LETTER TO THE EDITOR

Fluctuation-induced kinetics of reversible reactions

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Abstract. The influence of spatial density fluctuations on the kinetics of a reversible reaction $A + B \leftrightarrow C$ involving charged particles is investigated. New explicit expressions for the long-time approach of mean A and B densities to equilibrium are obtained.

Fluctuation effects in the theory of diffusion-controlled processes have gained considerable interest in recent years. On the one hand this is due to the growing number of its applications in physics, chemical physics and biology. On the other hand it can be accounted for by the fact that this problem has now taken an appropriate place among the related problems of statistical physics in which fluctuation-induced behaviour is essential. We should also mention a great number of fractal system investigations where the fluctuations of spatial structure determine an anomalous kinetic behaviour of diffusion-controlled processes.

In mean-field considerations it was assumed that after some characteristic time t_L ($t_L = L^2/D$ where L is the mean size of spatial inhomogeneity, and D is a diffusion coefficient) a steady regime is established when the kinetics of bimolecular reactions

$$A + B \leftrightarrow C \qquad \text{or} \qquad A + A \leftrightarrow S$$
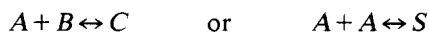
is independent of inhomogeneity in the initial spatial distribution of reagents A and B. In this approximation the long-time approach to the equilibrium values of the mean densities is determined by exponential dependence upon time.

It was first shown by Zeldovich (1977), Ovchinnikov and Zeldovich (1978) and Burlatsky (1978) and, subsequently, by Toussaint and Wilczek (1983) and Kang and Redner (1984) that in the case of an irreversible reaction $A + B \rightarrow$ inert at equal initial mean A and B densities, thermodynamical fluctuations in the spatial distributions of the reagents lead to a slowing down of the long-time kinetics (as compared to the mean-field predictions $C_A(t) = C_B(t) = C_d(t)$; $C_1(t) \sim t^{-1/2}$, $C_2(t) \sim \ln t/t$, $C_3(t) \sim t^{-1}$, where d is space dimensionality). The long-time stage is determined by the diffusive smoothing of initial random inhomogeneities which results in the dependence $C_d(t) \sim t^{-d/4}$.

Besides, Zeldovich and Ovchinnikov (1977, 1978) and Kang and Redner (1985) have shown that the long-time kinetics of reversible reactions involving uncharged particles is also determined by fluctuation effects and with $t \rightarrow \infty$ the approach to equilibrium is defined by a power law $C_A(t) - C_A(\infty) \sim (Dt)^{-d/2}$.

Fluctuation effects are essentially increased in the system prepared by a steady external source. If particles A and B are generated in the reaction bath independently of each other by an external source with Poissonian properties, the irreversible reaction between them leads to the appearance of spatial correlations in reagent distributions.

The long-wave asymptotics of the fluctuation spectrum are not of Poissonian type (Ovchinnikov and Burlatsky 1986, Zhang 1987, West *et al* 1989), which results in the long-time kinetics of irreversible recombination after the external source is turned off; for $d = 3$ $C_3(t) \sim t^{-1/4}$. For systems with d less then the dimension of random walk d_w (for compact spaces $d_w = 2$) the existence of an essential peculiarity in the steady-state fluctuation spectrum leads to the division of the reaction bath into macroscopic domains containing only one sort of reagent. This effect was predicted by Ovchinnikov and Burlatsky (1986), Zhang (1987), Burlatsky and Pronin (1989) and West *et al* (1989) and confirmed by numerical experiment on fractals (Anacker and Kopelman 1987).

The goal of the present letter is to investigate the long-time kinetics of the reversible bimolecular reaction $A + B \leftrightarrow C$ involving charged particles under different types of external generation of reagents.

The rate of local densities of diffusing species A and B charged by q_A and q_B respectively is governed by

$$\dot{C}_j(r, t) = -K\hat{L}_1[C_A(r, t)C_B(r_1, t)] + D_j \, \mathrm{div}(\mathrm{grad} - \beta q_j \, \mathrm{grad} \, U(r, t))C_j(r, t)$$

$$+ K_- C_C(r, t) + Z_j(r, t) + I_j(r, t)$$

$$\beta = 1/k_B T \qquad j = A, B \qquad q_A = -q_B = q \tag{1}$$

$$\hat{L}_1 = N_d \int dr_1 \, \delta(|r - r_1| - l)[\ldots] \qquad N_d \int dr_1 \, \delta(|r_1| - l) = 1.$$

Here l is the reaction radius, D_A and D_B are the diffusion coefficients (further on we shall regard $D_A = D_B = D_C = D/2$); $Z_j(r, t)$ are the terms which consider the fluctuations of diffusive fluxes (Gardiner 1983), $I_j(r, t)$ are random source terms, and K and K_- are the 'chemical' rate constants of direct and backward reactions. The potential $U(r, t)$ submits to the Poisson equation

$$\mathrm{div} \, \mathrm{grad} \, U(r, t) = -4\pi q(C_B(r, t) - C_A(r, t)). \tag{2}$$

The reagent densities are equal to

$$C_j(r, t) = C_j(t) + c_j^*(r, t) \qquad \langle c_j^*(r, t) \rangle = 0 \qquad j = A, B, C$$

where $C_j(t)$ are the mean values, while $c_j^*(r, t)$ are random spatial deviations and angle brackets refer to volume average. Averaging (1), we obtain that $C(t)$ (here we consider the case of equal initial mean A and B densities, $C(t) = C_A(t) = C_B(t)$) obeys the equation

$$\dot{C}(t) = -K(C^2(t) + \langle \hat{L}_1[c_A^*(r, t)c_B^*(r_1, t)] \rangle) + K_- C_C(t) + \langle I_{A,B}(r, t) \rangle$$

$$+ K_q \langle 2c_A^*(r, t)c_B^*(r, t) - (c_A^*(r, t))^2 - (c_B^*(r, t))^2 \rangle \tag{3}$$

where $K_q = 4\pi q^2 D\beta$. The rate of $C_C(t)$ is governed by the condition that the total number of reacting particles be conserved, $\dot{C}(t) + \dot{C}_C(t) = 0$.

Let us determine the pair correlation functions

$$G_{ij}(R, t) = \langle \hat{L}_R[c_i^*(r, t)c_j^*(r_1, t)] \rangle \qquad \hat{L}_R = \int dr_1 \delta(r - r_1 - R)[\ldots] \qquad i, j = A, B, C$$

where R is the d-dimensional correlation parameter. For G_{ij} we get the following system of reaction–diffusion equations:

$$\dot{G}_{jj} = -2C(t)(K - K_q)G_{AB} - 2C(t)(K + K_q)G_{jj} + 2K_- G_{jC} + D\Delta_R G_{jj} - DC(t)\Delta_R \delta(R)$$

$$+ I_{jj}(R, t) - 2KT_{AjB} + 2K_q(T_{AjB} - T_{jjj}) \qquad j = A, B \tag{4a}$$

$$\dot{G}_{AB} = -KC(t)(2G_{AB} + G_{AA} + G_{BB}) - K_q C(t)(2G_{AB} - G_{AA} - G_{BB}) + K_-(G_{AC} + G_{BC})$$

$$+ D\Delta_R G_{AB} + I_{AB}(R, t) - K(T_{AAB} + T_{ABB}) \tag{4b}$$

$$\dot{G}_{jC} = KC(t)(G_{jj} + G_{AB} - 2G_{jC}) + K_-(G_{CC} - G_{jC}) + D\Delta_R G_{jC} + I_{jC}(R, t)$$

$$+ K(T_{AjB} - T_{ABC}) + K_q(T_{ABC} - T_{jjC}) \qquad j = A, B \tag{4c}$$

$$\dot{G}_{CC} = KC(t)(G_{AC} + G_{BC}) - 2K_- G_{CC} + D\Delta_R G_{CC} - DC_C(t)\Delta_R \delta(R)$$

$$+ I_{CC}(R, t) + 2KT_{ABC} \tag{4d}$$

where Δ_R denotes the d-dimensional Laplacian, $\delta(R)$ is a delta function and T_{ijk} are third-order correlation functions.

In order to calculate the pair correlation functions G_{ij} we shall make the following assumption. Assume that the correlation functions of the fourth-order H_{ABij} can be decoupled and represented as a composition

$$H_{ABij}(R, t) = G_{AB}(l, t)G_{ij}(R, t) \tag{5}$$

then the system of equations which governs the time evolution of T_{ijk} will not have non-trivial solutions and (4) will be self-contained. As was shown by Burlatsky and Ovchinnikov (1987), such an assumption leads to an asymptotically exact description of the correlation properties of related diffusion–reaction systems at the large-R limit and, hence, to asymptotically exact long-time dependences of mean densities upon time. Besides, in the long-time dependence $C(t) = \mu t^{-w}$ the indicator w is determined exactly, while the coefficient μ, dependent on the diffusion coefficients and rate constants, is defined up to a numerical multiplier. In particular, in terms of such an assumption as (5), the well known dependence $C(t) \sim t^{-d/4}$ was obtained by Burlatsky (1978). In general, for intermediate R the representation (5) is not quite valid. It was shown by Burlatsky *et al* (1989) that for diffusion–reaction systems of uncharged species T_{ijj} has a singularity at $|R| = l - T_{ijj}(R, t) = N_d K^{-1} \dot{C}(t)\delta(|R| - l)$, caused by the discrete nature of the spatial distributions of the particles. This singularity leads to the appearance of short-wave pair correlations and, hence, Smoluchowsky-type renormalisation of the rate constants in the equation for the mean density evolution

$$\dot{C}(t) = -K_{\text{eff}}(t)/(C^2(t) + G_{AB}(l, t)) + K_{\text{eff}}^-(t)C_C(t) + \langle I_{A,B}(r, t)\rangle. \tag{6}$$

Let us emphasise that this renormalisation is essential only for intermediate times (when we can neglect $G_{AB}(l, t)$) and determines a correct Smoluchowsky-type intermediate exponential dependence, while the goal of our letter is to define the long-time fluctuation-induced laws, connected with the decrease of pair correlations $G_{AB}(l, t)$ and independent of $K_{\text{eff}}(t)$. Hence, we shall present asymptotic expressions for $K_{\text{eff}}(t)$ omitting intermediate derivations which go beyond the framework of this paper and will be published elsewhere:

$$K_{\text{eff}}(t) = K_c K_d/(K_c + K_d) \qquad K_{\text{eff}}^-(t) = K_- K_d/(K_c + K_d) \qquad K_c = K \exp(r_0/1)$$

where r_0 is the Onsager radius. Smoluchowsky–Debye-type constants are equal to

$$K_3 = \tfrac{1}{2}K_q(1 + \coth(r_0/2l)) \qquad K_2 = 4\pi D/\ln(Dt/l^2) \qquad K_1 = (D/\pi t)^{1/2}.$$

Thus, we have derived the self-contained system of reaction–diffusion equations (4) (with $T_{ijk} = 0$) and (6) determining the kinetics of reversible reactions involving charged particles.

Let us consider a few cases of initial conditions for equations (4) and (6).

(i) In the case of instant generation of non-correlated particles when A and B are 'quickly' (time of generation is much less than the 'chemical' time $t_{ch} = (2K_cC(0) + K_-)^{-1}$) injected into the reaction bath with constant mean densities $C(0)$ and $C_C(0)$ and statistically independent fluctuations, the initial distribution can be considered Gaussian and δ-correlated

$$G_{ij}(R, 0) = C_j(0)\delta_{ij}\delta(R) \qquad i, j = A, B, C$$

where δ_{ij} is the Kroneker delta.

(ii) Under the instant A and B generation by correlated pairs of radius r_g the initial value of $G_{AB}(R, 0)$ is not equal to zero, contrary to case (i),

$$G_{AB}(R, 0) = N_d C(0)\delta(|R| - r_g) \qquad \text{while} \qquad G_{AC}(R, 0) = G_{BC}(R, 0) = 0.$$

This case is essentially important since it imitates the majority of reaction–diffusion processes involving charged particles—electrons and holes, radical pairs.

Under instant generation from (4) (with $T_{ijk} = 0$) we obtain the following long-time expressions for $G_{AB}(l, t)$.

For initial conditions (i):

$$G_{AB}(l, t) = G_{AB}(l) - \tfrac{1}{2}\Delta C K_-^2 t_{ch}^2 (Dt)^{-d/2} + \text{small corrections.}$$

Here $\Delta C = C(0) - C_A$, where C_A is a steady-state solution of (6) with $\langle I \rangle = 0$ and $G_{AB}(l)$ is an equilibrium solution of (4).

For initial conditions (ii):

$$G_{AB}(l, t) = G_{AB}(l) + \tfrac{1}{2}(C_A - C(0)r_g^2/(Dt))(Dt)^{-d/2} + \text{small corrections.}$$

Linearising (6) near the steady-state value C_A we find that the long-time approach of the mean density to equilibrium is defined by the decrease of pair correlations and described by power-law dependence, contrary to the predictions of exponential mean-field theories:

for (i) $\qquad C(t) = C_A + A\Delta C(Dt)^{-d/2} \qquad A = K_c K_-^2 t_{ch}^2 / 2(2K_c C_A + K_-) \qquad (7a)$

for (ii) $\qquad C(t) = C_A - A(C_A - C(0)r_g^2/Dt)(Dt)^{-d/2} \qquad (7b)$

It is important that at the large-t limit $C(t)$ (7b) is less than C_A and, hence, $C(t)$ can be a non-monotonic time function.

(iii) Let us consider one more type of A and B external generation often used in radiation physics. In the reaction bath where the reversible reaction takes place there acts an external source which breaks the direct reaction product C into a pair of reagents A and B. The radius of the generated pair is equal to r_g. The kinetics of such a process is determined by the system of equations (4), (6), where the averaged source terms are equal to

$$I_{jj}(R, t) = -I_{jC}(R, t) = I_{CC}(R, t) = IC_C(t)\delta(R)$$

$$I_{AB}(R, t) = IN_d C_C(t)\delta(|R| - r_g) \qquad \langle I(r, t)\rangle = IC_C(t)$$

where I is the mean intensity of the external source. From (4), (6) we get the following expression for the leading terms at $t \to \infty$ of the Fourier image of G_{AB}

$$G_{AB}(p, t) = G_{AB}(p)(1 - \exp(-Dtp^2))$$

where

$$G_{AB}(p)_{p \to 0} = -\tfrac{1}{2}IC_C F(p, r_g)K_-^2 t_{ch}^2 / Dp^2.$$

Here $F(p, r_g)$ is the Fourier image of the function $F(R, r_g) = \delta(R) - N_d\delta(|R| - r_g)$. The expression given above for $G_{AB}(p)$ is valid for dimensionality of space. When $r_g \to \infty$ an equilibrium fluctuation spectrum $G_{AB}(p)$ has a peculiarity, $G_{AB} \sim p^2$ at $p \to 0$, which leads to the effect of macroscopic segregation in reversible reactions of charged particles. Let us note that this effect was recently predicted for irreversible reactions of uncharged species by Ovchinnikov and Burlatsky (1986), Zhang (1987), West *et al* (1989). For reversible reactions of charged species we get from (4) and (6) that in 3D the essential peculiarity in an equilibrium fluctuation spectrum causes the change of time degree indicator in the long-time approach to equilibrium

$$C(t) = C_A^* - B(Dt)^{-1/2} \tag{7c}$$

where constant $B = K_c C_C^* K_-^2 t_{ch}^2 / D(2K_c C_A^* + I + K_-)$; C_A^*, C_C^* are the steady-state solutions of (6) with $\langle I(r, t)\rangle = IC_C(t)$. With finite values of r_g the steady-state spectrum of fluctuations is of Poissonian type due to the geminate recombination and the mean density approach to equilibrium is determined by the power dependence

$$C(t) = C_A^* - Br_g^2(Dt)^{-d/2}.$$

Equations (4) and (6), together with some assumptions about the structure and eigenvalue spectrum of diffusion-type equations, allow us to obtain an enclosed description of fluctuation-induced kinetics of bimolecular reactions on fractal structures. It was shown by Cates (1985), O'Shaughnessy and Procaccia (1985) that the Green function of a diffusive-type equation has the following structure on fractals:

$$S(R, t) = D\hat{\mathscr{L}}_R S(R, t) \qquad S(R, t) = (Dt)^{-d_f/d_w} W(R/(Dt)^{1/d_w})$$

$$\lim_{t \to \infty} W = \text{constant}$$

where $\hat{\mathscr{L}}_R$ is a Laplacian-type operator, d_f and d_w are the fractal dimension and the dimension of the random walk respectively. From (4) and (6) we get:

for (i) $$C(t) = C_A + A\Delta C(Dt)^{-d_f/d_w} \tag{8a}$$

for (ii) $$C(t) = C_A(1 - A(Dt)^{-d_f/d_w}). \tag{8b}$$

For the reversible reactions of charged species followed by external generation (iii) the equilibrium spectrum of fluctuations $G_{AB}(p)$ is not of Poisson type for any values of r_g: $G_{AB}(p) \sim p^{2-d_w}$ when $p \to 0$, contrary to the case of compact spaces. Evidently, such a difference can be accounted for by the suppression of the geminate recombination—particles A and B generated in one pair turn out to be on different sites of a fractal and the 'chemical' path between them will be much longer then r_g. Correspondingly, the long-time approach to the equilibrium state is defined by following dependence:

$$C(t) = C_A^* - Br_g^2(Dt)^{-\mu} \qquad \mu = (d_f + 2 - d_w)/d_w.$$

The obtained results on the slow-down of the kinetics of the reversible reaction involving charged species have the following physical grounds. Random deviations of local densities of reagents from the mean values can be of two types.

(*a*) Fluctuations of different signs, i.e. local regions depleted or enriched by particles of one sort. In the case of an irreversible reaction with uncharged A and B these fluctuations determine the long-time kinetics. For charged particles these regions induce local electric fields which along with diffusion contribute to the smoothing of spatial inhomogeneity. It was shown by Zeldovich (1977) and Ohtsuki (1986) that in this case fluctuation effects are suppressed and the mean-field approximation is valid.

(*b*) Fluctuations of the same sign, where the density deviations from the mean value both for *A* and *B* have the same value and sign. For irreversible reactions such fluctuations can only accelerate the mean density decrease. However, for reversible reactions, where the value

$$M(r, t) = C_A(r, t) + C_B(r, t) + 2C_C(r, t) \qquad \dot{M}(r, t) = D\Delta_r M(r, t)$$

is conserved and the total charge in such regions equals zero, these deviations are smoothed only by diffusion which causes the power-law approach to the equilibrium fluctuation spectrum.

Our results and those for uncharged species (Zeldovich and Ovchinnikov 1977, 1978, Kang and Redner 1985) allow us to make some general conclusions.

Fluctuation peculiarities and the structure of the equilibrium state in reversible bimolecular (and higher-order) reactions can be accounted for by the existence of linear combinations of reagent local densities which do not change in the course of the elementary reaction. For instance, it is the sum of reagents and reaction product local densities $M(r, t)$. Since the law of conservation of matter is valid for any set of successive and parallel reactions, at least one such combination exists for any reversible conversions. Hence, the long-time approach to the equilibrium state for any reversible reactions (higher than first order) with diffusion transport of species is a diffusion-controlled process and is described by power dependences upon time. The time degree indicator is determined by the fluctuation spectrum of the initial equilibrium spatial distribution of reagents.

In low-dimensional systems (with $d_f(d)$ less then the dimension of random walk $d_w(2)$) where the external source breaks the direct reaction product into non-correlated pairs of reagents (r_g is equal to infinity) diffusion process fail to smooth the spatial fluctuations generated by the source. In such systems despite the fact that the mean density equation has the steady-state solution, fluctuation effects become essentially increased and the equilibrium is destroyed.

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