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LETTER TO THE EDITOR

On a noise-induced transition in a reactive system

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Abstract. The reaction of a two-component system is studied both under the influence of a stochastic reaction rate and additional fluctuations of the concentrations. There results a noise-induced transition in the case of a coupling between the two kinds of randomness with a characteristic exponent $\beta = 1$. The typical time of the dynamics is approximately calculated by means of a perturbation expansion for a mean first passage time.

A large number of problems in non-equilibrium statistical mechanics may be formulated in terms of nonlinear differential equations for the time evolution of certain physical quantities. Typical examples are reaction–diffusion phenomena which are of current interest [1–7]. Here, the consideration of the reaction gives rise to nonlinear terms proportional to the product of the reactants concentrations. In general, the resulting equations are not of potential type [8], which may lead to deviations from conventional behaviour (compare [9]).

In addition to the deterministic part, there occur also noise source terms representing the influence of different kinds of fluctuations. An additive noise term, for example, may simulate random reaction events. A multiplicative noise could be originated by a fluctuating reaction rate.

An example for reaction phenomena is the process caused by an ion-exchange in a glass. Ag^+ ions covered on the surface will react with Fe^{2+} ions within the glass matrix. The resulting neutral Ag^+ atoms will change the optical properties of the material, which is of practical interest [10].

The present letter addresses a simple modelling of this situation. In particular, we study a model with two kinds of randomness which are coupled to the concentrations in an additive and in a multiplicative way.

We consider a two-component system. The concentrations are denoted by $n_+(t)$, $n_-(t)$. They are space averaged quantities. In the example mentioned above $n_+(t)$ and $n_-(t)$ stand for the concentration of Ag^- ions and Fe^- ions, respectively.

The conventional deterministic evolution equation reads

$$\partial_t n_+ = \partial_t n_- = -An_+ n_- \tag{1}$$

where A is the reaction rate. The system is placed under the non-equilibrium initial conditions $n_+(0) = N$ and $n_-(0) = N - n_e$. Without loss of generality the excess concentration n_e is assumed to be negative. It follows immediately that

$$n_+(t) = n_-(t) + n_e \qquad \forall t. \tag{2}$$

Inserting (2) into (1) we get as the solution

$$n_+(t) = \frac{Nn_e}{N - (N - n_e)\,e^{-An_e t}}. \tag{3}$$

From here one concludes the typical timescale for the relaxation to be $\tau = -(An_e)^{-1}$. We remark that, for $t \to \infty$, n_+ tends to zero, which is the stationary solution. This means physically that the whole amount of one of the substances will be exhausted.

Let us stress that the exponential decay is originated by the non-zero excess concentration. If $n_e = 0$ $(n_+ = n_-)$ there results from (3) asymptotically a decay like t^{-1} which should be exact even in the presence of diffusion and spatial fluctuations if the space dimensionality is larger than 2 [1], rederived recently in [3].

The time t_f necessary for reaching a certain concentration $n_f < N$ is calculated from (3) as

$$t_f = \tau \ln \frac{(n_f - n_e)N}{(N - n_e)n_f} \qquad \tau = -(An_e)^{-1}. \qquad (4)$$

However, the model defined by (1) neglects any kind of fluctuations. Random reaction events cause a noise term additive to (1). A fluctuating reaction rate can be described by a multiplicative noise term. Both kinds of fluctuations could have a common origin, e.g. chemical changes in the environment (varying concentrations of the reaction products etc). Consequently, an extension of the model should describe two kinds of noise, which can be coupled to each other. We start with the following stochastic differential equation:

$$\partial_t n_+ = -\langle A \rangle n_+(n_+ - n_e) - n_+(n_+ - n_e)\xi_t + \kappa \xi_t. \qquad (5)$$

Here ξ_t denotes a stochastic process, which is assumed to be Gaussian with

$$\langle \xi_t \rangle = 0 \qquad \langle \xi_t, \xi_{t'} \rangle = \sigma^2 \delta(t - t') \qquad \forall t, t'.$$

The second term in (5) results from the reaction rate fluctuations, and the third one is the additive noise mentioned above. Since we have assumed a common origin for both of the noises, (5) includes only one stochastic source. The parameter σ is the strength of the noise; κ measures the rate of the strengths of the two noisy terms. It can be positive or negative as well.

The model with a purely multiplicative noise $(\kappa = 0)$ reveals a stationary solution which describes the deterministic state resulting from (1). This will be shown below. On the other hand, a purely additive noise does not qualitatively change the stationary solution either. As is well known [11], the only effect is a broadening of the probability density, which is δ-shaped in the deterministic case. The same is to be concluded if both of the noises are independent. A new situation arises only in the case of a coupling between the noises, which is considered in (5).

Contrary to the deterministic model, equation (5) allows solutions with a momentarily increasing concentration, which corresponds to the backward reaction.

Following a standard procedure [14] we get from (5) the Fokker–Planck equation for the time dependent probability density $p(n_+, t)$:

$$\partial_t p(n_+, t) = -\partial_{n_+}[f(n_+)p(n_+, t)] + \tfrac{1}{2}\partial_{n_+}^2[g^2(n_+)p(n_+, y)] \qquad (6)$$

with

$$f(n_+) = -\langle A \rangle(n_+ - n_e)n_+ + \sigma^2[(n_+ - n_e)n_+ - \kappa](n_+ - n_e/2)$$
$$g^2(n_+) = \sigma^2[(n_+ - n_e)n_+ - \kappa]^2.$$

As usual $f(n_+)$ and $g^2(n_+)$ are called drift and diffusion, respectively.

The stochastic differential equation (5) is interpreted according to Stratonovich. This seems to be meaningful, since the white noise is understood as the limit of a coloured noise [12].

Provided the diffusion term g^2 does not vanish in the physically accessible region for n_+ the stationary probability density is easily obtained as:

$$p_s(n_+) = Z^{-1} \frac{(n_+ - n_e/2 + b)^{a-1}}{|n_+ - n_e/2 - b|^{a+1}} \exp \frac{c(n_+ - n_e/2)}{b^2(n_+ - n_e/2 + b)(n_+ - n_e/2 - b)} \tag{7}$$

with

$$a = \frac{2\langle A \rangle}{\sigma^2} \frac{2\kappa + n_e^2}{(4\kappa + n_e^2)^{3/2}} \qquad b = \sqrt{\kappa + n_e^2/4} \qquad c = \frac{\kappa \langle A \rangle}{\sigma^2}.$$

Normalization to 1 gives a condition to Z.

Next we will discuss three different situations.

(i) $\kappa > 0$. In this case there occurs a special point

$$n_s = n_e/2 + b \tag{8}$$

in the physically meaningful interval $0 \leqslant n_+ < \infty$. At this point the diffusion term vanishes whereas the drift term is negative. Since the stationary solution (7) does not exist there, it is necessary to study the dynamics of the system using (5). Starting with a concentration $N > n_s$ the system will reach the point n_s due to the non-zero diffusion term for all $n_+ > n_s$. Since $g^2(n_s) = 0$ and $f(n_s) < 0$ the system will be driven to the region $n_+ < n_s$ with probability 1. Approaching n_s from the left the system will be reflected there. Consequently, it will be confined to the region $0 \leqslant n_+ < n_s$ after a certain time t_s, which will be calculated below. Since the stationary solution corresponds to the limit $t \to \infty$, it is given by (7) within the interval $[0, n_s)$ and equals zero outside. We remark that $p_s(n_+ \to n_s - 0) = 0$.

The stationary probability density exhibits a maximum at $n_m \in (0, n_s)$ where n_m is given as the solution of a cubic equation. n_m is a monotonously increasing function of κ. The following approximations are valid:

$$n_m \propto \kappa \text{ for } \kappa \ll n_e^2, \sigma^{-4}\langle A \rangle^2 \qquad n_m \propto \sqrt{\kappa} \text{ for } \kappa \gg n_e^2, \sigma^{-4}\langle A \rangle^2. \tag{9}$$

A typical stationary solution is shown in figure 1.

Contrary to the deterministic model the most probable result of the process is a non-vanishing concentration n_+ here. The physical reason is the influence of the backward reaction, modelled by the two competing stochastic terms. One of the stochastic terms causes an increasing concentration while the other one causes a decreasing n_+.
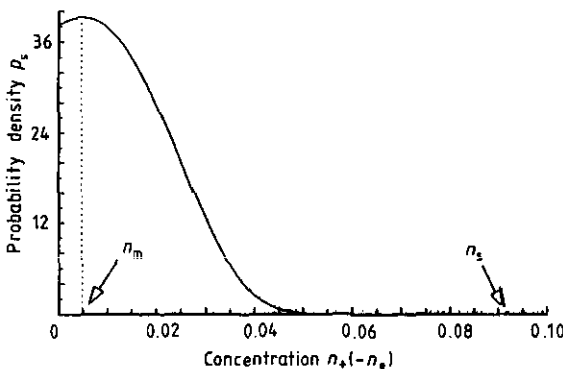

Figure 1. Stationary probability density p_s of n_+ for $\kappa = 0.1 n_e^2$; $\sigma^2 = -0.1\langle A \rangle n_e^{-1}$.

(ii) $\kappa = 0$. There is no additive noise. At the point $n_+ = 0$ both diffusion and drift are equal to zero. The system remains at this point once it has reached it. Hence the stationary probability density has a δ-peak. It is easily proved that $\delta(n_+)$ is a solution of the stationary Fokker–Planck equation for a vanishing current. Such a behaviour corresponds exactly to the deterministic case mentioned above.

(iii) $\kappa < 0$. Contrary to cases (i) and (ii) the stationary solution (7) exists everywhere in $0 \leq n_+ < \infty$. p_s is a monotonously decreasing function, giving a non-zero value to every n_+. The most probable concentration is $n_+ = 0$, resulting also in the deterministic model. A typical shape for p_s is shown in figure 2.

In summary, the most probable values n_m for the concentration n_+ in the stationary case ($t \to \infty$) are given in figure 3 as a function of the control parameter κ. Obviously, there occurs a noise induced transition at $\kappa = 0$. In analogy to classical phase transition phenomena we are able to calculate a characteristic exponent $\beta = 1$, defined by $n_m \propto \kappa^\beta$ (for small κ). β is different to the classical critical exponent $\frac{1}{2}$ [11].

Next the dynamics of the system will be studied briefly. The time necessary for reaching a stationary probability density is infinite. A complete description of the evolution of the probability density is given by the Fokker–Planck equation (6). Typical times can be found by an eigenfunction expansion; see e.g., [12]. This will not be performed here. Besides, the time scales of the dynamics of the system are in general
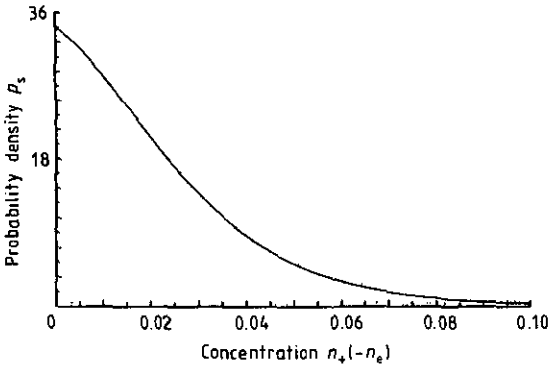

Figure 2. Stationary probability density p_s of n_+ for $\kappa = -0.1 n_c^2$; $\sigma^2 = -0.1 \langle A \rangle n_c^{-1}$.
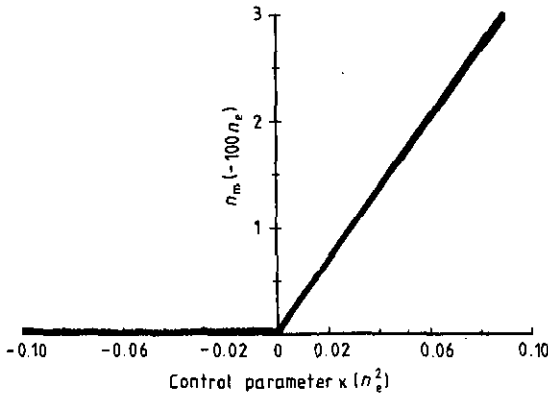

Figure 3. Most probable resulting concentration n_m as a function of the control parameter κ for small κ and for $\sigma^2 = -\langle A \rangle n_c^{-1}$.

not identical to those for the probability density. (Even in the case of a stationary distribution the system itself changes its state.) For the most interesting case $\kappa > 0$, where the noise changes the steady state qualitatively, we are able to find a characteristic time of the system dynamics by an approximation for small noise.

The system starts with certainty at $n_+ = N$. (We assume $N > n_s$.) After reaching n_s it will be driven to $n_+ < n_s$ and will never return. Hence the average time t_s necessary for reaching n_s has a physical meaning very similar to the corresponding time for the deterministic model. t_s can be calculated as a mean first passage time. As a function of N, t_s obeys the following differential equation [13]:

$$f(N)\partial_N t_s(N) + \tfrac{1}{2}g^2(N)\partial_N^2 t_s(N) = -1. \tag{10}$$

Considering the Kolmogorov backward equation the boundary conditions for the problem are obtained as:

$$t_s(n_s) = 0 \qquad \partial_N t_s(N)|_{N \to \infty} = 0. \tag{11}$$

Since we have not found a general solution we use a perturbative approach with respect to σ^2. Writing $f(N)$ as $f(N) = f_0(N) + \sigma^2 f_1(N)$, $g^2(N)$ as $g^2(N) = \sigma^2 g_1^2(N)$ and expanding $t_s(N) = t_s^{(0)}(N) + \sigma^2 \theta(N) + o(\sigma^4)$ we get as a perturbative approximation

$$t_s^{(0)}(N) = -\int_{n_s}^N f_0^{-1}(n)\,\mathrm{d}n = \tau \ln \frac{(n_s - n_e)N}{(N - n_e)n_s} \tag{12}$$

$$\theta(N) = -\int_{n_s}^N f_0^{-1}(n)[f_1(n)\partial_n t_s^{(0)}(n) + \tfrac{1}{2}g_1^2(n)\partial_n^2 t_s^{(0)}(n)]\,\mathrm{d}n$$

$$= \langle A \rangle^{-2} \frac{N^2 n_e^2 - 2Nn_e(N^2 - \kappa) + (N^2 - \kappa)^2}{4N^2(N - n_e)^2} \tag{13}$$

where logarithmic terms occurring in the expression for θ cancel each other.

Inserting (12) and (13) into the expansion for t_s we obtain:

$$n_s \approx \frac{Nn_e}{N - (N - n_e)\,\mathrm{e}^{(t_s - \sigma^2\theta)/\tau}}. \tag{14}$$

Here t_s is a quantity averaged over all sample paths starting at N and ending at n_s. hence (14) can be understood as the law governing (on average) the approach of the system to n_s and it corresponds to the deterministic law (3) in the sense described above. Remark that for $\sigma = 0$, which means a vanishing randomness, (3) and (14) are identical.

For $\kappa \lll N^2$, θ is approximately independent on N; $\theta \approx \langle A \rangle^{-2}/4$. That means physically the noise does not change the timescale of the evolution. Only a shift occurs. The time necessary to reach the concentration n_s is increased by addition of a definite amount due to the randomness.

Summarizing, we have discussed a chemical reaction model with a multiplicative and an additive noise coupled to each other. It exhibits a noise-induced transition with a characteristic exponent $\beta = 1$. We have studied the dynamics of one of the phases. In the case of small noise and a small control parameter κ, the randomness does not change the timescale. It causes only an additive increasing of the deterministic relaxation time.

Further investigations should concern the dynamics of the probability density or the relation of the equations used here to a deterministic description in a higher-dimensional phase space. The inclusion of explicit diffusive terms is considered in a forthcoming paper [14].

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