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A Stochastic Approach to Nonequilibrium Chain Reactions in Disordered Systems: Breakdown of Eikonal Approximation[1]

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A stochastic description of chain reactions occurring in disordered systems is suggested by considering a statistical distribution of time-dependent rate coefficients. The possibilities of constructing a thermodynamic formalism for nonequilibrium chain reactions are investigated by testing the validity of the eikonal approximation in the thermodynamic limit. If the fluctuations of the rate coefficient are restricted to a finite range, then for large systems the probability of concentration fluctuations obeys the eikonal scaling condition, which makes possible the development of a nonequilibrium thermodynamic formalism. For an infinite range of variation of the rate coefficient, however, the eikonal scaling does not hold anymore: the probability of concentration fluctuations has a long tail of the negative power-law type and the system displays statistical fractal features. The passage from the stochastic eikonal behavior to the fractal scaling is characterized by a change in the deterministic kinetic equations of the process: in the eikonal regime the effective reaction order with respect to the active intermediate is 1, whereas for fractal scaling it is equal to 2. Due to this change in the effective reaction order for fractal scaling, the reaction is much faster than in the eikonal regime and the explosion threshold may be reached after a finite time interval.

KEY WORDS: chain reactions in disordered systems, eikonal scaling; nonequilibrium thermodynamics; renormalized kinetic equations; statistical fractal scaling.

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1. INTRODUCTION

A number of thermodynamic and stochastic approaches have been suggested in the literature for the description of nonequilibrium processes [1–4]. These theories start out from a stochastic description of a nonequilibrium process and try to establish a connection between the macroscopic behavior of the system and the probability of fluctuations. The main assumption of these theories is that for a large system the probability of fluctuations at time t, $P(\mathbf{X}; t)\, d\mathbf{X}$, corresponding to a set $\mathbf{X} = (X_1, X_2,...)$ of extensive macrovariables, obeys the scaling condition

$$P(\mathbf{X}; t)\, d\mathbf{X} \sim \exp[-\Omega J(\mathbf{X}/\Omega; t)]\, d\mathbf{X} \qquad \text{as} \quad \Omega \to \infty \tag{1}$$

where Ω is the size of the system, expressed in terms of volume, surface, or total number of particles, and $J(\mathbf{X}/\Omega; t)$ is a stochastic action similar to the action function from classical mechanics. The scaling condition, Eq. (1), is similar to the eikonal approximation from optics or to the WKB approximation from quantum mechanics. Equation (1) was introduced by Kubo et al. [5]. For the stochastic and thermodynamic theories of nonequilibrium processes, Eq. (1) plays a role similar to Einstein's fluctuation formula from equilibrium thermodynamics, whereas the function $\Omega J(\mathbf{X}/\Omega; t)$ plays the role of a stochastic thermodynamic potential similar to the entropy or the Gibbs or Helmholtz free energies.

The possibility of constructing a nonequilibrium thermodynamic theory is generally limited to systems for which the scaling condition expressed by Eq. (1) is fulfilled. Equation (1) fails to describe systems for which the large fluctuations have the main contribution to the temporal evolution of the process, because for systems obeying Eq. (1) the very large fluctuations, although possible, are exponentially rare. It follows that for the general understanding of the evolution of nonequilibrium processes, it is very important to know in what circumstances the scaling condition [Eq. (1)] may fail. A class of very simple processes for which an approximation of the type of Eq. (1) may not hold is made up of different types of chain processes, including chemical chain reactions. The general study of chain processes is not limited to the field of chemical kinetics; chain processes have been used for describing a broad class of natural phenomena from physics, chemistry, and biology [6]. For a chain process the fluctuations of the number of particles may play an important role, because the chain mechanism not only leads to the multiplication of the number of individuals but also amplifies the fluctuations. An alternative to the eikonal scaling, Eq. (1),is the statistical fractal scaling [7],

$$P(\mathbf{X}; t)\, d\mathbf{X} \sim [\Omega/(\mathbf{X}/\Omega; t)]^{(1+H)}\, d\mathbf{X} \qquad \text{as} \quad \Omega \to \infty, \quad H > 0 \tag{2}$$

where $H > 0$ is a positive fractal exponent. A straightforward analysis shows that a chain reaction occurring in a homogeneous system and evolving according to the stochastic version of the mass action law does not lead to a breakdown of the eikonal scaling Eq. (1), despite the occurrence of relatively large fluctuations. A chain reaction occurring in a disordered system, however, may lead to a fractal scaling of the type of Eq. (2) and to the violation of the eikonal approximation. For a disordered system the random structure of the medium in which the reaction takes place leads to a statistical distribution of the rate coefficients which become random variables. The population fluctuations are relatively large even for a homogeneous chain reaction; for a disordered system these fluctuations are further amplified by the random structure of the medium, resulting in a statistical fractal behavior described by Eq. (2).

The structure of the article is the following. In Section 2 we give a mathematical formulation of the problem in terms of a compound master–Liouville stochastic equation and evaluate the probability of population fluctuations. Sections 3 and 4 deal with the eikonal and fractal scaling conditions, respectively. Section 5 deals with the determination of the effective deterministic kinetic equations. Finally, in Section 6 we discuss the main implications of the model.

2. EVOLUTION EQUATIONS

We consider a simplified description of a chain reaction taking place in a disordered medium. We assume that there is a single type of active intermediate and take into account only a propagation step of the type

$$A + X \xrightarrow{k} 2X \tag{3}$$

where A is a stable species with concentration kept constant, X is the active intermediate, and k is an effective first-order rate coefficient which is proportional to the concentration of the stable species A. The possibility of a thermal explosion generated by the accumulation of heat in the system is neglected and therefore the process is assumed to be isothermal.

A chemical reaction occurring in a disordered system is characterized by two main features [8]. (a) Due to the disordered structure of the medium the motion of the reacting particles is very slow and therefore the rate coefficients are time dependent. (b) The random structure of the medium leads to a statistical distribution of rate coefficients. In this article we limit ourselves to the study of systems with static disorder, for which a structural fluctuation, once it has occurred, lasts forever, that is, in the system the disorder is completely frozen. As a result, the random structure of the medium leads to an initial random distribution of the rate coefficient k. This initial distribution is characterized by a probability density

$$\eta(k)\,dk \qquad \text{with} \quad \int \eta(k)\,dk = 1 \tag{4}$$

The time evolution of the rate coefficient is described by the differential equation [8]

$$dk(t)/dt = -\nu(t)\,k(t) \qquad \text{with} \quad k(t=0) = k_0 \tag{5}$$

where the initial value $k(t=0) = k_0$ is randomly selected from the probability law, Eq. (4), and $\nu(t)$ is the frequency of decay of the rate coefficient. We note that relationships of the type of Eq. (5) have been commonly used in chemical engineering for describing the process of catalyst poisoning [9]. Since the disorder leads to a decrease in the mobility of particles, the rate coefficient should be a nonincreasing function of time. In this article we consider two situations which fulfill this condition. (a) The decay frequency $\nu(t)$ is equal to zero and thus the rate coefficient is time independent:

$$k(t) = k \qquad \text{independent of } t \text{ for } \nu(t) = 0 \tag{6}$$

(b) The decay rate $\nu(t)$ tends to a value different from zero for large times,

$$\lim_{t \to \infty} \nu(t) = \nu(\infty) \neq 0 \tag{7}$$

In this second case the rate coefficient at time t,

$$k(t) = k_0 \exp\left[-\int_0^t \nu(t')\,dt' \right] \tag{8}$$

decreases to zero for large times,

$$\lim_{t \to \infty} k(t) = 0 \tag{9}$$

For describing the dynamics of the process we introduce the joint probability density

$$\Phi(N, k; t)\,dk \qquad \text{with} \quad \sum_N \int \Phi(N, k; t)\,dk = 1 \tag{10}$$

$\Phi(N, k; t)\,dk$ is the probability that at time t the number of active intermediates is N and that the value of the rate coefficient is between k and

$k + dk$. By taking into account the above-introduced assumptions, we can derive an irreversible stochastic master–Liouville equation for $\Phi(N, k; t)$:

$$\frac{\partial}{\partial t}\Phi(N, k; t) = \frac{\partial}{\partial k}[\nu(t)\,k\Phi(N, k; t)] + k[(N-1)\,\Phi(N, k; t) - N\Phi(N, k; t)] \tag{11}$$

with the initial condition,

$$\Phi(N, k; t=0) = \eta(k)\,P(N; t=0) \tag{12}$$

where

$$P(N; t) = \int \Phi(N, k; t)\,dk \qquad \text{with} \quad \sum_N P(N; t) = 1 \tag{13}$$

is the probability that at time t the number of active intermediates is N.

For solving the evolution equation, Eq. (11), we combine the method of characteristics with the technique of characteristic functions. We define the characteristic functions of $\Phi(N, k; t)$ and $P(N; t)$ as discrete Fourier transforms:

$$G(b, k; t) = \sum_N \exp(ibN)\,\Phi(N, k; t) \tag{14}$$

$$g(b; t) = \sum_N \exp(ibN)\,P(N; t) \tag{15}$$

where b is the Fourier variable conjugate to the number N of active intermediates. By expressing Eqs. (11) and (12) in terms of the characteristic functions $G(b, k; t)$ and $g(b; t)$, we come to

$$\frac{\partial}{\partial t}G(b, k; t) = \frac{\partial}{\partial k}[\nu(t)\,kG(b, k; t)] - ik[\exp(ib) - 1]\frac{\partial}{\partial b}G(b, k; t) \tag{16}$$

$$G(b, k; t=0) = g(b; t=0)\,\eta(k) \tag{17}$$

The partial differential equation, Eq. (16), can be integrated along the characteristics. The solution corresponding to the initial condition (17) is

$$G(b, k; t) = \varphi^{-1}(t)\,\eta[k\varphi^{-1}(t)]\; g\left\{i\ln\left\{1 - [1 - \exp(-ib)] \times \exp\left[k\varphi^{-1}(t)\int_0^t \varphi(t')\,dt'\right]\right\};\; t=0\right\} \tag{18}$$

where

$$\varphi(t) = \exp\left[-\int_0^t \nu(t')\,dt'\right] \tag{19}$$

is the coefficient of attenuation of the rate coefficient k at time t. The probability $P(N; t)$ of the number N of active intermediates at time t and the corresponding moments

$$\langle N^m(t)\rangle = \sum_N N^m P(N; t), \qquad m = 1, 2,... \tag{20}$$

can be evaluated from Eq. (18) by applying the equations

$$P(n; t) = \frac{1}{N!}\int dk\,\frac{d^N}{dz^N}\,G(b = -i\ln z, k; t)\Big|_{z=0} \tag{21}$$

$$\langle N^m(t)\rangle = (-i)^m \int dk\,\frac{d^m}{db^m}\,G(b = 0, k; t) \tag{22}$$

which can be easily derived from the definition, Eq. (14), of the characteristic function $G(b, k; t)$. By combining Eqs. (18), (21), and (22), we obtain

$$\begin{aligned} P(N; t) = \int dk_0\,\eta(k_0) \sum_{N_0 \geqslant 1} P(N_0; t=0)\,&\frac{(N-1)!}{(N_0-1)!\,(N-N_0)!} \\ &\times [\lambda(k_0; t)]^{N_0}\,[1-\lambda(k_0; t)]^{N-N_0} \end{aligned} \tag{23}$$

$$\begin{aligned} \langle N^m(t)\rangle = \sum_{q=1}^{m} \frac{1}{q!}\,\langle N^q(t=0)\rangle &\sum_{\substack{n_1,\ldots,n_q \geqslant 1 \\ \sum n_u \leqslant m}} \cdots \sum (-1)^{m-\sum n_u}\,\$_m^{(\sum n_u)} \\ &\times \frac{(\sum_u n_u)!}{\prod_u n_u!} \int \eta(k_0)\,dk_0 \exp\left\{\left(\sum_u n_u\right) k_0\varphi(t)\right\} \end{aligned} \tag{24}$$

where

$$\$_m^{(a)} = \sum_{k=0}^{a} \frac{(-1)^{a-k}\,k^m}{k!(a-k)!} \tag{25}$$

are the Stirling numbers of the second kind and

$$\lambda(k_0; t) = \exp\left\{-k_0\int_0^t \varphi(t')\,dt'\right\} \tag{26}$$

From Eq. (23) we notice that the probability distribution of the number of intermediates at time t is made up of the additive contributions of a number of negative binomials, corresponding to the different initial possible values of the rate coefficient $k(t=0)=k_0$.

We distinguish at least two regimes for the evolution of chain reactions. (a) A "normal" process for which all positive moments $\langle N^m(t)\rangle$ are finite for any finite time and the probability $P(N;t)$ has a short tail; in this case we normally expect that the eikonal approximation, Eq. (1), holds. (b) A statistical fractal regime for which the moments $\langle N^m(t)\rangle$ of order bigger than a certain positive threshold value H are infinite

$$\langle N^m(t)\rangle = \infty, \qquad \text{for} \quad m \geqslant H \tag{27}$$

and the probability $P(N;t)$ has a long tail of the power-law type,

$$P(N;t) \sim \text{const.}\, N^{-(1+H)} \qquad \text{for} \quad N \gg 0 \tag{28}$$

which corresponds to the scaling condition, Eq. (2). The conditions for the occurrence of these two different regimes can be established by investigating the behavior of the moments $\langle N^m(t)\rangle$ of the number of active intermediates at time t.

3. EIKONAL SCALING

We assume that the chain reaction starts out with a relatively low number N_0 of active intermediates obeying the constraint

$$1 \leqslant N_0 \leqslant N_0^{\max}, \qquad \text{i.e.,} \quad P(N > N_0^{\max}; t=0) = 0 \tag{29}$$

where the threshold value $N_0^{\max}$ of the initial number of active intermediates is much smaller than the typical number $N(t)$ of intermediates at time t. In these circumstances all sums in Eq. (24) are made up of finite numbers of terms and the only possible source of divergence for $\langle N^m(t)\rangle$ is given by the integral over the initial values $k(t=0)=k_0$ of the propagation rate.

If there is a finite range for the initial value of the reaction coefficient

$$k_{\max} \geqslant k_0 \geqslant 0, \qquad \text{where} \quad k_{\max} = \text{finite} \tag{30}$$

the integral over $k(t=0)=k_0$ in Eq. (24) is normally finite; indeed, $\eta(k_0)$ is a probability density for k_0 and cannot normally produce a singularity in the integral; similarly, the exponential term $\exp[(\sum n_u)\, \varphi(t)\, k_0]$ does not lead to a divergence for finite values of the initial rate constant k_0. If the restriction, Eq. (30), is fulfilled, then the shape of the tail of the probability $P(N; t)$ can be easily evaluated. We have

$$P(N; t) \sim \int dk_0\, \eta(k_0) \sum_{N_0=1}^{N_0^{\max}} P(N_0; t=0) \exp\left\{N_0 \ln\left[\frac{\lambda(k_0, t)}{1-\lambda(k_0, t)}\right]\right\} \times \frac{N^{N_0-1}}{(N_0-1)!} \exp\{-N \ln[(1-\lambda(k_0, t))^{-1}]\} \qquad \text{for} \quad N \gg N_0^{\max} \tag{31}$$

that is, for $N \gg N_0^{\max}$ the probability distribution of the number of active intermediates, $P(N; t)$, is given by a superposition of gamma distributions obeying a scaling condition similar to the KNO scaling law from nuclear physics [10]. In particular, if there is only a single value k_0 of the initial infection rate, the tail of the probability distribution $P(N; t)$ is given by

$$P(N; t) \sim \sum_{N_0=1}^{N_0^{\max}} P(N_0; t=0) \exp\left\{N_0 \ln\left[\frac{\lambda(k_0, t)}{1-\lambda(k_0, t)}\right]\right\} \times \frac{N^{N_0-1}}{(N_0-1)!} \exp\{-N \ln[(1-\lambda(k_0, t))^{-1}]\} \qquad \text{for} \quad N \gg N_0^{\max} \tag{32}$$

that is, it is an exponential modulated by a polynomial in N. For large values of the number N of particles the exponential term outweighs the contribution of the polynomial and the scaling condition, Eq. (32), is equivalent to the eikonal scaling (1.1). This conclusion can be easily extended to the more general expression, Eq. (31), for which, in the limit $N \gg N_0^{\max}$, the integral over k_0 can be evaluated by means of the method of steepest descent, resulting in an expression similar to Eq. (32), and thus the eikonal scaling still holds.

4. STATISTICAL FRACTAL SCALING

For systems obeying the restrictions, given by Eqs. (29) and (30), the only possibility for the occurrence of statistical fractal scaling is that there are no restrictions concerning the maximum initial value of the rate coefficient:

$$k_{\max} \to \infty \tag{33}$$

In this case in Eq. (2.22) the integral over k_0 may diverge. A typical situation is the one in which very large values of the initial propagation rate may exist and their probability of occurrence is exponentially rare, that is, the tail of the probability density $\eta(k)$ has an exponential shape. For simplicity we assume not only that the tail of $\eta(k)$ has an exponential shape, but also that the whole function does:

$$\eta(k) = \langle k_0 \rangle^{-1} \exp(-k/\langle k_0 \rangle) \tag{34}$$

where

$$\langle k_0 \rangle = \int k\eta(k)\, dk \tag{35}$$

is the average value of the initial rate coefficient. The distribution, Eq. (34), is commonly used in studies of reaction kinetics in disordered systems. Note that it is the most unbiased distribution of the initial rate coefficients consistent with the constraint given by Eq. (35). Equation (34) may be derived by searching for the extremum of the information entropy attached to the probability density $\eta(k)$,

$$\mathscr{H} = -\int \eta(k) \ln[\eta(k)\, \Delta k]\, dk \tag{36}$$

subject to the constraint (35).

If the distribution $\eta(k)$, of the initial rates is given by Eq. (34), then the integrals over k_0 in Eqs. (23) and (24) can be computed exactly. By combining Eqs. (23), (24), (33), and (34), we obtain

$$P(N; t) = H(t) \sum_{N_0=1}^{N_0^{\max}} P(N_0; t=0) \frac{(N-1)!\, \Gamma[N_0 + H(t)]}{(N_0-1)!\, \Gamma[N+1+H(t)]} \tag{37}$$

$$\langle N^m(t) \rangle = \sum_{q=1}^{m} \frac{1}{q!} \langle N^q(t=0) \rangle \sum_{\substack{n_1, \dots, n_q \geqslant 1 \\ \sum n_u \leqslant m}} \cdots \sum (-1)^{m - \sum n_u} \mathcal{S}_m^{(\sum n_u)}$$
$$\times \frac{(\sum n_u)!\, H(t)}{\prod n_u!\, [H(t) - \sum n_u]} \qquad \text{for} \quad m < H(t) \tag{38}$$

where

$$\langle N^m(t) \rangle = \infty \qquad \text{for} \quad m \geqslant H(r) \tag{39}$$

where

$$\Gamma(a) = \int_0^\infty t^{a-1} \exp(-t)\, dt, \qquad a > 0 \tag{40}$$

is the complete gamma function and

$$H(t) = \left[\langle K_0\rangle \int_0^t \varphi(t')\,dt'\right]^{-1} \tag{41}$$

It is easy to check that Eq. (37) has a long tail of the negative power-law type:

$$P(N; t) \sim \left\{\sum_{N_0=1}^{N_0^{\max}} P(N_0; t=0)\, H(t)\, \frac{\Gamma[N_0 + H(t)]}{(N_0 - 1)!}\right\} N^{-[H(t)+1]}$$

$$\text{for} \quad N \gg N_0^{\max} \tag{42}$$

Equation (42) has the same structure as Eqs. (2) and (28), with the difference that now the parameter H is not an arbitrary scaling exponent but a function of time given by Eq. (42).

From the above calculation it follows that an exponential distribution of the initial rate coefficient leads to the violation of the eikonal condition (1) and to a statistical fractal scaling of the type of Eq. (2). In Eq. (33) the reciprocal value $1/H(t)$ of the exponent $H(t)$ is a measure of the statistical fractal character of the probability distribution $P(N; t)$: the bigger $1/H(t)$, the more pronounced are the statistical fractal features. For $t = 0$ the fractal exponent H is infinite

$$H(t=0) = \infty, \qquad \text{i.e.,} \quad 1/H(t=0) = 0 \tag{43}$$

all positive moments $\langle N^m(t=0)\rangle$ are finite and the statistical fractal features are nonexistent. As the chain reaction is going on, the time integral $\int_0^t \varphi(t')\,dt'$ increases from zero to increasing positive values, the fractal exponent $H(t)$ decreases, the tail of the probability $P(N; t)$ becomes longer and longer and more and more moments $\langle N^m(t)\rangle$ become infinite. When the condition, Eq. (7), is fulfilled the integrand $\varphi(t')$ has an exponential tail and thus the integral $\int_0^\infty \varphi(t')\,dt'$ exists and is finite; the corresponding fractal exponent is the smallest one,

$$0 < H(\infty) = \left[\langle K_0\rangle \int_0^\infty \varphi(t')\,dt'\right]^{-1} < H(t) \tag{44}$$

In this case for large times a stationary probability of the number of active intermediates emerges in the limit $t \to \infty$,

$$P(N; \infty) = H(\infty) \sum_{N_0=1}^{N_0^{\max}} P(N_0; t=0) \frac{(N-1)!\,\Gamma[N_0 + H(\infty)]}{(N_0 - 1)!\,\Gamma[N + 1 + H(\infty)]} \tag{45}$$

for which the statistical fractal features are the most pronounced.

5. KINETIC EQUATIONS

A typical feature for chemical reactions in disordered systems is that, for them, a purely deterministic description is generally incomplete. This type of behavior is clearly displayed by the fractal scaling regime studied in the preceding section. For fractal scaling the moments of the number $N(t)$ of the active intermediates X with an order m at least equal to the scaling exponent $H(t)$ are divergent $\langle N^m(t)\rangle = \infty$, $m \geqslant H(t)$. In particular, the average value $\langle N(t)\rangle$ is finite only if $H(t) > 1$. From Eqs. (24) and (34) we obtain

$$\langle N(t)\rangle = \frac{\langle N(t=0)\rangle}{1-\langle k_0\rangle \int_0^t \exp\left[-\int_0^{t'} \nu(t'')\,dt''\right] dt'} \qquad \text{for} \quad H(t) > 1 \tag{46}$$

$$\langle N(t)\rangle = \infty \qquad \text{for} \quad H(t) \leqslant 1 \tag{47}$$

It is easy to check that the expression, Eq. (46), is the solution of an effective kinetic equation which is of second order with respect to the average value $\langle N(t)\rangle$,

$$\frac{d\langle N(t)\rangle}{dt} = \langle k(t)\rangle \frac{\langle N(t)\rangle^2}{\langle N(0)\rangle} \qquad \text{for} \quad \langle N(0)\rangle \neq 0, \quad H(t) > 1 \tag{48}$$

where $\langle k(t)\rangle$ is the ensemble average of the propagation rate at time t,

$$\langle k(t)\rangle = \int_0^\infty k(t)\,\eta(k_0)\,dk_0 = \langle k_0\rangle \exp\left[-\int_0^t \nu(t')\,dt'\right] \tag{49}$$

On the other hand, for an ordered system for which the propagation rate is time independent and nonrandom,

$$\langle k(t)\rangle = \langle k_0\rangle = \text{constant}, \qquad \nu = 0, \qquad \text{and} \qquad \eta(k) = \delta(k - \langle k_0\rangle) \tag{50}$$

the average value $\langle N(t)\rangle$ increases exponentially in time,

$$\langle N(t)\rangle = \langle N(0)\rangle \exp(\langle k_0\rangle t) \tag{51}$$

which corresponds to a kinetic equation of first order,

$$d\langle N(t)\rangle/dt = \langle k_0\rangle\langle N(t)\rangle \tag{52}$$

From the above computation it follows that the passage from the eikonal to the fractal scaling regime corresponds to a passage from an overall kinetic equation of the first order to a kinetic equation of the second order. For a second-order process the increase in time of the number of active intermediates is much faster than in the case of a first-order process characteristic for homogeneous systems. This effect is due to the contribution of very large propagation rates; although according to Eq. (34) very large rates are exponentially rare, their contribution leads to the modification of the dynamical behavior of the process. In addition to the random distribution of the initial propagation rates, a second feature of a reaction taking place in a disordered system is the decrease in time of the rate coefficient, which tends to diminish the contribution of very large initial rates. The balancing between these two opposite factors, the random selection of large initial rates, which are exponentially rare, and their decrease in time, may lead to interesting effects.

For investigating the effects of balancing of the two factors influencing the values of the rate coefficient, we limit ourselves to the particular case when the frequency of decay of the rate coefficient is constant,

$$\nu(t) = \nu_0 \text{ constant} \tag{53}$$

In this case the relative influence of the two factors is characterized by the ratio

$$\lambda = \nu_0 / \langle k_0 \rangle \tag{54}$$

between the frequency of decay ν_0 and the initial average value $\langle k_0 \rangle$ of the propagation rate; the numerical value of λ characterizes the relative intensity of the damping of the initial values of the propagation rate. Depending on the numerical value of the damping parameter λ, we distinguish the following cases.

(a) If the damping of the propagation rate is missing, then

$$\nu_0 = 0, \qquad \text{i.e.,} \quad \lambda = 0 \tag{55}$$

and there is no decrease in the values of the propagation rate. A given realization of the propagation rate coefficient k, once it is initially selected from the exponential probability density, Eq. (34), remains constant. In this case the statistical fractal features of the system are the most pronounced. The expressions for the average number of active intermediates $\langle N(t) \rangle$ and for the scaling exponent $H(t)$ are

$$\langle N(t) \rangle = \langle N(0) \rangle / [1 - \langle k_0 \rangle t] \tag{56}$$

$$H(t) = 1/[\langle k_0 \rangle t] \tag{57}$$

The hyperbolic law, Eq. (56), leads to an increase in the average number of particles $\langle N(t)\rangle$ which is faster than the one predicted by the exponential law, Eq. (51). According to Eq. (56) the average number of active intermediates $\langle N(t)\rangle$ diverges to infinity after a finite time interval equal to the reciprocal value of the average propagation rate:

$$\langle N(t)\rangle \to \infty \qquad \text{as} \quad t \to t_{\text{critical}} \quad \text{with} \quad t_{\text{critical}} = 1/\langle k_0\rangle \tag{58}$$

which, as expected, corresponds to a scaling exponent $H(t)$ equal to unity, $H(t_{\text{critical}}) = 1$. For comparison, we mention that in the case of exponential law, Eq. (51), $\langle N(t)\rangle$ diverges to infinity only for $t \to \infty$.

(b) For slow (supercritical) damping we have

$$\langle k_0\rangle > \nu_0 > 0, \qquad \text{i.e.,} \quad 1 > \lambda > 0 \tag{59}$$

and the expressions for the average number of active intermediates $\langle N(t)\rangle$ and for the scaling exponent $H(t)$ are given by

$$\langle N(t)\rangle = \frac{\langle N(0)\rangle\, \nu_0 \exp(\nu_0 t)}{\langle k_0\rangle - (\langle k_0\rangle - \nu_0) \exp(\nu_0 t)} \tag{60}$$

$$H(t) = \frac{\nu_0 \exp(\nu_0 t)}{\langle k_0\rangle [\exp(\nu_0 t) - 1]} \tag{61}$$

In this case the contribution of the process of decay of the rate coefficient is smaller than the contribution of very large initial rates. As a result, the average number of active intermediates diverges after a finite time interval; the only difference is that the critical time is longer than in the case corresponding to $\lambda = 0$,

$$\langle N(t)\rangle \to \infty \qquad \text{as} \quad t \to t_{\text{critical}} \quad \text{with} \quad t_{\text{critical}} = \frac{1}{\nu_0} \ln\left[\frac{\langle k_0\rangle}{\langle k_0\rangle - \nu_0}\right] > \frac{1}{\langle k_0\rangle} \tag{62}$$

(c) For critical damping we have

$$\nu_0 = \langle k_0\rangle, \qquad \text{i.e.,} \quad \lambda = 1 \tag{63}$$

In this case the contribution of very large initial rates is compensated exactly by their decay and the time evolution of the average value $\langle N(t)\rangle$ is given by the exponential law, Eq. (51), characteristic for homogeneous systems. In this case $\langle N(t)\rangle$ diverges to infinity after an infinite time interval.

(d) For fast (subcritical) damping we have

$$\nu_0 > \langle k_0 \rangle \gg 0, \qquad \text{i.e.,} \quad \lambda > 1 \tag{64}$$

and the expressions for the average number of active intermediates $\langle N(t) \rangle$ and for the scaling exponent $H(t)$ are given by

$$\langle N(t) \rangle = \frac{\langle N(0) \rangle \, \nu_0}{\nu_0 - \langle k_0 \rangle [1 - \exp(-\nu_0 t)]} \tag{65}$$

$$H(t) = \frac{\nu_0}{\langle k_0 \rangle [1 - \exp(-\nu_0 t)]} \tag{66}$$

In this case the contribution of damping outweighs the contribution of very large initial rates and the process is even slower than in the critical case (c) characterized by $\lambda = 1$. In the limit of large times, $t \to \infty$, the average number of active intermediates $\langle N(t) \rangle$ and the scaling exponent $H(t)$ tend toward finite values:

$$\langle N(\infty) \rangle = \frac{\langle N(0) \rangle \, \nu_0}{\nu_0 - \langle k_0 \rangle}; \qquad H(\infty) = \lambda = \nu_0 / \langle k_0 \rangle > 1 \tag{67}$$

By examining Eq. (65) we note that in this case the average number of active intermediates, $\langle N(t) \rangle$, evolves according to a logistic equation.

It is interesting that all these four cases can be derived from a unique deterministic kinetic equation which, unlike the relationship (48), depends only on apparent rate coefficients which are independent of time. We emphasize that the derivation of such a kinetic equation is possible only when the attenuation frequency is constant, $\nu(t) = \nu_0$. For deriving this kinetic equation we differentiate with respect to the time variable Eqs. (51), (56), (60), and (65) for $\langle N(t) \rangle$ and eliminate the time variable from the resulting equation by expressing it in terms of $\langle N(t) \rangle$. After some calculations we obtain the overall kinetic equation:

$$\frac{d}{dt} \langle N(t) \rangle = \nu_0 \langle N(t) \rangle + \frac{(\langle k_0 \rangle - \nu_0)}{\langle N(0) \rangle} \langle N(t) \rangle^2 \tag{68}$$

For $\nu(t) = \nu_0$ Eqs. (48) and (68) are equivalent to each other. Equation (68) has the advantage that it does not contain time-dependent apparent rate coefficients and thus it has a structure similar to that of the evolution equations of homogeneous chemical kinetics.

In case (a), the damping process is missing, $\lambda = 0$, and Eq. (68) reduces to a kinetic equation of second order with respect to $\langle N(t) \rangle$; such an equation corresponds to an equivalent homogeneous propagation process of second order with respect to the active intermediate X,

$$A + 2X \xrightarrow{k'} 3X \tag{69}$$

where the apparent rate coefficient k' is given by

$$k' = \langle k_0 \rangle / \langle N(0) \rangle \tag{70}$$

In case (b), $1 > \lambda > 0$, the damping of the propagation rate is slow (supercritical) and Eq. (68) corresponds to an equivalent homogeneous reaction mechanism of the type

$$A + X \xrightarrow{\nu_0} 2X; \qquad A + 2X \xrightarrow{k''} 3X \tag{71}$$

with

$$k'' = (\langle k_0 \rangle - \nu_0) / \langle N_0 \rangle \tag{72}$$

that is, to two propagation steps of first and second order with respect to the active intermediate, respectively.

In case (c), $\lambda = 1$, the damping process is compensated by the very large initial values of the propagation rate and Eq. (68) corresponds to an equivalent homogeneous propagation reaction of first order in X,

$$A + X \xrightarrow{\langle k_0 \rangle} 2X \tag{73}$$

In case (d), $\lambda > 1$, the damping process outweighs the contribution of very large initial rates and the equivalent homogeneous mechanism corresponding to Eq. (68) is

$$A + X \xrightarrow{\nu_0} 2X; \qquad 2X \xrightarrow{k'''} \text{products} \tag{74}$$

with

$$k''' = (\nu_0 - \langle k_0 \rangle) / \langle N(0) \rangle \tag{75}$$

The equivalent homogeneous mechanism, Eq. (74), is made up of a propagation reaction of first order with respect to X and by a second-order termination reaction.

The above analysis shows that the key factor in determining the kinetic behavior of the average number of active intermediates is the damping parameter λ. Very small changes in this parameter may generate major changes in the evolution of the chemical process. This fact is clearly

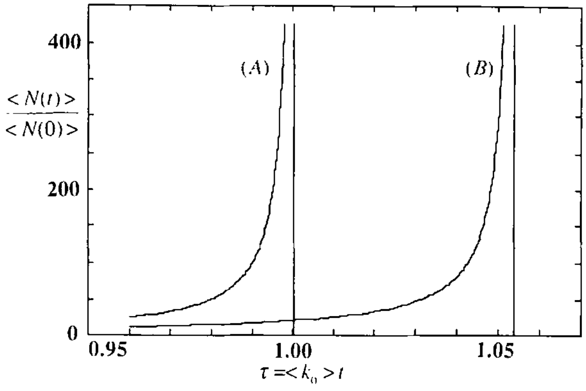

Fig. 1. The dependence of the relative average number of active intermediates X, $\langle N(t)\rangle/\langle N(0)\rangle$, on the dimensionless time variable $\tau = \langle k_0\rangle t$ (A) for a process with no damping ($\lambda = 0$) and (B) for a process with slow damping ($\lambda = 0.1$).

illustrated by Figs. 1 and 2. Figure 1 shows the time evolution of the ratio $\langle N(t)\rangle/\langle N(0)\rangle$ as a function of the dimensionless time variable, $\tau = \langle k_0\rangle t$ for a system with no damping, $\lambda = 0$, and for a system with small damping, $\lambda = 0.1$, respectively. This small variation in the damping coefficient slows down the reaction and leads to a time delay in the occurrence of the explosion. A similar pattern is displayed in Fig. 2, which shows the time dependence of the ratio $\langle N(t)\rangle/\langle N(0)\rangle$ for a system with critical damping characterized by $\lambda = 1$ and for which the number of particles increases exponentially and for a system with subcritical damping characterized by a slightly larger value of the damping coefficient, $\lambda = 1.05$, for which the ratio $\langle N(t)\rangle/\langle N(0)\rangle$ evolves toward a finite asymptotic value.

Figure 3 shows the dependence of the relative rate of the process, $\langle \dot{N}(t)\rangle/(\langle k_0\rangle\langle N(0)\rangle)$ as a function of the ratio $\langle N(t)\rangle/\langle N(0)\rangle$ for different values of the damping coefficient λ corresponding to the four cases discussed before. We notice that the increase in the damping coefficient λ leads to the decrease in the rate of the process. For $\lambda = 0$ the rate of the process is proportional to the square of the number of particles, whereas for the compensated regime corresponding to $\lambda = 1$, the parabolic dependence is replaced by a linear dependence. Finally, for fast damping, $\lambda > 1$, the attenuation of the rate coefficient is rate determining and the rate of the process is an increasing function only for small values of the ratio $\langle N(t)\rangle/\langle N(0)\rangle$; as the number of X particles increases, an extremum point is reached for which the rate of the process has a maximum value; afterward the rate decreases toward the final value of zero.

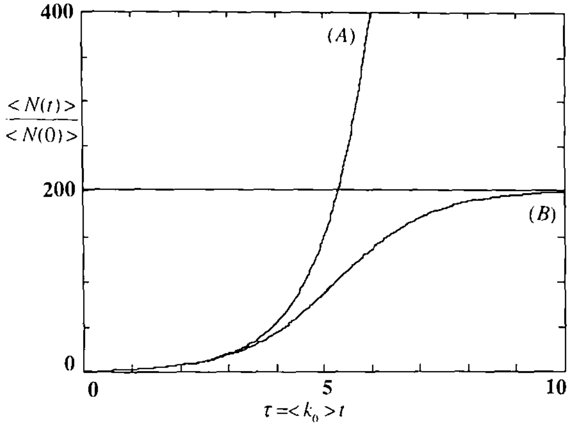

Fig. 2. The dependence of the relative average number of active intermediates $X\langle N(t)\rangle/\langle N(0)\rangle$, on the dimensionless time variable $\tau=\langle k_0\rangle t$ (A) for a process with no damping ($\lambda=1.00$) and (B) for a process with slow damping ($\lambda=1.05$).

The above analysis shows that for a chain reaction in a disordered systems the macroscopic evolution of the system is deeply influenced by the fluctuations dynamics. The evolution equations, Eqs. (48) and (68), for the average number of active intermediates are in fact renormalized macroscopic equations [11] which describe the influence of the fluctuation dynamics on the macroscopic behavior of the system. An interesting feature

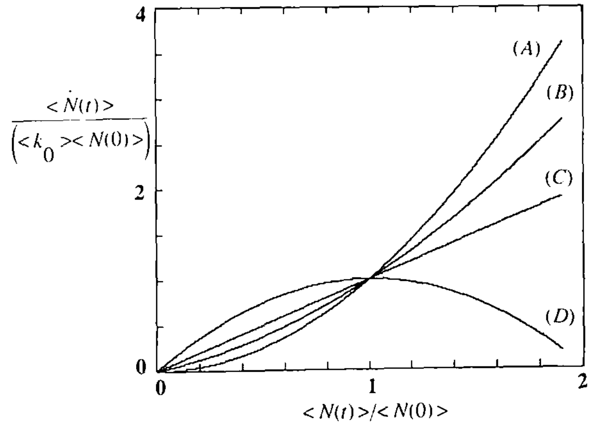

Fig. 3. The dependence of the relative reaction rate, $\langle \dot{N}(t)\rangle/(\langle k_0\rangle\langle N(0)\rangle)$ on the relative average number of active intermediates X, $\langle N(t)\rangle/\langle N(0)\rangle$, for $\lambda=0$ (A), $\lambda=0.5$ (B), $\lambda=1$ (C), and $\lambda=2$ (D).

of the models described by Eqs. (48) and (68) is that they may lead to explosion after a finite time. A chain reaction model with a similar behavior has recently been suggested by Cerofolini for the description of adsorption kinetics on reconstructable surfaces [12]. Further research should clarify the possible connections between our approach and Cerofolini's model.

6. CONCLUSIONS

In this article a simple stochastic description of a chain reaction occurring in a disordered system has been suggested in terms of a compound master–Liouville equation. It has been shown that in certain circumstances, the behavior of the system in the thermodynamic limit is described by a scaling condition of the statistical fractal type. For fractal scaling the nonequilibrium thermodynamic formalisms suggested in the literature [1–4] are not valid. In this article we have investigated only the effect of dynamical disorder on macroscopic behavior. Further research should lead to the development of a nonequilibrium thermodynamic formalism for which the fractal scaling condition (1.2) should play a role similar to the Einstein fluctuation formula in equilibrium thermodynamics.

DEDICATION

This article is dedicated to the memory of Edward A. Mason, an outstanding scientist with the highest standards of scholarship, a fellow graduate student with John Ross nearly 50 years ago, and a life-long friend.

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