"Noise-limited" reactions: Effects of noise-induced transitions in a distributed system

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The problem of the induction of intermittent behavior by fluctuations in the rate constant of a reaction in a system described by the Smoluchowski equation is solved. The critical values of the noise level above which the system separates into regions with enhanced and reduced concentrations of a substance are obtained. Engineering applications of this behavior are proposed. [S1063-7761(96)02201-1]

1. INTRODUCTION

Theoretical investigations of the Smoluchowski equation,[1] which describes the diffusion of molecules in a potential field and their reactions with molecules of the medium, pertain to a traditional and fundamental subject in physics. This equation is encountered in descriptions of phenomena in diverse areas of science, such as the passage of particles through a membrane,[2] biochemical reactions within a protein globule,[3] and intramolecular reactions[4] (the transfer of an electron, electron energy, a photon, or individual groups of atoms):

$$\partial n(r,t)/\partial t = D\nabla[\nabla n(r,t) + \nabla U(r) n(r,t)/\vartheta] - k(r)n(r,t). \tag{1}$$

Here $n(r,t)$ is the local density of some reactant R; $k(r)$ is the coordinate-dependent rate of the reaction between molecules of R and molecules of the medium s, whose concentration is assumed to be constant; ∇ is the gradient operator; D is the diffusion constant; and $\vartheta = k_B T_a$ is a parameter that determines the intensity of fluctuations (the so-called noise level), where k_B is Boltzmann's constant and T_a is the absolute temperature. The term in square brackets in Eq. (1) takes fluctuations of the medium into account, which can be described by Brownian motion in the potential field $U(r)$.

In the absence of a reaction, i.e., when $k(r)=0$, Eq. (1) has a solution that describes a state of equilibrium:

$$n_{\text{eq}} = Z^{-1}\exp(-U(r)/\vartheta),$$

$$Z = \int dr[\exp(-U(r)/\vartheta)]. \tag{2}$$

In the absence of diffusion, i.e., when $D=0$, each state $n(r,t)$ decays at a characteristic rate $k(r)$:

$$n(r,t) = n(r,0)\exp[-k(r)t]. \tag{3}$$

A description with consideration of the combined effect of a reaction and diffusion was given in Ref. 5.

Growing interest has recently been aroused by a description with consideration of fluctuations of the control parameter, i.e., the rate constant of the reaction,[8] which are taken into account by introducing an additional stochastic term, i.e., the so-called multiplicative noise, into Eq. (1). The purpose of the present work is to describe the contribution of such fluctuations to the dynamics of the system (1) in the rate-limiting step of the reaction.

Let us consider a one-component system with a reaction and diffusion, whose behavior is described by the following stochastic partial differential equation:

$$\partial n(r,t)/\partial t = D\nabla[\nabla n(r,t) + \nabla U(r) n(r,t)/\vartheta] + k(r)n(r,t) + h(n(r,t))\eta(r,t). \tag{4}$$

Here we took into account fluctuations of the rate constant of the reaction by introducing the stochastic term $h(n)\eta(r,t)$ into Eq. (1), where $h(n)$ is a certain function of n that describes the noise-induced deviations from deterministic behavior of the system, and $\eta(r,t)$ represents ordinary Gaussian white noise with zero mean and intensity $\sigma = \sigma(T_a)$:

$$s(r-r',t-t') = \langle \eta(r,t)\eta(r',t')\rangle = \sigma\delta(r-r')\delta(t-t'). \tag{5}$$

A formal solution of Eq. (4) in terms of path integrals along trajectories was given in Ref. 7. Each trajectory $n=n(r,t)$, which is a solution of Eq. (4), is realized with a certain probability, specified by the probability functional $P[n(r,t)]$:

$$P[n(r,t)] = \int Dp(r,t)\exp(\mathscr{F}), \tag{6}$$

where

$$\mathscr{F} = \int dr\, dt[\sigma(ph-\gamma h')^2/2 + p(g + D\Delta n - \partial n/\partial t) - \gamma g']. \tag{7}$$

Here $p(r,t)$ is a certain real auxiliary field, and we have introduced the notation $h' = \delta h/\delta n$,

$$g(n) = \frac{D}{\vartheta}\nabla[\nabla U(r) n(r,t)] - k(r)n(r,t), \tag{8}$$

$$g'(r) = -\left(\frac{D}{\vartheta}\nabla^2 U + k(r)\right). \tag{9}$$

The discretization constant γ $(0 \leqslant \gamma \leqslant 1)$, which is equal to 1/2 in the Stratonovich interpretation of the stochastic differential equation (1) and is equal to zero in the Itoh interpretation,[8] is used for generality. As will be shown, our approach presupposes a definite choice of γ.

We calculate the trajectory that makes the largest contribution to the probability functional (6) using the saddle-point method.[7] Then the most probable (optimal) trajectory satisfies the following variational equation

$$\delta\left\{\int dr\ dt\mathscr{F}(n,p)\right\}=0, \tag{10}$$

$$\begin{cases} \partial n/\partial t=g(n)+D\Delta n+\sigma h(ph-\gamma h') \\ -\partial p/\partial t=pg'-\gamma g''+D\Delta p+\sigma(ph'-\gamma h'')(ph-\gamma h'). \end{cases} \tag{11}$$

The system of two coupled deterministic reaction–diffusion equations obtained as a result of this procedure for the initial component and a certain auxiliary field makes it possible, in principle, to describe both very rare events, in which the behavior of the system is determined mainly by one trajectory, and the optimal, i.e., most probable, behavior of the system, which is averaged over an ensemble of realizations. However, to obtain solutions in explicit form, it is necessary to invoke additional arguments regarding the domain in which noise plays a significant role.

The correct interpretation of the equations must be based on the fact that the solutions of this system are the most probable (optimal) trajectories of the random process described by the stochastic differential equation (4). Then the most probable behavior of the system is described for the most part by the Smoluchowski equation (1), which is represented by the first three terms in the equation for the concentration of the system (11). The influence of noise becomes significant in the final stage of the reaction, when an approximate balance is established between the forces representing free diffusion, which strives to transform the initial distribution into a uniform distribution, the potential field, which strives to lead the initial distribution to the state described by the potential minimum, and the reaction, which takes place at a coordinate-dependent rate.

Since σ appears in explicit form in Eq. (7), it should be possible to isolate a small parameter related directly to the noise. This would make it possible to directly supplement the optimal trajectory method with procedures from the multiple-scales method and perturbation theory. As a result, the dynamics of the system (4) will separate into motion in two mutually orthogonal subspaces, the behavior of the solutions lying in the "noise-induced" subspace being represented by solutions of the Ginzburg–Landau equation, and the dynamics of the system in the other orthogonal space being described by the Smoluchowski equation (1). We shall describe the observed intermittency in terms of the concentration peaks and troughs which appear.

2. PERTURBATION THEORY

It was shown in Ref. 9 that a noise-induced transition[10] can be observed in a system with a reaction, diffusion, and external multiplicative noise of intensity σ somewhat a critical value ($\sigma=\sigma_c$) in the absence of an external field $U(r)$. We now refine the value of σ_c for a system described by the stochastic differential equation (4).

We introduce the small parameter

$$\varepsilon=\pm[|\sigma-\sigma_c|/\sigma]^m(m\geqslant 1), \tag{12}$$

where selection of the value of m makes it possible to "keep" the value of ε small in order to describe the behavior of the system both in the immediate vicinity of $\sigma_c(m\sim 1)$ and far from the critical value of the noise ($m\gg 1$).

It was shown in Ref. 11 that the effect of multiplicative noise reduces to the fact that the concentration of a substance can increase at random points in space (noise-induced attractors) at the expense of a decrease in its concentration in other regions of space. In effect, the noise plays the role of a "janitor" who sweeps molecules of the substance into the attractors/piles.

It is natural to assume that white noise does not influence the reaction rate or the effects of external forces. In this sense there is a certain similarity between our approach and the method proposed in Ref. 5 to describe the kinetics of reactions with restricted diffusion "perpendicular to the reaction coordinate." For example, the following "noise-induced" variables will be "perpendicular coordinates" to r and t, respectively, in our case:

$$R=\sigma^{1/2}r, \quad T=\sigma t. \tag{13}$$

We introduce the following functional relations:

$$h(n)=\varepsilon n_1(R,T), \tag{14}$$

$$\begin{cases} n=n_{\text{det}}(r,t)+h(n_1), \\ \quad p=\varepsilon^{-1}p(R,T). \end{cases} \tag{15}$$

Next, we assume that the new and old variables are independent, yielding the following replacements in the differentiation operations in Eq. (7):

$$\partial/\partial r=\partial/\partial r+\sigma^{1/2}\partial/\partial R; \quad \partial/\partial t=\partial/\partial t+\sigma\partial/\partial T. \tag{16}$$

Assuming that $n_{\text{det}}(r,t)$ is a solution of the Smoluchowski equation (1), we rewrite the functional $\mathscr{F}$ in the following form:

$$\mathscr{F}=\sigma^{-1/2}\int dr\ dt\ dR\ dT[(ph-\gamma h')^2 + p(-wn_1+D\Delta_R n_1-\partial n_1/\partial T)-\gamma g'], \tag{17}$$

where

$$g'(r)/\sigma\equiv -w. \tag{18}$$

We note that by modifying $\mathscr{F}$ in such a manner, we simply neglected the trajectories associated with solutions of the Smoluchowski equation that are realized with a probability of unity. Then the most probable fluctuation satisfies the variational equation

$$\delta\left\{\int dr\ dt\ dR\ dT\mathscr{F}(n_1,p)\right\}=0. \tag{19}$$

From (19) we have a system of coupled equations,

$$\begin{cases} \partial n_1/\partial T = -wn_1 + D\Delta_R n_1 + n_1(\rho n_1 - \gamma\varepsilon), \\ -\partial\rho/\partial T = -w\rho - \gamma g''\varepsilon + D\Delta_R\rho + \rho(\rho n_1 - \varepsilon\gamma). \end{cases} \quad (20)$$

Neglecting terms that are small when $\varepsilon \to 0$, we obtain

$$\begin{cases} \partial n_1/\partial T = -wn_1 + \rho n_1^2 + D\Delta_R n_1, \\ -\partial\rho/\partial T = -wp + \rho^2 n_1 + D\Delta_R\rho. \end{cases} \quad (21)$$

Returning now to the original variable p, we note that we have obtained the same system of equations as if we had chosen the Itoh interpretation of the stochastic differential equation (1) from the start. This means[10] that at the phase transition point $\sigma = \sigma_c$ instantaneous fluctuations do not correlate with the state of the system at the same moment in time. In other words, in the vicinity of the critical point the phase space of the system $\{n,p\} \in N$ is actually the direct sum of two mutually orthogonal subspaces

$$N = N_{\rm det} \oplus N_1, \quad (22)$$

with the subspace $N_{\rm det}$ comprising all attractors of the deterministic Eq. (1), $n_{\rm det} \in N$, while the "noise-induced" subspace N_1 is a direct product, $n_1 \otimes p = N_1$.

The resulting system of equations (21) can be greatly simplified and reduced to a single equation via the following replacements:

$$\tau = -iT, \quad x = D^{-1/2}R, \quad \psi = n_1, \quad \psi^* = \rho. \quad (23)$$

Then (21) transforms into the nonlinear Schrödinger equation:

$$i\partial\psi/\partial\tau - w\psi + \Delta_x\psi + |\psi|^2\psi = 0. \quad (24)$$

Performing the reverse replacements, we obtain solutions of the original system of equations (21):

$$\begin{cases} n = n_{\rm det} + \varepsilon[W(R,T)]^{\rm real}, \\ p = \varepsilon^{-1}[W^*(R,T)]^{\rm real}, \end{cases} \quad (25)$$

where $W(R,T)$ satisfies the Ginzburg–Landau equation

$$\partial W/\partial T = -wW + D\Delta_R W + |W|^2 W. \quad (26)$$

The operation $[...]^{\rm real}$ in the expressions (25) indicates that the solution of the Ginzburg–Landau equation must be made "real" by analytic continuation of the free parameters in a way that satisfies the original system of equations (21).

The Ginzburg–Landau equation (26) naturally appears in many problems when small deviations from supercriticality are described, being a so-called amplitude equation, to which numerous partial differential equations reduce.[12]

The following solution of the Ginzburg–Landau equation (26) was obtained in Refs. 9 and 11:

$$\begin{cases} [W]^{\rm real} = (2q)^{1/2}\cosh^{-1}[(q/D)^{1/2}R]\exp[(q-w)T], \\ [W^*]^{\rm real} = (2q)^{1/2}\cosh^{-1}[(q/D)^{1/2}R]\exp[-(q-w)T]. \end{cases} \quad (27)$$

The limiting case in which the reaction constant does not depend on the coordinate and there is no potential, i.e.,

$$k(r) = \alpha = \text{const}, \quad U(r) = 0, \quad (28)$$

was thoroughly analyzed in Refs. 9, 11, and 13. For example, the following solutions of the corresponding stochastic differential equation were found:

$$\begin{cases} n = n_{\rm det}(r,t) + 2^{1/2}\varepsilon\cosh^{-1}[(\sigma/D)^{1/2}r]\exp[(\sigma-\alpha)t], \\ p = 2^{1/2}\varepsilon^{-1}\cosh^{-1}[(\sigma/D)^{1/2}r]\exp[-(\sigma-\alpha)t]. \end{cases} \quad (29)$$

Then, comparing the solutions (25) and (29) in the limit (28) with consideration of the definitions (13) for R and T, we ultimately obtain the following solution of the stochastic differential equation (4):

$$\begin{cases} n = n_{\rm det}(r,t) + 2^{1/2}\varepsilon\cosh^{-1}[(\sigma/D)^{1/2}r]\exp[(\sigma+g'(r))t], \\ p = 2^{1/2}\varepsilon^{-1}\cosh^{-1}[(\sigma/D)^{1/2}r]\exp[-(\sigma+g'(r))t]. \end{cases} \quad (30)$$

The replacement of $g'(r)$ by the expression (9) leads to the following equation for the noise level σ at which an increase in the exponential term in (30) is possible:

$$\sigma(T_a) > \sigma_c(r) = \frac{D}{k_B T_a}\nabla^2 U + k(r). \quad (31)$$

The conditions under which the critical noise level is exceeded are determined by the regions in space within which a local increase in concentration occurs. It should be noted that the Ginzburg–Landau equation (26) is invariant under the replacement $R \to (R+A)$, but it is not invariant under the replacement $r \to (r+a)$, where A and a are arbitrary parameters. It can be concluded from this that the coordinate R is the "intrinsic" coordinate of the "center of mass" of the noise-induced perturbation, which can appear at arbitrary points in space within the regions defined by the condition (31).

3. DESCRIPTION OF NOISE-INDUCED INTERMITTENCY

As noted in Refs. 13 and 14, a field distribution $n(r,t)$ that gives rise to structures accompanied by high peaks with a large concentration of the substance and a short lifetime or a small spatial expanse is typical of systems described by a stochastic differential equation with multiplicative noise. The gaps between these structures are characterized by a low concentration of the substance and a large expanse. The general term describing such a situation is intermittency.

The behavior of a system described by the stochastic differential equation (4) exhibits intermittency when the critical values of the noise level $\sigma_c(r)$ are exceeded [the set of these values is a continuum owing to the fact that each point in space has its own value of $\sigma_c(r)$]. The solutions describing peaks and troughs are represented, with consideration of (12), by the plus and minus signs, respectively, in the expression

$$n = n_{\rm det} \pm 2^{1/2}|\varepsilon|\cosh^{-1}[(\sigma/D)^{1/2}r]\exp[(\sigma-w)t]. \quad (32)$$

We note that these solutions refer to different points in space for which the condition (31) is satisfied.

We can now refine the meaning of the term "rate-limiting step of a reaction:" it is the step in which both terms in the solution (32) are of the same order at $t > t_*$:

$$n_{\rm det}(r,t_*) \sim \varepsilon\cosh^{-1}[(\sigma/D)^{1/2}r]\exp[(\sigma+g'(r))t_*]. \quad (33)$$

As follows from (6), (17), and (30), the probability of the realization (existence) of the optimal trajectory after a certain time $t_{\rm real}$, up to some multiplicative factor, is

$$\mu(t_{\rm real}) = P[n_{\rm opt}] \sim \exp\left[-\sigma\int dr\ dt(ph)^2/2\right]$$
$$= \exp\left[-(\sigma/2)^{-1/2}\int dR\ dT(\rho n_1)^2\right]. \qquad (34)$$

Then for the solutions (30) we have

$$\mu(t_{\rm real}) \sim \exp\left[-\frac{4}{3}(\sigma D/2)^{1/2} t_{\rm real}\right]. \qquad (35)$$

Thus, we have confirmed our main assumption that white noise does not influence the reaction rate or the action of external forces: the probability of the realization of a noise-induced structure does not depend on external factors, which determine only the regions in space where intermittency can occur.

4. CONCLUSIONS

We have shown that consideration of fluctuations in the reaction rate constant of a system described by the Smoluchowski equation leads to behavior of the system that differs significantly from the deterministic case when certain critical values of the noise level are exceeded. A definite similarity to another familiar type of reaction known as a diffusion-limited reaction[15] can be drawn.

In the long-term stage of such a reaction the pure reaction rate no longer appears in the asymptotic expressions for the concentration and (or) in the expressions characterizing the statistical properties of the various structures formed as a result of the reaction. The diffusion coefficient, in these expressions is indeed the source of the name of this type of reaction.

As we have shown, reactions which can be described by Eq. (4) and proceed at a multiplicative noise level above the critical level are also characterized in the long term by the formation of random structures. Although the pure reaction rate $k(r)$ appears in Eq. (32), the noise level, which controls this process, takes on decisive importance in the long run. In analogy to diffusion-limited reactions, we call such reactions noise-limited. Although the term random-force-dominated reaction kinetics was proposed in Ref. 16, our term is more appropriate, since the word limited refers directly to the final stage of the reaction.

The possible engineering applications of this phenomenon relate to chemical analyzers and separators. Essentially all of these devices have some minimal sensitivity threshold, which the designers endeavor to reduce by isolating the system from all sources of noise. An alternative and more productive approach from an economic standpoint might involve solutions that allow a source of external multiplicative noise to reach the critical noise level for the particular system.

It can also be expected that the proposed theoretical approach will be employed frequently to describe phenomena in systems with biomolecular kinetics[17] owing to its descriptive nature and broad capabilities for interpreting the origin of the external noise.

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