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Non-Poisson statistics of reactive events and nonexponential kinetics

Dmitrii E. Makarov and Maria Topaler
School of Chemical Sciences, University of Illinois, 505 S. Mathews Avenue, Urbana, Illinois 61801
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We consider a model of a chemical reaction where the transition is possible only if the environment of the reacting complex attains a certain configuration. For example, electron transfer between two electronic states occurs when a fluctuation of the environment brings these states into resonance. Non-Poisson statistics of reactive events may lead to nonexponential kinetics characterized by short- and long-time rate constants. The transition from the nonadiabatic to adiabatic (environment-controlled) regime of the reaction is shown to have different character in the cases of attractive and repulsive statistics.

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It has been realized, both experimentally [1] and theoretically [2–7] that an elementary chemical reaction will exhibit nonexponential kinetics if the relaxation time of the environment of the reaction complex is slower than or comparable with the time scale of the reaction itself. The limit where the relaxation time is infinite is the well understood case of an inhomogeneous environment or "static disorder" that leads to a distribution of reaction rates (see, e.g., [2–4]).

The regime of "dynamical disorder" where fluctuations of the environment occur on a time scale comparable with that of the reaction itself is not so well understood. Zwanzig [5] proposed a procedure to treat rate processes with dynamical disorder in the case where rate fluctuations are described by a Markovian process. Chandler *et al.* [6] discussed nonexponential kinetics due to rate fluctuations using a cumulant approximation. Recently Wang and Wolynes [7] set forth a path integral formalism to obtain population kinetics in the general case where the reaction and environmental relaxation occur on similar time scales. They introduced a "survival path" followed by the environment in order to produce the dominant contribution to the kinetics and applied their formalism to cases with moderate dependence of the reaction rate on the environmental coordinates, such as "geometrical bottlenecks."

In this Rapid Communication we propose a different language suited to describe the case of a very sharp dependence of the rate on the environmental variables (that is, the reaction only happens when the environment assumes a favorable configuration). In this case the continuous stochastic process can be mapped onto a sequence of points corresponding to such favorable configurations in much the same way as a discrete Poincaré map provides a convenient description of chaotic systems that are continuous in time. We describe reactions in fluctuating environments in terms of statistics of *reactive events*, i.e., occurrences of the favorable configurations that allow the reaction to proceed.

The examples where such a physical situation is realized are abundant in chemistry and physics. A recent example was given by Chandler *et al.* [6] and Gehlen *et al.* [8] in connection with the primary charge transfer in photosynthesis. Following these papers, consider two electronic states, the energy gap between which, $\varepsilon(t)$, is a stochastic variable that depends on the configuration of the environment. Suppose for simplicity that the transition from the initial to the final state is irreversible. The "reactive event" in this case is zero-crossing: whenever $\varepsilon(t)=0$ the two states are on resonance and the transition from the initial to the final state occurs with probability p. Two models will be considered, in which p is a constant (model 1) or depends on the crossing velocity $\dot{\varepsilon}(t)$ according to the Landau-Zener formula, $p(\dot{\varepsilon})=1-\exp(-\alpha/|\dot{\varepsilon}|)$ (model 2). For electron transfer α is proportional to the square of the coupling matrix element between the electronic states.

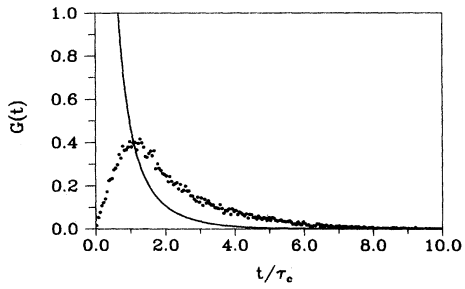

FIG. 1. Distribution function of the time interval between two adjacent reactive events obtained from Monte Carlo sampling the Gaussian-correlated process (markers). The solid line is the unnormalized analog of this function [given by the second time derivative of Eq. (4)] for the Ornstein-Uhlenbeck process.

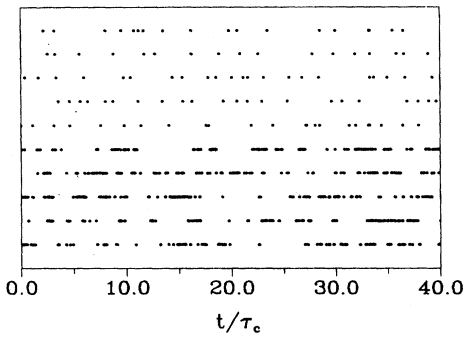

FIG. 2. Typical sequences of zero-crossings for the Gaussian-correlated (upper five sequences) and Ornstein-Uhlenbeck (lower five sequences) noise.

Model 2 is generally more realistic but model 1 is usually easier to solve. Replacing $\dot{\varepsilon}$ by a constant effective velocity model 2 becomes model 1; the conditions under which this can be done will be discussed below.

For model 1 the probability to survive in the initial state is given by

$$S(t)=\langle(1-p)^{N(t)}\rangle, \tag{1}$$

where $N(t)$ is the number of reactive events during time t and $\langle\cdots\rangle$ indicates ensemble averaging. Note that this quantity coincides with the standard definition of the characteristic function of a random point process, $g(u)=\langle\exp(iuN)\rangle$, if $iu=\ln(1-p)$. For a stationary stochastic process $\langle N(t)\rangle$ grows linear in time so if the operations of averaging and raising to a power could be interchanged, we would get the survival probability, $S(t)=(1-p)^{\langle N(t)\rangle}$, to decay exponentially in time. In a more realistic case energy crossings are considered independent of one another such that $N(t)$ obeys Poisson statistics with the probabilities to have N crossings in the time interval t equal to $\rho(N)=(t/\tau)^N\exp(-t/\tau)/N!$, where τ is the average time interval between two reactive events. The survival probability is exponential in this case [8], $S(t)=\exp(-pt/\tau)$. The statistics of crossings can be considered Poisson if the time t is much greater than the correlation time of energy gap fluctuations, τ_c, and otherwise correlations between crossings will lead to nonexponential behavior of $S(t)$ which will be the subject of the following analysis.

In this preliminary report of our results we assume $\varepsilon(t)$ to be a stationary Gaussian random variable with zero mean and the correlation function $A(t-t')=\langle\varepsilon(t)\varepsilon(t')\rangle$. A detailed account of our work including the nonsymmetric case $\langle\varepsilon\rangle\neq 0$ will be given elsewhere. For a Gaussian process, the averaging operation can be understood as a path integral

$$\langle\cdots\rangle=\int D[\varepsilon(t)](\cdots)\exp\left(-\frac{1}{2}\int_0^t\int_0^t dt'dt''B(t'-t'')\varepsilon(t')\varepsilon(t'')\right), \tag{2}$$

where $B(t)$ is the kernel of the integral operator inverse to $A(t)$ (see, e.g., [10]). In practice, Eq. (2) is evaluated by expanding $\varepsilon(t)$ in a Fourier series and Monte Carlo sampling of the resulting multidimensional Gaussian integral.

Calculating the full distribution of zero-crossings, $\rho(N)$, is a formidable task; one might hope though that by studying the most important pairwise correlations between reactive events and approximately extrapolating to large N's the qualitative picture will be captured. Specifically, the behavior of $S(t)$ is qualitatively different in the cases of *attraction* of reactive events (i.e., where the crossings tend to occur in clusters) and *repulsion* (where two reactive events cannot subsequently happen during a short time). Introducing the distribution of time intervals between two successive crossings, $G(t)$, the repulsive statistics are indicated by $G(0)=0$, while in the attractive case $G(t)$ is a monotonically decreasing function. An example of attractive statistics is the Ornstein-Uhlenbeck process(see, e.g., [11,12]), $A(t-t')=D\exp(-t/\tau_c)/\tau_c$, while the Gaussian-correlated noise, $A(t-t')=D\exp[-(t/\tau_c)^2]/\tau_c$, exhibits repulsive statistics, as demonstrated in Fig. 1.

The Ornstein-Uhlenbeck process. Although this is a Markovian process, the statistics of zero-crossings are not described by the Poisson law. The average number of crossings $\langle N(t)\rangle$ is infinite, as indicated by the formula [12]

$$\langle N(t)\rangle=|A''(0)/A(0)|^{1/2}t/\pi\equiv t/\tau. \tag{3}$$

However, this does not lead to an infinitely fast decay for two reasons: First, most of the crossings occur with infinite velocity such that the Landau-Zener probability of transition is zero; this argument shows that model 1 cannot be used in place of model 2 for this case. Second, although $\langle N(t)\rangle=\infty$, the probability that no crossings occur during the time t is nonzero and given by [12,9]

$$S_e(t)=(2/\pi)\sin^{-1}[\exp(-t/\tau_c)]. \tag{4}$$

This is a manifestation of the attractive statistics: the reactive events tend to occur in infinitely dense clusters which are separated by long (on the order of τ_c) time intervals (see Fig. 2).

In fact, the survival probability $S(t)$ becomes $S_e(t)$ in the limit of $p\to 1$ or $\alpha\to\infty$, since even a single crossing leads to

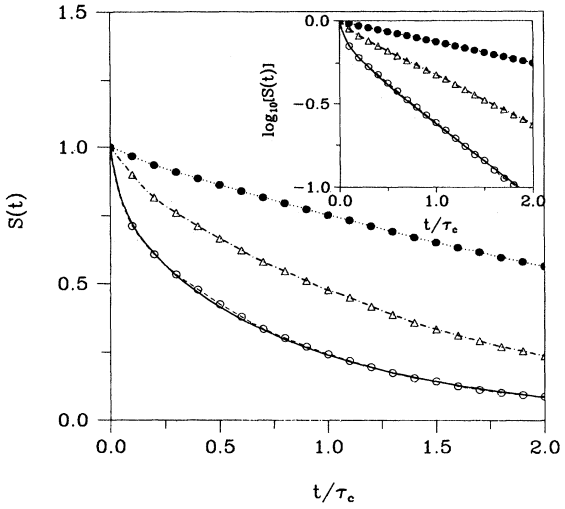

FIG. 3. Survival probability obtained by Monte Carlo sampling of Eq. (5) plotted as a function of time for the Ornstein-Uhlenbeck process with $D=16$, $\tau_c=1$, and $\alpha=3.5$ (filled circles), 14.1 (triangles), and 630 (hollow circles). The solid line is the analytical result for the environment-controlled regime Eq. (4). Inset: the same data replotted on a semilogarithmic scale.

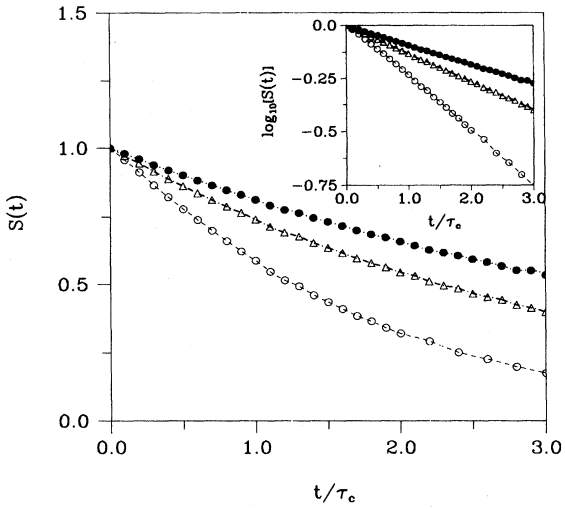

FIG. 4. Survival probability obtained by Monte Carlo sampling of Eq. (5) plotted as a function of time for the Gaussian-correlated process with $D=16$, $\tau_c=1$, and $\alpha=3.5$ (filled circles), 6.3 (triangles), and 630 (hollow circles). Inset: the same data replotted on a semilogarithmic scale.

the complete population transfer. This is the limit of environment-controlled reaction whose rate is independent of p. At long times $S_e(t)$ describes an exponential decay with the rate $1/\tau_c$; this can be thought of as the rate of entering or leaving a cluster.

Consider next the short-time behavior of $S(t)$. In model 2, the survival probability

$$S(t)=\left\langle \exp\left(-\alpha\sum_{j=1}^{N} |\dot{\varepsilon}_j|^{-1} \right) \right\rangle = \left\langle \exp\left(-\alpha\int_0^t dt'\,\delta(\varepsilon(t')) \right) \right\rangle \tag{5}$$

can be represented as a double series both in t and in α:

$$S(t)=1-\sum_{n=1}^{\infty}\frac{(-\alpha)^n}{(2\pi)^n n!}\int_0^t dt_1\cdots\int_0^t dt_n\int_{-\infty}^{\infty}d\lambda_1\cdots \times\int_{-\infty}^{\infty}d\lambda_n\left\langle \exp\left(\sum_{k=1}^{n} i\lambda_k\varepsilon(t_k) \right) \right\rangle, \tag{6}$$

where the spectral expansion of the δ function has been used. For the Ornstein-Uhlenbeck case this series is calculated to be of the form

$$S(t)=1-(\tau_c/2\pi D)^{1/2}\alpha t+(2\tau_c)^{3/2}\alpha^2 t^{3/2}/(3\pi D)+\cdots \tag{7}$$

such that the short-time rate constant $k(0)=-\dot{S}(0)$ is equal to $(\tau_c/2\pi D)^{1/2}\alpha$. In the environment-controlled case this rate becomes infinite. Another important quantity is the long-time rate limit, $k(\infty)=-\lim_{t\to\infty}[\dot{S}(t)/S(t)]$. As seen from Fig. 3 for small α $S(t)$ decays exponentially for all times, $k(0)\approx k(\infty)$, while in the environment-controlled limit $k(\infty)=1/\tau_c\ll k(0)$. We found that the formula

$$k(\infty)^{-1}=k(0)^{-1}+\tau_c \tag{8}$$

works well for arbitrary α reproducing the above limiting cases. This expression can be obtained from the following heuristic reasoning: Consider an ensemble of realizations of the random noise $\varepsilon(t)$. At a given time t $\varepsilon(t)$ can either be in the "cluster state" corresponding to frequent crossings or outside a cluster, in the "nonreactive state." In order for the transition to occur, the "cluster state" should be attained, which happens with the rate $1/\tau_c$. Being in the cluster state, the transition back to the nonreactive state can happen with the rate $1/\tau_c$ or the reaction can occur with the rate $k(0)$, such that the fraction of clusters participating in the reaction is $k(0)/[k(0)+\tau_c^{-1}]$. Multiplying this by the probability of entering a cluster one obtains Eq. (8). In fact, this equation is known in the context of solvent-controlled electron transfer [13]; what we have shown is that its validity relies heavily on the "clustering" of the reactive events, which is indicated by the singularity of derivatives of the correlation function and is a consequence of the Markovian character of the noise. Since in reality such a singularity should always be smoothed, special consideration should be given to the non-Markovian case where $A(t)$ is regular at $t=0$.

Gaussian-correlated noise. In this case, unlike the Ornstein-Uhlenbeck process, model 1 provides a good approximation to model 2, since the reactive events do not cluster (see Fig. 2) and the effective crossing velocity is a well-defined quantity. From the numerical data of Fig. 4 we find that (i) $k(\infty)>k(0)$ and (ii) at short times $S(t)$ decays linearly rather than exponentially. The second finding is readily understood: For a time t short enough $\rho(1)=t/\tau$, $\rho(0)\approx 1-\rho(1)$ and $\rho(N>1)\approx 0$ because, as seen from Fig. 1, two successive crossings are an unlikely

event. From Eq. (1) then one obtains the linear dependence $S(t)\approx 1-k(0)t$ where $k(0)=p/\tau$.

The short-time rate constant $k(0)$ for model 2 can be found exactly [9] along the lines of Zusman [14]; those derivations suggest that the transition probability can be set constant $p=1-\exp(-\alpha/|\dot{\varepsilon}_{eff}|)$, where the effective crossing velocity is constant for small α and increases weakly, $\dot{\varepsilon}_{eff} \propto \alpha^{1/3}$, for $\alpha\rightarrow\infty$.

To find the long-time rate we resort to the approximation of "nonapproaching points" [12]. In this approximation the repulsion of the reactive events is characterized by the correlation coefficient $R(t_2-t_1)=1-\tau^2 f_2(t_1,t_2)$ where $f_2(t_1,t_2)$ is the joint probability density to encounter crossings at the moments t_1 and t_2, a quantity that can be evaluated using the techniques described in [12,9]. Using the characteristic function given in [12] one obtains from Eq. (1)

$$S(t)=\exp\left(\int_0^t dt' \frac{\ln(1-k(0)\int_0^t dt'' R(t'-t''))}{\int_0^t dt'' R(t'-t'')}\right) \quad (9)$$

with the long-time rate limit given by

$$k(\infty)=T_c^{-1}\ln[1-k(0)T_c], \quad T_c=\int_{-\infty}^{\infty} dt\, R(t). \quad (10)$$

In the case of the Gaussian-correlated noise we found numerically that $T_c\approx 0.477\tau_c$ and the current approximation reproduces the correct long-time behavior with accuracy within a few percent. According to Eq. (10), for positive T_c the long-time decay of $S(t)$ is faster than the short-time decay, the result confirmed by our numerical data in Fig. 4. This is in contrast to the Markovian case where the decay is fastest at short times. One arrives at the same conclusion by analyzing the cumulant approximation of Ref. [6], which can be obtained by truncating and exponentiating the series of Eq. (6).

To conclude, we have shown that non-Poisson statistics of reactive events lead to nonexponential behavior of the survival probability at times shorter than the correlation time of the noise, τ_c. Depending on whether the reactive events tend to attract or repel one another, the decay rate decreases or increases as time evolves until the exponential decay sets in with a constant rate $k(\infty)$. As the parameter α that controls the transition probability p increases, transition from the "nonadiabatic regime" where $k(\infty)\propto\alpha$ to the environment-controlled regime where $k(\infty)$ is independent of α occurs. This transition is qualitatively different in the case of attractive and repulsive statistics as seen by comparing Eqs. (8) and (10). In the first case the transition is determined by the competition of the "electronic" transition and the processes of entering or leaving a cluster, while in the second case this is essentially a Landau-Zener-type transition which occurs as $p\rightarrow 1$ $(\alpha\rightarrow\infty)$.

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