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Metastable states in diffusion-controlled processes

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Abstract. A two-component system with diffusion, annihilation of particles of different types and reproduction and recombination of particles of the same type is considered. It is shown that if the initial concentrations of the reactants are equal, the existence of small density fluctuations leads to the formation of an extremely long-living metastable mozaic distribution of particles, where average concentrations largely exceed the mean-field values. If the initial concentrations differ significantly the relaxation has a slow power-law character. In the system of reduplicating particles annihilating with mobile and not self-reproducing non-ideal traps at long times the concentration of the particles grows (however small it might be initially) while that of traps vanishes—in contrast with formal kinetics.

The study of fluctuation kinetics in diffusion-controlled reactions attracts considerable attention. These effects are essential for the description of exciton migration and capture in molecular solids and solutions, carrier and defect annihilation in crystals, aggregation and coagulation processes and survival problems in biology, ecology and synergetics.

It has been shown (Balagurov and Vaks 1973, Donsker and Varadhan 1975, Ovchinnikov and Zeldovich 1978, Burlatskii 1978, Zeldovich and Ovchinnikov 1977, 1978, Meakin and Stanley 1984, Berezhkovskii *et al* 1986) that small thermodynamic fluctuations of the initial distribution of particles change the long-time asymptotics of density relaxation. Some of these results were later rederived (Grassberger and Procaccia 1982, Kayser and Hubbard 1983, Toussaint and Wilczek 1983, Anacker *et al* 1984, Kang and Redner 1984, 1985, Sokolov 1986). Stationary fluctuation effects in bimolecular systems with external sources lead to stochastic segregation of reactants (Ovchinnikov and Burlatskii 1986, Burlatskii *et al* 1987, Anacker and Kopelman 1987, Zhang Yi-Cheng 1987). The Poisson fluctuations in the distribution of immobile traps after a long waiting period lead to an explosive growth of particle concentration for any non-zero (arbitrarily small) rate of particle reduplication (Burlatskii and Ovchinnikov 1987).

In this paper we study the influence of density fluctuations on the kinetic processes in bimolecular reaction systems with diffusion, pair annihilation of particles of different types, slow recombination of particles of one type, along with particle reproduction, and also in systems with reduplicating particles and mobile non-ideal traps. For the case of equal initial concentrations of reactants it is shown that an extremely long-living metastable state is formed so that the whole system is split into areas or domains each consisting of only one type of particle. The average size of such clusters grows slowly (logarithmically) with time and the mean densities largely exceed the predictions of mean-field theories. If the initial concentrations in this situation differ significantly, the relaxation has a slow power-law character. We obtain another case if the concentration of type B particles is much greater than that of type A, but the rate of reproduction for B equals zero. Then at long times the concentration of particles A will grow, while for B it will vanish—in contrast with formal kinetics that does not take fluctuations into account.

In the general case the reaction kinetics of the system under consideration are governed by the following equations:

$$\dot{c}_A(\boldsymbol{r}, t) = D\Delta c_A(\boldsymbol{r}, t) + k_1^+ c_A(\boldsymbol{r}, t) - k^- c_A(\boldsymbol{r}, t) c_B(\boldsymbol{r}, t) - \alpha_1 c_A^2(\boldsymbol{r}, t) \qquad (1a)$$

$$\dot{c}_B(\boldsymbol{r}, t) = D\Delta c_B(\boldsymbol{r}, t) + k_2^+ c_B(\boldsymbol{r}, t) - k^- c_A(\boldsymbol{r}, t) c_B(\boldsymbol{r}, t) - \alpha_2 c_B^2(\boldsymbol{r}, t) \qquad (1b)$$

where D is the diffusion coefficient and $k_1^+, k_2^+, k^-, \alpha_1, \alpha_2$ are the rate constants corresponding to reproduction, annihilation and recombination processes respectively.

First, let us consider the symmetric case:

$$k_1^+ = k_2^+ = k^+ \qquad \alpha_1 = \alpha_2 = \alpha \qquad k^- \gg \alpha \qquad c_0 a^d \ll 1$$

$$c_A^0 = c_B^0 = c_0 \qquad c_A^0 = \langle c_A(\boldsymbol{r}, 0)\rangle \qquad c_B^0 = \langle c_B(\boldsymbol{r}, 0)\rangle$$

$$\langle [c_A(\boldsymbol{r}, 0) - c_A^0][c_B(\boldsymbol{r}', 0) - c_B^0]\rangle = 0$$

$$\langle [c_A(\boldsymbol{r}, 0) - c_A^0][c_A(\boldsymbol{r}', 0) - c_A^0]\rangle = \langle [c_B(\boldsymbol{r}, 0) - c_B^0][c_B(\boldsymbol{r}', 0) - c_B^0]\rangle = c_0 \delta(\boldsymbol{r} - \boldsymbol{r}')$$

where a is the particle (or the annihilation) radius. The initial density distribution is of the Poissonnian type with mean c_0.

In the framework of formal kinetics the evolution of the system includes two stages. First, concentrations relax to

$$c_1^* = k^+(k^- + \alpha)^{-1}. \qquad (2)$$

For $k^- > \alpha$ this state is unstable with respect to fluctuations of the total concentration, so after a long waiting time period (greater than the quantity $(c_1^* V)^{1/2}/k^+$) where V is the volume of the system, there occurs a transition to the state of stable equilibrium (see figure 1):

$$c_{A(B)} = 0 \qquad c_{B(A)} = c_2^* = k^+/\alpha. \qquad (3)$$

For $k^- = \alpha$ we have an indifferent equilibrium on the critical line so the proportions of reactant concentrations fluctuate freely (figure 2).

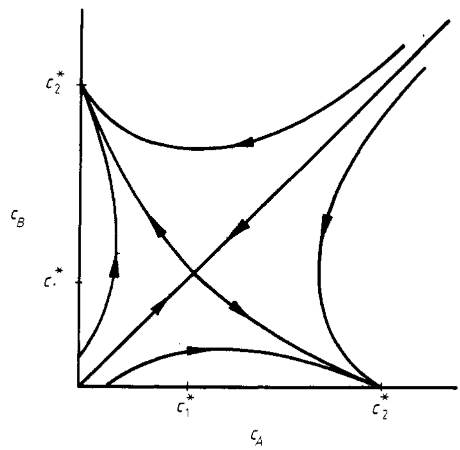

Figure 1. The phase diagram of the system for $k^- > \alpha$.

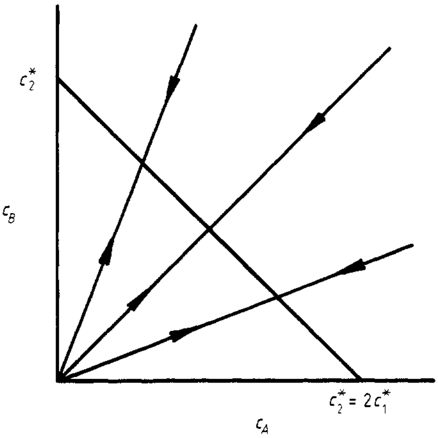

Figure 2. The phase diagram of the system for $k^- = \alpha$.

Now we take into account local density fluctuations. In (1) we go over to the new variables

$$z(\boldsymbol{r}, t) = c_A(\boldsymbol{r}, t) - c_B(\boldsymbol{r}, t) \qquad \Sigma(\boldsymbol{r}, t) = c_A(\boldsymbol{r}, t) + c_B(\boldsymbol{r}, t) \tag{4}$$

and obtain

$$\dot{z}(\boldsymbol{r}, t) = \Delta z(\boldsymbol{r}, t) + z(\boldsymbol{r}, t) - z(\boldsymbol{r}, t)\Sigma(\boldsymbol{r}, t) \tag{5a}$$

$$\dot{\Sigma}(\boldsymbol{r}, t) = \Delta\Sigma(\boldsymbol{r}, t) + \Sigma(\boldsymbol{r}, t) - (k^- + \alpha)(2\alpha)^{-1}\Sigma^2(\boldsymbol{r}, t) + (k^- - \alpha)(2\alpha)^{-1}z^2(\boldsymbol{r}, t). \tag{5b}$$

Here the coordinates are expressed in units $(D/k^+)^{1/2}$, the time t in units $(k^+)^{-1}$ and the densities in units c_2^*.

The diffusion and density fluctuations have little effect on the initial stage—the relaxation to the formal equilibrium state $c_A = c_B = c_1^*$. But as can be seen from (5), the corresponding homogeneous solution is unstable with respect to small long-wave perturbations. With the help of the methods proposed by Balagurov and Vaks (1973), Ovchinnikov and Zeldovich (1978) and Toussaint and Wilczek (1983) one can show that the local equilibrium state, characterised by

$$\Sigma(\boldsymbol{r}, t) = |z(\boldsymbol{r}, t)| \tag{6}$$

is reached after a period of time $\tau' = \ln(c_0 a^d k^+ \alpha^{-1})$. In this state the system is formed of domains of varying sizes, each consisting of only one type of particle. In the narrow layer at the domain wall equation (6) is violated, but for $k^- \gg \alpha$ the non-linear term in (5) (transformed with the help of (6)) is much smaller than the linear term in a larger layer, so the use of (6) in the whole space would not lead to appreciable discrepancies. For the stationary regime in one dimension, integration in (5a) and (6) can be performed to give

$$(\mathrm{d}z/\mathrm{d}x)^2 = F(z) \qquad F(z) = \tfrac{2}{3}|z|^3 - z^2 + \beta \qquad 0 \leqslant \beta \leqslant \tfrac{1}{3}. \tag{7}$$

Here β is an arbitrary integration constant that determines the cluster size

$$L = \int_0^{z_\mathrm{m}} [F(z)]^{-1/2}\,\mathrm{d}z \tag{8}$$

and z_m is the maximum value of the density in the cluster, defined by the equation $F(z_\mathrm{m}) = 0$.

As $\beta \to \frac{1}{3}$, the size of the cluster tends to infinity. For large clusters we have $\beta = \frac{1}{3} - \Delta$, $\Delta \ll 1$, and

$$\tfrac{1}{6}(\Delta/2)^{1/2} = \mathrm{e}^{-2L} \qquad z_{\mathrm{m}} = 1 - (\Delta/2)^{1/2} \qquad \Psi = \left|\frac{\mathrm{d}z}{\mathrm{d}x}\right|_{z=0} = \beta^{1/2}. \tag{9}$$

The flow Ψ through the border of an equilibrium cluster is larger for large clusters, so big domains would absorb the smaller ones. For a large quasi-equilibrium cluster, contacting with an infinite cluster, we have

$$\mathrm{d}z_{\mathrm{m}}^2/\mathrm{d}t = \Psi^2 - \tfrac{1}{3}.$$

This equation gives an estimate for the lifetime of a domain of size L

$$\tau(L) = \exp(2L) \tag{10}$$

that corresponds to the logarithmic growth of the mean cluster size. Systems of higher dimensionality have a more complicated structure; the estimate (10), however, remains valid because the particle density reaches its stationary value in a thin layer at the boundary, which can be considered flat if $L \gg 1$. Average concentrations of A and B particles in the metastable system equal $c_2^*/2$, which exceeds the mean-field value c_1^* significantly.

So, if the initial concentrations of the reactants are equal, a long-living mozaic distribution of the two types of particles is formed. But if at $t = 0$ the concentrations differ significantly, say, $c_B^0 \gg c_A^0$, while the reproduction and recombination rates remain symmetric, the less numerous component vanishes and the concentration of the other reaches its stationary value. At the final stage of the relaxation the concentration can be estimated with the help of the method of optimal fluctuation (Balagurov and Vaks 1973, Ovchinnikov and Zeldovich 1978, Berezhkovskii *et al* 1986). We consider the survival probability of A particles in a spherical area initially containing no traps. For the Poisson initial distribution the probability of the formation of such a cavity depends on its volume exponentially and its lifetime is determined by (10), so the concentration of the vanishing component can be obtained by integration over the size distribution of these cavities:

$$c_A(t) = k^+ \alpha^{-1} c_B^0 \int \mathrm{d}r \exp[-c_B^0 V - t \exp(-2r\sqrt{k^+/D})]. \tag{11}$$

Calculation by the method of steepest descent leads to power-law asymptotics, which differ radically from exponential mean-field results:

$$c_A(t \to \infty) \sim t^{-(c_B^0/2)(D/k^+)^{1/2}} \qquad d = 1 \tag{12a}$$

$$c_A(t \to \infty) \sim t^{-(\pi c_B^0/4)(D/k^+)\ln t} \qquad d = 2 \tag{12b}$$

$$c_A(t \to \infty) \sim t^{-(\pi c_B^0/6)(D/k^+)3/2\ln^2 t} \qquad d = 3. \tag{12c}$$

The exponents in (12*a*)–(12*c*) are not universal.

Now consider the non-symmetric case when particles A annihilate with diffusing and non-self-reproducing traps B ($k_2^+, \alpha_2 = 0$). When the trap concentration is sufficiently high $c_B^0 \gg c_A^0$, k^+/k^-, the mean-field-like solution forecasts an exponential vanishing of the concentration of type A particles. Let us take into account density fluctuations. For the Poissonian initial distribution there would always occur with a small probability such areas where the density of A particles is anomalously high, and there are no traps. In three dimensions the flow of particles out of a spherical cavity of radius $R \gg (D/k^+)^{1/2}$, where reproduction and recombination of A particles takes place is equal to $4\pi DR^2 c_2^*(k^+/3D)^{1/2}$ (see (9)). The maximum flow of traps onto the absorbing sphere is $4\pi DRc_B^0$ so, if the radius of the cavity exceeds $R_c = (c_B^0/c_2^*)(3D/k^+)^{1/2}$, the 'out' flow of particles exceeds the 'in' flow of traps. Then the size of these fluctuation areas grows with time. The probability of finding spherical cavities of the critical radius is defined by

$$\ln P(R_c) = -4\pi R_c^3 (c_B^0)^2 / 3c_A^0.$$

So, in systems with slow reproduction, recombination and annihilation of particles on non-ideal diffusing traps on the first stage the concentration of the particles falls exponentially to the low value $c_0 P(R_c)$ and then, after a long period of time, that is larger than $P^{-1}(R_c)$, the particle density grows to the equilibrium value c_2^*, while the trap concentration vanishes.

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