Generalized Huber kinetics for nonlinear rate processes in disordered systems: Nonlinear analogs of stretched exponential

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This paper deals with one-variable nonlinear rate processes occurring in disordered systems. A general stochastic approach is introduced for these processes based on the following assumptions. The total rate coefficient is made up of the additive contributions of a large number of individual reaction channels. These contributions are random functions of time and their stochastic properties are characterized by a functional random point process. Exact analytical expressions for the time dependence of the average concentration are derived by using a characteristic functional technique. These expressions are valid for systems with both dynamic and static disorder and are nonlinear analogs of the general kinetic law derived by Huber [Phys. Rev. B **31**, 6070 (1985); Phys. Rev. E **53**, 6544 (1996)] for linear rate processes in systems with static disorder. For independent rate processes with static disorder and a self-similar distribution of reaction channels we derive a nonlinear analog of the stretched exponential. A closed analytic expression of the nonlinear stretched exponential is given in terms of Fox's *H* functions. As expected, when the reaction order of the process is one, the nonlinear kinetic law reduces to a stretched exponential with a scaling exponent characterizing the self-similar distribution of the individual reaction channels. For nonlinear processes the tail of the averaged kinetic curve is self-similar and obeys a scaling law with a negative power law. Surprisingly, the scaling exponent of the tail depends only on the reaction order of the process and is independent of the scaling exponent that characterizes the self-similar distribution of the individual channels. We examine the possibilities of experimental evaluation of the statistical distribution of the total rate coefficient: The moments of different orders of the rate coefficient can be evaluated from the time derivatives of the survival function. [S1063-651X(98)10906-6]

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I. INTRODUCTION

In recent years the relaxation and reaction processes occurring in disordered systems have been studied from both the experimental and theoretical points of view [1]. In this field most papers focus on the experimental and theoretical study of processes with linear kinetics described by stretched exponential survival functions. There are relatively few attempts to extend the research to the case of nonlinear processes [2]. For nonlinear kinetics in random media exact theoretical results are scarce; most studies rely on numerical simulations. For linear processes in disordered systems a theoretical model was suggested by Huber in 1985 [3]. Based on a careful study of different linear rate processes, he proposed the kinetic law

$$\langle l(t)\rangle = \exp\left\{ -\int_0^\infty \rho(k)[1-\exp(-kt)]dk \right\}, \qquad (1)$$

where $\langle l(t)\rangle$ is the average relaxation (survival) function of the process and $\rho(k)$ is the average density of relaxation channels with an individual relaxation rate between k and $k+dk$. In particular, if the distribution of individual rates is self-similar and obeys a scaling relation with a negative power law

$$\rho(k)dk \sim \text{const} \times k^{-(1+\beta)}dk \quad \text{with} \quad 1>\beta>0, \qquad (2)$$

which is consistent with the general ideas of self-similarity of disordered systems reported in the literature, Huber's equation (1) leads to a stretched exponential kinetic law

$$\langle l(t)\rangle = \exp\{-(\Omega t)^\beta\}. \qquad (3)$$

More recently it has been shown that Huber's equation (1) is exact for a Poissonian distribution of independent channels [4]. Moreover, this equation also holds beyond the range of validity of the Poissonian distribution: It emerges as a universal scaling law for a uniform random distribution of reaction channels characterized by nonintermittent fluctuations [5]. This result is consistent with the idea that Huber's equation (1) and the stretched exponential relaxation law (2) derived from it can be generated by a central limit behavior of the Lévy type that expresses the contribution of a large number of weakly connected relaxation channels [6–8].

Huber's law (1) has been extended for systems with dynamical disorder [4,5,9]. By assuming that each individual relaxation rate attached to a reaction channel is a random function obeying Poissonian statistics, it has been shown that

$$\langle l(t)\rangle = \exp\left\{ -\iint \mathcal{R}[k(t')]\mathcal{D}[k(t')] \times \left[1-\exp\left(-\int_0^t k(t')dt' \right) \right] \right\}, \qquad (4)$$

where, due to dynamical disorder, the relaxation rate corre-

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sponding to an individual relaxation channel $k=k(t')$, $t \geqslant t' \geqslant 0$, is a random function of time; $\mathcal{R}[k(t')]\mathcal{D}[k(t')]$ is an average density of channels characterized by different random functions $k=k(t')$, $t \geqslant t' \geqslant 0$; $\mathcal{D}[k(t')]$ is a suitable integration measure over the space of functions $k=k(t')$, $t \geqslant t' \geqslant 0$; and $\iint$ stands for the operation of path integration. Just as in the case of Eq. (2), it has been shown that Eq. (4) emerges as a universal scaling law for a uniform random distribution of reaction channels characterized by nonintermittent fluctuations.

The theoretical studies of Huber's relaxation equation and of its generalizations have been motivated mainly by the analysis of physical relaxation processes occurring in disordered systems. However, these equations can be also applied to chemical reactions in disordered systems provided the kinetics of the process is of first order. Such kinetic systems are important, but the kinetics of most chemical reactions are nonlinear. The purpose of this paper is to present a simple approach for the time evolution of a chemical process of the type

$$\nu X \rightarrow (\text{products}), \tag{5}$$

occurring in a disordered system and for which the kinetic is nonlinear. Although our present research is mainly motivated by studies of chemical kinetics, the results presented in this paper are also of interest for the study of nonlinear physical processes in disordered media.

II. NONLINEAR RATE PROCESSES WITH DYNAMICAL DISORDER

In analogy to similar approaches developed in the literature in the case of linear kinetics, we assume that the chemical reaction (5) is the result of the contribution of a large number of different reaction channels. Each channel is characterized by a different rate coefficient $k_u(t)$, $u=1,2,...$, which is a random function of time. The total rate coefficient of the process $W(t)$ is the sum of the individual rates $k_u(t)$, $u=1,2,...$,

$$W(t)=\sum_u k_u(t). \tag{6}$$

Formally, the stochastic properties of an ensemble of N reaction channels can be described by generalizing the formalism of random point processes suggested by Ramakrishnan [10]. We introduce a set of grand canonical functional probability densities

$$Q_0, Q_1[k_1(t)]\mathcal{D}[k_1(t)], Q_N[k_1(t),...,k_N(t)]\mathcal{D}[k_1(t)]\cdots\mathcal{D}[k_N(t)]\cdots, \tag{7}$$

with the normalization condition

$$Q_0+\sum_{N=1}^{\infty}\frac{1}{N!}\iint\cdots\int Q_N[k_1(t),...,k_N(t)]\mathcal{D}[k_1(t)]\cdots\mathcal{D}[k_N(t)]=1 \tag{8}$$

and the characteristic functional

$$\mathcal{G}[Z[k(t)]]=Q_0+\sum_{N=1}^{\infty}\frac{1}{N!}\iint\cdots\int Q_N[k_1(t),...,k_N(t)]Z[k_1(t)]\cdots Z[k_N(t)]\mathcal{D}[k_1(t)]\cdots\mathcal{D}[k_N(t)], \tag{9}$$

where $Z[k(t)]$ is a suitable test functional.

For a given realization of the total rate coefficient $W(t)$ the differential kinetic equation attached to the chemical process (5) is

$$dc(t)/dt=-W(t)[c(t)]^{\nu} \quad \text{with} \quad c(t=0)=c_0, \tag{10}$$

where $c(t)$ is the concentration of the substance X at time t. The solution of the differential equation (9) for a given realization of the total rate coefficient $W(t')$, $t \geqslant t' \geqslant 0$, can be expressed as

$$\frac{c[t;W(t')]}{c_0}=\left\{1+(\nu-1)(c_0)^{\nu-1}\int_0^t W(t')dt'\right\}^{-1/(\nu-1)}$$

$$=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^{\infty} z^{1/(\nu-1)-1}\exp\left\{-z\left[1+(\nu-1)\times(c_0)^{\nu-1}\int_0^t W(t')dt'\right]\right\}dz, \tag{11}$$

where $\Gamma(x)=\int_0^{\infty} z^{x-1}\exp(-z)dz$, $x>0$, is the complete gamma function. In Eq. (10) we have made use of the equality

$$(1+y)^{-\alpha}=\frac{1}{\Gamma(\alpha)}\int_0^{\infty} z^{\alpha-1}\exp[-(1+y)z]dz. \tag{12}$$

The macroscopic observable is the average value of the survival function $l(t)$ of species X, which can be expressed as the ratio between the average value $\langle c(t)\rangle$ of the concentration $c(t)$ of the substance X and the initial concentration $c(t=0)=c_0$ for $t=0$,

$$\langle l(t)\rangle=\langle c(t)\rangle/c_0=\iint\frac{c[t;W(t')]}{c_0}\mathcal{P}[W(t')]\mathcal{D}[W(t')], \tag{13}$$

where

$$\mathcal{P}[W(t')]\mathcal{D}[W(t')] \quad \text{with} \quad \int\int \mathcal{P}[W(t')]\mathcal{D}[W(t')]=1 \tag{14}$$

is the probability density functional of the total rate coefficient $W(t')$, $t \geqslant t' \geqslant 0$. From Eqs. (11)–(14) we notice that the average survival function $\langle l(t)\rangle$ can be expressed in terms of the characteristic functional

$$\begin{aligned}\mathfrak{B}[\mathfrak{Y}(t')]&=\left\langle \exp\left[i\int_0^t W(t')\mathfrak{Y}(t')dt' \right]\right\rangle \\ &=\int\int \exp\left[i\int_0^t W(t')\mathfrak{Y}(t')dt' \right]\mathcal{P}[W(t')]\mathcal{D}[W(t')]\end{aligned} \tag{15}$$

of the probability density functional $\mathcal{P}[W(t')]\mathcal{D}[W(t')]$. We have

$$\langle l(t)\rangle=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^\infty z^{1/(\nu-1)-1}\exp(-z) \times\mathfrak{B}[i\mathfrak{Y}(t')=-z(\nu-1)(c_0)^{\nu-1}\theta(t)]dz, \tag{16}$$

where $\theta(t)$ is the usual Heaviside step function.

In principle, there are two different ways of computing the average survival function from Eq. (17). The first approach is a generalization of the ''random rate approach'' used in the literature for chemical processes with linear kinetics. We assume that the stochastic properties of the total rate coefficient are known and are expressed in terms of the cumulants $\langle\langle W_1(t_1)\rangle\rangle$, $\langle\langle W(t_1)W(t_2)\rangle\rangle$,... . We represent the characteristic functional $\mathfrak{B}[\mathfrak{Y}(t')]$ in Eq. (16) by a cumulant expansion, resulting in

$$\langle l(t)\rangle=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^\infty z^{1/(\nu-1)-1}\exp\left\{\sum_{m=1}^\infty \frac{1}{m!}[-\delta_{m1}-z(\nu-1)(c_0)^{\nu-1}]^m\int_0^t\cdots\int_0^t\langle\langle W(t_1')\cdots W(t_m')\rangle\rangle dt_1'\cdots dt_m'\right\}dz. \tag{17}$$

The expression (17) for the average survival function is similar to the virial expansion in equilibrium statistical mechanics. Similar expansions have been suggested for reactions with linear kinetics occurring in disordered systems.

The second method for evaluating the average survival function $\langle l(t)\rangle$ is a generalization of the random channel approach suggested in the literature for linear processes. We try to evaluate the dynamical average in Eq. (13) in terms of the grand canonical probability functionals (7) or in terms of the corresponding characteristic functional $\mathcal{G}[Z[w(t)]]$ defined by Eq. (9). We notice that $\mathfrak{B}[\mathfrak{Y}(t')]$ can be expressed as a grand canonical average

$$\begin{aligned}\mathfrak{B}[\mathfrak{Y}(t')]&=\left\langle \exp\left(i\int_0^t W(t')\mathfrak{Y}(t')dt' \right)\right\rangle \\ &=Q_0+\sum_{m=1}^\infty \frac{1}{m!}\int\cdots\int \exp\left(i\sum_{u=1}^m \int_0^t k_u(t')\mathfrak{Y}(t')dt' \right) \\ &\quad\times Q_m[w_1(t),\ldots,w_m(t)]Z[w_1(t)]\cdots Z[w_m(t)]\mathcal{D}[w_1(t)]\cdots\mathcal{D}[w_m(t)] \\ &=\mathcal{G}\left[Z[k(t)]=\exp\left(i\int_0^t k(t')\mathfrak{Y}(t')dt' \right)\right].\end{aligned} \tag{18}$$

By combining Eqs. (16) and (18) we arrive at

$$\langle l(t)\rangle=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^\infty z^{1/(\nu-1)-1}\exp(-z)\mathcal{G}\left[Z[k(t)]=\exp\left(-z(\nu-1)(c_0)^{\nu-1}\int_0^t k(t')dt' \right)\right]dz. \tag{19}$$

In particular, if the different reaction channels are statistically independent, the grand canonical probability density functionals defined by Eq. (7) obey Poissonian statistics and are given by

$$Q_0=\exp\left(-\int\int \rho[k(t)]\mathcal{D}[k(t)]\right), \tag{20}$$

$$Q_N[k_1(t),\ldots,k_N(t)]\mathcal{D}[k_1(t)]\cdots\mathcal{D}[k_N(t)]=\exp\left(-\int\int \mathcal{R}[k(t)]\mathcal{D}[k(t)]\right)\mathcal{R}[k_1(t)]\mathcal{D}[k_1(t)]\cdots\mathcal{R}[k_N(t)]\mathcal{D}[k_N(t)]. \tag{21}$$

The corresponding characteristic functional $\mathcal{G}[Z[k(t)]]$ is exponential,

$$\mathcal{G}[Z[k(t)]]=\exp\left(-\iint\{1-Z[k(t)]\}\mathcal{R}[k(t)]\mathcal{D}[k(t)]\right), \tag{22}$$

and Eq. (19) leads to

$$\langle l(t)\rangle=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^\infty z^{1/(\nu-1)-1}\exp(-z)\times\exp\left\{-\iint\mathcal{R}[k(t)]\mathcal{D}[k(t)]\times\left[1-\exp\left(-z(\nu-1)(c_0)^{\nu-1}\int_0^t k(t')dt'\right)\right]\right\}dz. \tag{23}$$

Equation (23) is the nonlinear analog of the Huber equation (4).

III. STATIC DISORDER AND GENERALIZED HUBER KINETICS

For illustration, in the following we consider a particular case of systems with static disorder. For such systems, a fluctuation, once it occurs, is frozen and lasts forever. By using the random rate approach, it follows that the total rate coefficient W is a random variable selected from a given probability distribution $P(W)dW$. In terms of this probability distribution the probability density functional $\mathcal{P}[W(t')]\mathcal{D}[W(t')]$ can be expressed as the average of the delta functional $\Delta[W(t)-W']\mathcal{D}[W(t')]$. We have

$$\mathcal{P}[W(t')]\mathcal{D}[W(t')]=\int_0^\infty dW'P(W')\times\Delta[W(t')-W']\mathcal{D}[W(t')]. \tag{24}$$

Similarly, in terms of the random channel approach, the individual channels with a rate coefficient between k and $k+dk$ are distributed according to an average density function $\rho(k)dk$. The average functional density of channels $\mathcal{R}[k(t')]\mathcal{D}[k(t')]$ can be expressed in terms of the density function $\rho(k)dk$ by a relationship similar to Eq. (24):

$$\mathcal{R}[k(t)]\mathcal{D}[k(t)]=\int_0^\infty dk'P(k')\Delta[k(t)-k']\mathcal{D}[k(t)]. \tag{25}$$

For static disorder the expressions (16), (17), and (19) for the average kinetic curve $\langle l(t)\rangle$ turn into a simpler form. We have

$$\langle l(t)\rangle=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^\infty z^{1/(\nu-1)-1}\exp(-z)\times\mathfrak{B}[iy=-z(\nu-1)(c_0)^{\nu-1}t]dz=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^\infty z^{1/(\nu-1)-1}\exp\left\{\sum_{m=1}^\infty\frac{1}{m!}\times[-\delta_{m1}-z(\nu-1)(c_0)^{\nu-1}]^m\langle\langle W^m\rangle\rangle t^m\right\}dz \tag{26}$$

and

$$\langle l(t)\rangle=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^\infty z^{1/(\nu-1)-1}\exp(-z)\times\mathfrak{C}\{\mathfrak{Z}(k)=\exp[-z(\nu-1)(c_0)^{\nu-1}kt]\}dz, \tag{27}$$

where

$$\mathfrak{B}(y)=\int_0^\infty\exp(iWy)P(W)dW \tag{28}$$

is the Fourier transform of the probability distribution $P(W)dW$, $\langle\langle W\rangle\rangle,\langle\langle W^2\rangle\rangle,\ldots$ are the cumulants of this distribution, and

$$\mathfrak{C}[\mathfrak{Z}(k)]=\mathfrak{Q}_0+\sum_{N=1}^\infty\frac{1}{N!}\int_0^\infty\cdots\int_0^\infty\mathfrak{Q}_N(k_1,\ldots,k_N)\mathfrak{Z}(k_1)\cdots\mathfrak{Z}(k_N)dk_1\cdots dk_N \tag{29}$$

is the characteristic functional attached to the set of ''static'' grand canonical distributions

$$\mathfrak{Q}_0,\ldots,\mathfrak{Q}_N(k_1,k_2,\ldots)dk_1dk_2\ldots$$

$$\text{with}\quad \mathfrak{Q}_0+\sum_{N=1}^{\infty}\frac{1}{N!}\int_0^{\infty}\cdots\int_0^{\infty}\mathfrak{Q}_N(k_1,\ldots,k_N)dk_1\cdots dk_N=1, \tag{30}$$

which describe the fluctuations of the individual values of the rate coefficients for a system with static disorder.

The random-rate and random-channel description of the process are related to each other by means of a relationship between the characteristic functional $\mathfrak{C}[\mathfrak{Z}(k)]$, which describes the statistical properties of the individual channels and the Fourier transform $\mathfrak{B}(y)$ of the probability distribution $P(W)dW$ of the total rate coefficient W:

$$\mathfrak{B}(y)=\mathfrak{C}[\mathfrak{Z}(k)=\exp(iky)]. \tag{31}$$

Equation (31) can be derived in the same way as Eq. (18).

IV. NONLINEAR ANALOGS OF THE STRETCHED EXPONENTIAL

Systems with static disorder for which the different reaction channels are independent deserve special attention. In this case the grand canonical probability distributions $\mathfrak{Q}_0,\ldots,\mathfrak{Q}_N(k_1,k_2,\ldots)dk_1dk_2,\ldots$ are Poissonian,

$$\mathfrak{Q}_0=\exp\left(-\int_0^{\infty}\rho(k)dk\right),$$

$$\mathfrak{Q}_N(k_1,\ldots,k_N)dk_1\cdots dk_N=\exp\left(-\int_0^{\infty}\rho(k)dk\right)\rho(k_1)dk_1\cdots\rho(k_N)dk_N, \tag{32}$$

and the characteristic functional $\mathfrak{C}[\mathfrak{Z}(k)]$ is exponential,

$$\mathfrak{C}[\mathfrak{Z}(k)]=\exp\left\{\int_0^{\infty}[\mathfrak{Z}(k)-1]\rho(k)dk\right\}. \tag{33}$$

By combining Eqs. (27) and (33) we arrive at

$$\langle l(t)\rangle=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^{\infty}z^{1/(\nu-1)-1}\times\exp\left\{-z-\int_0^{\infty}\rho(k)\{1-\exp[-z(\nu-1)\times(c_0)^{\nu-1}kt]\}dk\right\}dz. \tag{34}$$

Equation (34) is the nonlinear analog of Huber's relaxation equation (1) for systems with static disorder. As expected, in the limit $\nu\to1$, Eq. (34) reduces to Eq. (4).

Following Huber, we assume a self-similar distribution of individual rates of the type (2),

$$\rho(k)dk\sim[\Gamma(1-\beta)]^{-1}\Omega^{\beta}k^{-(1+\beta)}dk, \tag{35}$$

where Ω is a constant with the physical dimension of a rate coefficient for the nonlinear chemical process (5). In Eq. (35) the proportionality constant was determined from the condition that in the limit $\nu\to1$, Eqs. (34) and (35) lead to the stretched exponential (2).

By inserting Eq. (35) into Eq. (34) and carrying out the integral over k we arrive at

$$\langle l(t)\rangle=\frac{1}{\Gamma\left(\frac{1}{\nu-1}\right)}\int_0^{\infty}z^{1/(\nu-1)-1}\exp\{-z-[z(\nu-1)\times(c_0)^{\nu-1}\Omega t]^{\beta}\}dz. \tag{36}$$

Equation (36) is the nonlinear analog of the stretched exponential law (3). It is easy to check that, in the limit $\nu\to1$, Eq. (36) reduces to Eq. (1). A simple way of proving this is to expand in Eq. (36) the exponential term $\exp\{-[z(\nu-1)(c_0)^{\nu-1}\Omega t]^{\beta}\}$ in a Taylor series, integrate the resulting equation term by term, and pass to the limit $\nu\to1$. By collecting the different terms of the resulting equation we arrive at Eq. (3).

By following a common approach in the theory of statistical fractals [13], the integral in Eq. (36) can be expressed in terms of the Fox H functions. We can rewrite Eq. (36) by substituting $u=z(c_0)^{\nu-1}\Omega t$, resulting in

$$\langle l(t)\rangle=\frac{((c_0)^{\nu-1}\Omega t)^{-1/(\nu-1)}}{\Gamma\left(\frac{1}{\nu-1}\right)}\times\int_0^{\infty}\exp\left[-\frac{u}{(c_0)^{\nu-1}\Omega t}\right]u^{1/(\nu-1)-1}\times\exp\{-[(\nu-1)u]^{\beta}\}du, \tag{37}$$

which can be viewed as a Laplace transform from u to the $1/(c_0)^{\nu-1}\Omega t$ space:

$$\langle l(t)\rangle=\frac{[(c_0)^{\nu-1}\Omega t]^{-1/(\nu-1)}}{\Gamma[1/(\nu-1)]}\mathcal{L}(u^{1/(\nu-1)-1}\times\exp\{-[(\nu-1)u]^{\beta}\};1/(c_0)^{\nu-1}\Omega t). \tag{38}$$

To evaluate this transform we express the original function in terms of a Fox function as

$$u^{1/(\nu-1)-1}\exp\{-[(\nu-1)u]^{\beta}\} = \frac{(\nu-1)^{(\nu-2)/(\nu-1)}}{\beta} H_{0,1}^{1,0}\left[(\nu-1)u\,\middle|\left(\frac{2-\nu}{\beta(\nu-1)},\frac{1}{\beta}\right)\right], \tag{39}$$

from which we can calculate the Laplace transform [13]

$$\langle l(t)\rangle = \frac{(\nu-1)^{(2-\nu)/(\nu-1)}}{\beta\Gamma[1/(\nu-1)]}[(c_0)^{\nu-1}\Omega t]^{(2-\nu)/(\nu-1)} \times H_{1,1}^{1,1}\left[(\nu-1)(c_0)^{\nu-1}\Omega t\,\middle|\begin{matrix}(0,1)\\ \left(\frac{2-\nu}{\beta(\nu-1)},\frac{1}{\beta}\right)\end{matrix}\right]. \tag{40}$$

This exact analytical representation of the nonlinear stretched exponential law (36) can be used to investigate the asymptotic behavior of the process for long times. We make use of a formula given by Braaksma [14],

$$H_{p,q}^{m,n}(z)\sim\sum \mathrm{Res}[\chi(s)z^{s}] \quad \text{as} \quad |z|\to\infty. \tag{41}$$

In Eq. (41) the residues have to be taken in the points $s=(a_j-1-\nu)/A_j$, where $j=1,...,n$. The meaning of the symbols are given in the Appendix.

In our case Eq. (41) is given by

$$H_{1,1}^{1,1}\left[[(c_0)^{\nu-1}\Omega t]\,\middle|\begin{matrix}(0,1)\\ \left(\frac{2-\nu}{\beta(\nu-1)},\frac{1}{\beta}\right)\end{matrix}\right] \sim \sum_{\mu=0}^{\infty}\mathrm{Res}\left\{\Gamma(1+s)\Gamma\left[\frac{2-\nu}{\beta(\nu-1)}-\frac{s}{\beta}\right]\times[(c_0)^{\nu-1}\Omega t]^{s}\right\}\Bigg|_{s=-1-\mu}. \tag{42}$$

By evaluating the first residues we obtain

$$\langle l(t)\rangle = \frac{1}{\beta\Gamma[1/(\nu-1)]}[(\nu-1)(c_0)^{\nu-1}\Omega t]^{-1/(\nu-1)} \times\left\{\Gamma\left(\frac{1}{\beta(\nu-1)}\right)-[(c_0)^{\nu-1}\Omega t]^{-1}\Gamma\left(\frac{1+(\nu-1)}{\beta(\nu-1)}\right) +[(c_0)^{\nu-1}\Omega t]^{-2}\Gamma\left(\frac{1+2(\nu-1)}{\beta(\nu-1)}\right) +\mathcal{O}\{[(c_0)^{\nu-1}\Omega t]^{-3}\}\right\}, \tag{43}$$

where $\mathcal{O}$ is the Landau symbol. The asymptotic expansion (43) is reminiscent of the standard geometric series expansion for $1/(1+x)$. This analogy is also reflected in the identity

$$(1+y)^{-\alpha}=\frac{1}{\Gamma(\alpha)}H_{1,1}^{1,1}\left[y\,\middle|\begin{matrix}(1-\alpha,1)\\ (1,0)\end{matrix}\right]. \tag{44}$$

An alternative expression of the asymptotic behavior of the survival function for long times can be derived by expressing the exponential in Eq. (36) as a product of two exponentials, expanding $\exp(-z)$ in a McLaurin series, and integrating the resulting expression term by term. We obtain

$$\langle l(t)\rangle = \frac{[(\nu-1)(c_0)^{\nu-1}\Omega t]^{-1/(\nu-1)}}{\beta\Gamma(1/(\nu-1))}\sum_{m=0}^{\infty}\frac{[-(\nu-1)(c_0)^{\nu-1}\Omega t]^{-m}}{m!}\Gamma\left(m+\frac{1}{\beta(\nu-1)}\right) \quad \text{as} \quad (\nu-1)(c_0)^{\nu-1}\Omega t\to\infty. \tag{45}$$

As expected, both asymptotic expansions lead to the same result. For long times the average survival function has a long tail of the negative power law type:

$$\langle l(t)\rangle\sim\frac{\Gamma(1/\beta(\nu-1))}{\beta\Gamma(1/(\nu-1))}[(\nu-1)(c_0)^{\nu-1}\Omega t]^{-1/(\nu-1)} \quad \text{as} \quad (\nu-1)(c_0)^{\nu-1}\Omega t\to\infty. \tag{46}$$

It is interesting to compare the asymptotic law (46) with the integral kinetic law for a system without disorder for which

$$\rho(k)=\delta(k-\Omega). \tag{47}$$

In this case the general relation (34) reduces to

$$\langle l(t)\rangle=[1+(\nu-1)(c_0)^{\nu-1}\Omega t]^{-1/(\nu-1)} \sim[(\nu-1)(c_0)^{\nu-1}\Omega t]^{-1/(\nu-1)} \quad \text{as} \quad (\nu-1)(c_0)^{\nu-1}\Omega t\to\infty, \tag{48}$$

that is, for nonlinear kinetics the shape of the tail of the kinetic curve and the corresponding scaling exponents are identical for ordered and disordered systems. The only factor in which the influence of disorder shows up is in the proportionality coefficients of the tail; for disordered systems this proportionality coefficient depends both on the reaction order and on the scaling exponent β expressing the self-similar properties of the statistical distribution of the individual channels. In contrast, for a linear process with static disorder the scaling exponent β is the main parameter determining the shape of the tail of the kinetic curve. The independence of β of the scaling exponent of the tail for a reaction order differ-

ent from one is an unexpected nonlinear effect for which we do not have a simple physical explanation.

V. RATE STATISTICS AND EXPERIMENTAL DATA

For linear rate processes occurring in disordered systems an important issue is the spectral kinetic analysis [11]. Given an experimental kinetic curve $\langle l(t)\rangle$, it is possible to evaluate the statistical properties of the total rate coefficient W, expressed by the distribution $P(W)dW$ or the statistical properties of the contribution k of an individual reaction channel, expressed by the average density of states $\rho(k)dk$. The spectral kinetic analysis can be easily extended to nonlinear kinetics provided the value of the reaction order of the process is known.

We start our study of the nonlinear kinetic spectral analysis by establishing the relationships between the probability distribution $P(W)dW$ of the total rate coefficient and the average density of states $\rho(k)dk$ attached to an individual reaction channel. We restrict our analysis to the case of independent reaction channels obeying Poissonian statistics. By combining Eqs. (31) and (33) we arrive at the following expression for the Fourier transform $\mathfrak{B}(y)$ of the probability $P(W)dW$:

$$\mathfrak{B}(y)=\exp\left\{\int_0^\infty[\exp(iky)-1]\rho(k)dk\right\}, \tag{49}$$

from which, by performing an inverse Fourier transform and passing from complex exponential to trigonometric functions, we obtain

$$\begin{aligned}P(W)&=\frac{1}{2\pi}\int_{-\infty}^{+\infty}\exp\left\{-iyW+\int_0^\infty[\exp(iky)-1]\right.\\&\quad\left.\times\rho(k)dk\right\}dy\\&=\frac{1}{\pi}\int_0^\infty\exp\left\{-\int_0^\infty\rho(k)[1-\cos(ky)]dk\right\}\\&\quad\times\cos\left\{yW+\int_0^\infty\rho(k)\sin(ky)dk\right\}dy.\end{aligned} \tag{50}$$

In particular, if the distribution of reaction channels is self-similar and the average density of states $\rho(k)dk$ obeys the power law (35), the probability distribution $P(W)dW$ of the total rate coefficient can be evaluated from Eq. (50) by inserting Eq. (35) and evaluating the integrals over k,

$$\begin{aligned}P(W)&=\frac{1}{\pi}\int_0^\infty\exp\left\{-(y\Omega)^\beta\cos\left(\frac{\pi\beta}{2}\right)\right\}\\&\quad\times\cos\left\{yW+(y\Omega)^\beta\sin\left(\frac{\pi\beta}{2}\right)\right\}dy.\end{aligned} \tag{51}$$

The distribution (51) corresponds to the nonlinear generalization of the stretched exponential given by Eqs. (36) and (40).

To express the average density of channels $\rho(k)dk$ in terms of the probability distribution $P(W)dW$ we express Eq. (49) in the form

$$\int_0^\infty\exp(ikW)P(W)dW=\exp\left\{\int_0^\infty[\exp(iky)-1]\rho(k)dk\right\}. \tag{52}$$

Since the total rate coefficient W is a non-negative random variable, in Eq. (52) we can formally replace the Fourier transformation by a Laplace transformation. We introduce the Laplace variable $\sigma=-ik$ and take the logarithm of the resulting equation

$$\begin{aligned}&-\ln\left\{\int_0^\infty\exp(-\sigma W)P(W)dW\right\}\\&\quad=\int_0^\infty[1-\exp(-\sigma k)]\rho(k)dk.\end{aligned} \tag{53}$$

Now we differentiate Eq. (53) term by term with respect to σ, resulting in

$$\begin{aligned}\int_0^\infty\exp(-\sigma W)WP(W)dW&=\left[\int_0^\infty\exp(-\sigma W)P(W)dW\right]\\&\quad\times\left[\int_0^\infty\exp(-\sigma k)k\rho(k)dk\right].\end{aligned} \tag{54}$$

By applying the inverse Laplace transform to Eq. (54) we arrive at a linear integral equation for the average density of states $\rho(k)dk$,

$$\int_0^W k\rho(k)P(W-k)dk=WP(W). \tag{55}$$

The solution of Eq. (55) can be represented as an inverse Laplace transform

$$\begin{aligned}\rho(k)&=\frac{1}{2\pi ik}\int_{c-i\infty}^{c+i\infty}\left\{\frac{\int_0^\infty\exp(-\sigma W)WP(W)dW}{\int_0^\infty\exp(-\sigma W)P(W)dW}\right\}\\&\quad\times\exp(k\sigma)d\sigma.\end{aligned} \tag{56}$$

A remarkable property of Eqs. (49)–(56) is that they are independent of the value of the reaction order ν; it follows that they must have exactly the same form both for linear and for nonlinear kinetics. We notice that Eqs. (50), (51), and (56) have already been derived in the literature for the particular case of linear kinetics, by means of a method that is different from the one used here [12].

If the reaction order ν of the process, the initial concentration c_0, and the survival function $\langle l(t)\rangle$ are known, then at least in principle the distribution $P(W)dW$ of the total rate coefficient can be evaluated from experimental data. From Eqs. (26) and (28) we obtain

$$\langle l(t)\rangle = \int_0^\infty \frac{P(W)dW}{\{1+(\nu-1)(c_0)^{\nu-1}Wt\}^{1/(\nu-1)}}. \qquad (57)$$

Equation (57) is a linear integral equation for the distribution $P(W)dW$ of the total rate coefficient. This integral equation can be transformed, through discretization, into a linear matrix equation that can be solved numerically.

We notice that the positive moments of the total rate coefficient

$$\langle W^m\rangle = \int_0^\infty W^m P(W)dW, \quad m=1,2,\ldots, \qquad (58)$$

can be evaluated from the time derivatives of the average survival function $\langle l(t)\rangle$. By differentiating Eq. (57) m times with respect to t and setting $t=0$ we get

$$\langle W^m\rangle = [-(\nu-1)(c_0)^{\nu-1}]^{-m} \times \frac{\Gamma\left(m+\frac{1}{\nu-1}\right)}{\Gamma\left(\frac{1}{\nu-1}\right)} \frac{d^m}{dt^m}\langle l(t)\rangle \Bigg|_{t=0}. \qquad (59)$$

VI. CONCLUSIONS

In this paper we have suggested a statistical theory of one-variable nonlinear rate processes in disordered systems. By using the method of characteristic functionals combined with a functional generalization of the theory of random point processes we have derived analytical expressions of the averaged survival functions for both static and dynamical disorder. The theory has been applied to the particular case of a self-similar distribution of independent reaction channels obeying Poissonian statistics. In this particular case we have derived a nonlinear generalization of the well-known stretched exponential kinetic law. This nonlinear stretched exponential can be expressed analytically in terms of the Fox functions. We have investigated the possibilities of extending the spectral kinetic analysis to nonlinear processes. In the particular case of independent processes with static disorder we have derived a set of relations between the probability distribution of the total rate coefficient of the process and the average density of states of the individual rates corresponding to the different reaction channels. These relations may serve as a basis for extracting information about the local and global rate statistics from the experimental data.

In the particular case of linear rate processes with static or dynamical disorder it has been shown in the literature that the kinetic behavior of the Huber type emerges as a universal behavior in the limit of a large number of reaction channels with nonintermittent fluctuations. In addition, a renormalization-group approach has been used to show that for intermittent fluctuations a more complicated kinetic law emerges that includes the Huber kinetic law as a particular case. In our future research we intend to investigate the possibility to extend these results to the more complex case of nonlinear rate processes. Another interesting problem is the generalization for nonlinear processes of the method suggested by Allinger and Blumen for the study of linear rate processes with dynamic disorder [16]. Work on these problems is in progress.

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APPENDIX: FOX'S H FUNCTIONS

In 1961 Fox defined the H functions in his studies of symmetrical Fourier kernels as Mellin-Barnes path integrals in the complex plane (see, e.g., [13–15])

$$H_{pq}^{mn}(x) = H_{pq}^{mn}\left[x\left|\begin{matrix}(a_p,A_p)\\(b_q,B_q)\end{matrix}\right.\right] = H_{pq}^{mn}\left[x\left|\begin{matrix}(a_1,A_1),(a_2,A_2),\ldots,(a_p,A_p)\\(b_1,B_1),(b_2,B_2),\ldots,(b_q,B_q)\end{matrix}\right.\right] = \frac{1}{2\pi i}\int_L ds\ \chi(s)x^s, \qquad (A1)$$

with the integral density

$$\chi(s) = \frac{\prod_1^m \Gamma(b_j-B_js)\prod_1^q \Gamma(1-a_j+A_js)}{\prod_{m+1}^p \Gamma(1-b_j+B_js)\prod_{n+1}^p \Gamma(a_j-A_js)}. \qquad (A2)$$

The constraints for the parameters occurring in Eq. (38) are given in Ref. [15]. Note that the path integral in Eq. (37) represents just the inverse Mellin transform of the kernel $\chi(s)$.

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