is exact for a Poissonian distribution of independent channels.

In Eqs. (89)–(91) the first product density $\eta_1(w)$ is the average density of channels with an individual relaxation rate between w and $w+dw$. The integral of $\eta_1(w)$ over w is the average total number of channels

$$\langle N\rangle=\int_0^{\infty}\eta_1(w)dw. \tag{92}$$

In order to establish a relationship between the present approach and the model of static disorder suggested by Klafter and Shlesinger[2] we compare Eqs. (1) and (91). This comparison leads to the consistency condition

$$(\Omega t)^{\beta}=\int_0^{\infty} \eta_1(w)[1-\exp(-wt)]dw. \tag{93}$$

Equation (93) may be viewed as an integral equation for the average density of channels $\eta_1(w)$; it can be solved by differentiating with respect to t

$$\beta\Omega^{\beta}t^{\beta-1}=\int_0^{\infty} w\,\eta_1(w)\exp(-wt)dt. \tag{94}$$

The rhs of Eq. (94) is in fact the Laplace transform of the product $w\eta_1(w)$. By performing an inverse Laplace transformation we get an inverse power law for the average density of states

$$\eta_1(w)=\frac{\beta\Omega^{\beta}w^{-(1+\beta)}}{\Gamma(1-\beta)}. \tag{95}$$

Due to the nonanalytic singularity of the average density of states (95) for $w=0$ the average number of channels is infinite

$$\langle N\rangle=\infty. \tag{96}$$

For dynamic disorder the contribution $w(t)$ of an individual channel to the total relaxation rate is a random function of time. If there are N channels with the individual rates $w_1(t),\ldots,w_N(t)$ the total relaxation rate $W(t)$ is also a random function equal to

$$W(t)=w_1(t)+\cdots+w_N(t). \tag{97}$$

In order to generalize the formalism introduced in this section to systems with dynamic disorder we should extend the notion of random point process to the space of functions $w(t)$. Such a development can be carried out only in a formal way because we do not have a suitable definition of an integration measure $D[W(t)]$ over the space of functions $W(t)$.

Formally the stochastic properties of the number N of channels and of the corresponding individual rates can be described in terms of a set of functional Janossy densities

$$Q_0,Q_N[w_1(t),\ldots,w_N(t)]D[w_1(t)]\cdots D[w_N(t)], \tag{98}$$

with the normalization condition

$$Q_0+\sum_{N=1}^{\infty}\frac{1}{N!}\iint\cdots\iint Q_N[w_1(t),\ldots,w_N(t)]D[w_1(t)]\cdots D[w_N(t)]=1.$$

Within the framework of this functional formalism the product densities also become functionals of the individual rates

$$\eta_N[w_1(t),\dots,w_N(t)]D[w_1(t)]\cdots D[w_N(t)]$$
$$=D[w_1(t)]\cdots D[w_N(t)]\sum_{S=0}^{\infty}\frac{1}{S!}\iint\cdots\iint Q_{N+S}[w_1(t),\dots,w_{N+S}(t)]$$
$$\times D[w_{N+1}(t)]\cdots D[w_{N+S}(t)], \tag{99}$$

with

$$Q_N[w_1(t),\dots,w_N(t)]D[w_1(t)]\cdots D[w_N(t)]$$
$$=D[w_1(t)]\cdots D[w_N(t)]\sum_{S=0}^{\infty}\frac{(-1)^S}{S!}\iint\cdots\iint Q_{N+S}[w_1(t),\dots,w_{N+S}(t)]$$
$$\times D[w_{N+1}(t)]\cdots D[w_{N+S}(t)]. \tag{100}$$

The corresponding generating functionals become in fact functionals of functionals

$$\Lambda[Z[w(t)]]=Q_0+\sum_{N=1}^{\infty}\frac{1}{N!}\iint\cdots\iint Q_N[w_1(t),\dots,w_N(t)]$$
$$\times D[w_1(t)]\cdots D[w_N(t)]Z[w_1(t)]\cdots Z[w_N(t)], \tag{101}$$

$$\Xi[Z[w(t)]]=1+\sum_{N=1}^{\infty}\frac{1}{N!}\iint\cdots\iint \eta_N[w_1(t),\dots,w_N(t)]$$
$$\times D[w_1(t)]\dots D[w_N(t)]Z[w_1(t)]\cdots Z[w_N(t)], \tag{102}$$

$$\Lambda[Z[w(t)]]=\Xi[Z[w(t)]-1]. \tag{103}$$

In these equations $Z[w(t)]$ is a test functional of the random individual rate $w(t)$.

By using Eqs. (98)–(103) the relationship (88) for the average survival function can be easily extended for dynamic averages. We get

$$\langle \mathscr{\ell}(t)\rangle_{\text{dynamic}}=\Xi\left[Z[W(t)]=\exp\left(-\int_0^t W(t')dt'\right)-1\right]. \tag{104}$$

Equation (104) may be derived in the same way as Eq. (88) by introducing a probability density functional of the total rate $W(t)$ and using a functional analog of the Laplace transformation.

The case of independent channels corresponds to a functional Poisson process for which

$$Q_0=\exp\left(-\iint \eta_1[w(t)]D[w(t)]\right),$$
$$Q_N[w_1(t),\dots,w_N(t)]=\exp\left(-\iint \eta_1[w(t)]D[w(t)]\right)\eta_1[w_1(t)]\cdots\eta_1[w_N(t)], \tag{105}$$

and

$$\Xi[Z[w(t)]] = \exp\left(\iint \eta_1[w(t)]Z[w(t)]D[w(t)]\right). \tag{106}$$

By combining Eqs. (104)–(106) we come to a dynamic analog of the Huber equation (91)

$$\langle \mathscr{l}(t)\rangle_{\text{dynamic}} = \exp\left\{ -\iint \eta_1[w(t)]\left(1-\exp\left(-\int_0^t w(t')dt'\right)\right)D[w(t)]\right\}. \tag{107}$$

In these equations $\eta_1[w(t)]$ is the average functional density of channels and the functional integral over $w(t)$ is the total number of channels

$$\langle N\rangle = \iint \eta_1[w(t)]D[w(t)]. \tag{108}$$

By comparing Eq. (107) with Eq. (38) derived in Sec. III we get a consistency condition similar to Eq. (93)

$$\Omega^\beta \int_0^\infty d\not{\ell}\,\psi(\not{\ell}) \int_0^t dt'\ \omega(t')\left[\int_{t'}^{\min(t,\not{\ell}+t')} \varphi(t''-t')dt''\right]^\beta$$

$$= \iint \eta_1[w(t)]\left(1-\exp\left(-\int_0^t w(t')dt'\right)\right)D[w(t)], \tag{109}$$

which can also be viewed as an integral equation for the average functional density of channels $\eta_1[w(t)]$. However, unlike Eq. (93) Eq. (109) is only a formal equation which cannot be solved for $\eta_1[w(t)]$ because we do not have a suitable definition for the integration measure $D[w(t)]$.

VII. DISCUSSION

For analyzing the changes due to the passage from static to the dynamic disorder we compare the tails of the average relaxation laws (1), (43), (45), and (47)–(49) and the corresponding effective hazard rates

$$\mu(t) = -\partial \ln\langle \mathscr{l}(t)\rangle/\partial t. \tag{110}$$

By combining Eqs. (1), (43), (45) (47)–(49), and (110) we get the following expressions for the hazard rates:

(a) static disorder; $\langle \mathscr{l}(t)\rangle$ is given by Eq. (1) with $1>\beta>0$

$$\mu(t) = \beta\Omega^\beta t^{\beta-1}, \tag{111}$$

(b) dynamic disorder; $\langle \mathscr{l}(t)\rangle$ is given by Eqs. (47)–(49)

$$\mu(t) = \Omega^\beta \omega\langle\not{\ell}\rangle^\beta \gamma(\beta+1, t/\langle\not{\ell}\rangle),$$

$$\sim \Omega^\beta\omega\langle\not{\ell}\rangle^\beta\Gamma(\beta+1), \quad \text{as} \quad t\to\infty, \tag{112}$$

(c) dynamic disorder; $\langle \mathscr{l}(t)\rangle$ is given by Eq. (45)

$$\mu(t) = (\Omega A/H)^\beta \omega t^{\beta H}, \tag{113}$$

(d) dynamic disorder; $\langle \mathscr{S}(t) \rangle$ is given by Eq. (43)

$$\mu(t) = (\beta+1)\Omega^{\beta}\omega t^{\beta}. \tag{114}$$

In the succession of relaxation processes (a) $\to$ (b) $\to$ (c) $\to$ (d) the lengths of the tails of the average survival functions decrease, which shows an increase of the efficiency of the relaxation. This increase of efficiency is also displayed by the behavior of the effective hazard rates. For static disorder the hazard rate decreases from $\mu(0)=\infty$ to $\mu(\infty)=0$. In contrast, for systems with dynamic disorder the hazard rates (112)–(114) increase starting from $\mu(0)=0$; in case (b) it tends towards an asymptotic constant value and in cases (c) and (d) they tend to infinity as $t \to \infty$. The physical explanation of the increased efficiency for dynamic disorder is related to the fluctuation dynamics. The dynamic disorder is characterized by fluctuating relaxation rates which enter the expression of the survival function in a multiplicative way. As a result the average behavior of the system is influenced directly by the fluctuation dynamics: the stronger the fluctuations the faster the relaxation. We can make an analogy with the phenomenon of motional narrowing in spectroscopy described in terms of Anderson–Kubo theory:[11,12,45] in both cases a relaxation function depends multiplicatively on a random rate described by a stochastic process. The mechanism of fluctuations leads to a given type of relaxation behavior. In case (b) the generation of acceptors with a constant rate ω is compensated by their removal with a rate $\langle \mathscr{t} \rangle^{-1}$. For large time the statistical compensation between these two opposite factors leads to a constant hazard rate as $t \to \infty$ which corresponds approximately to a Markovian behavior for large time. In case (c) although there is no removal a similar compensation exists due to the decrease of the efficiency of acceptors [Eq. (44)]; however, the corresponding attenuation of an individual relaxation rate is slower than the process of removal and as a result even for very large times the process is still non-Markovian. The case (d) corresponds to a very efficient relaxation; in this case no compensation mechanism exists; the fast relaxation is due to the accumulation of the acceptors around the donor; this is essentially a transient effect which leads to the enhancement of the process of energy transfer.

Although the present approach has been suggested by the problem of direct energy transfer in fractal systems with dynamic disorder, our approach may also be used for investigating the dynamics of other types of relaxation processes. Of course our method is far from being universal: it is limited to the systems for which the dynamic disorder can be described in terms of the random point processes introduced in Secs. II and VI. However, even though the stochastic dynamics is different a basic feature of the present approach is still valid: the dynamic average of the survival function can always be represented in terms of the generating functional which describes the fluctuations of the total relaxation rate. It turns out that the evaluation of the average survival function is possible, at least in principle, for any stochastic system for which the generating functional can be computed analytically, for instance, for certain types of Markov processes or for some processes with long memory which can be embedded in a Markov process by increasing the number of degrees of freedom.[46] Such an approach can be applied for describing the decay of positrons or of positronium atoms trapped in dense fluids.[33]

In this article the main focus has been on the study of the average behavior of a relaxation system described in terms of a point process. Concerning the fluctuations of the number of surviving particles (or quasiparticles) for a relaxation process with dynamic disorder there are two different sources of stochasticity: (1) the fluctuations generated by the random variations of the relaxation rate $W(t')$ and (2) the sample fluctuations due to the intrinsic random nature of the relaxation process.

The first type of fluctuations due to dynamic disorder can be easily investigated by using the generating functional approach developed here. The one-time moments of the survival function $\langle \mathscr{S}(t) \rangle$ are given by

$$\langle \mathscr{S}^m(t)\rangle = \iint \exp\left(-\int_0^t mW(t')dt'\right)\mathscr{P}[W(t')]D[W(t')], \quad m>0. \tag{115}$$

By comparing Eqs. (21) and (115) we note that

$$\langle \mathscr{S}^m(t)\rangle = \langle \mathscr{S}(t, W(t') \to mW(t'))\rangle, \tag{116}$$

that is, the superior moments of the survival function can be computed from the expressions for the average survival function by replacing the relaxation rate $W(t')$ by $mW(t')$.

The study of interactions between the sample fluctuations and dynamical disorder is more complicated. In this case a double dynamic averaging procedure should be developed which will be presented elsewhere.[47] Here we mention only that the theory leads to a set of general fluctuation-dissipation relations

$$F_m(t)/F_m(0) = \langle \mathscr{S}^m(t)\rangle = \langle \mathscr{S}(t, W(t') \to mW(t'))\rangle, \tag{117}$$

which relate the factorial moments of the number $\mathscr{N}(t)$ of surviving particles at time t

$$F_m(t) = \langle \mathscr{N}(\mathscr{N}-1)\cdots(\mathscr{N}-m+1)\rangle(t), \quad m=1,2,\ldots \tag{118}$$

to the average survival function. The fluctuation-dissipation relations (117) are general: they are valid not only for the relaxation processes considered here but also for any independent decay process with dynamical disorder. Equations (117) are independent of the stochastic behavior of the random rate $W(t')$. An important consequence[47] of the fluctuation-dissipation relations (117) is that in the thermodynamic limit the fluctuations of the number of particles are intermittent: for large systems the relative fluctuation of the number of surviving particles does not decrease to zero but rather tends towards a constant positive value.

Although we have studied mainly the relaxation processes with dynamic disorder, some results obtained here are also of interest for the description of systems with static disorder. The formalism presented in Sec. VI may serve as a basis for a new physical interpretation of the Huber equation (91) leading to a new way of evaluating the experimental data. Such an approach would be of interest in the study of protein relaxation, for instance, the photodissociation of carbonmonoxy myoglobin.[25]

There are still some unsolved problems related to our approach, especially in connection with the relationships between the two types of random point processes introduced in Secs. II and VI. For the clarification of these relationships further investigations are necessary.

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