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LETTER TO THE EDITOR

Fluctuation slow-down of the death of Brownian particles in the case of movable traps

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Abstract. The influence of trap diffusion on the fluctuation slow-down of death of Brownian particles, discovered earlier in the case of stationary traps, is analysed. It is shown that fluctuation slow-down also takes place with movable traps if the diffusion is slow enough.

Normally, in describing diffusion-controlled reactions of the type $A+B\rightarrow B$ (death of particles (A) on traps (B)) one uses the approach which was first suggested by von Smolukhovsky [1]. According to this approach the death of particles on each trap takes place independent of the others. This approach is accurate when the particles are at rest and the reagents draw closer at the expense of trap diffusion. If the particles are movable then it gives only an approximate solution of the problem since it neglects many-body effects present in this case. In recent years much effort has been devoted to evolving a rigorous theory of such processes where many-body effects could be taken into account (see the recently issued monographs [2, 3] and reviews [4–6] as well as the papers cited therein).

Inadequacy of the traditional approach manifests itself most vividly with stationary traps in the effect of the so-called fluctuation slow-down of the death of particles. As is shown in [7–10], for asymptotically large times the probability of particle survival is appreciably higher than that predicted by the conventional expression. The effect is due to the survival of particles found in those regions of space which are free from traps owing to fluctuations in their distribution. The larger the size of such a fluctuation cavity the longer the particle lives in it, since its death outside the cavity is preceded by a prolonged walk over the region free from traps. On the other hand, the larger the cavities the smaller the probability of their presence. It is these two factors that determine the nature of the fluctuation slow-down. As a result, the dependence of probability of particle survival on the time takes the form [7–10]

$$P(t)\propto\exp\left[-\frac{d+2}{2}\left(\frac{2\beta_d}{d}(nv_d)^{2/d}D_A t\right)^{d/(d+2)}\right] \tag{1}$$

where n is the concentration of traps, $v_d=\pi^{d/2}/\Gamma(1+d/2)$ is the volume of the d-dimensional sphere of the unit radius, D_A is the coefficient of particle diffusion and β_d is the square of the first zero of the Bessel function of the first kind of the order $\frac{1}{2}(d-2)$. The particles, according to the expression (1), die appreciably more slowly than predicted by the conventional expression

$$P_{tr}(t)=\exp[-nv_d d(d-2)b^{d-2}D_A t] \tag{2}$$

where b is the trap radius.

The problem of the influence of trap motion on the fluctuation slow-down of particle death was considered by us in detail in [11] for the spaces with dimensions $d=1$, 2, 3. In the present letter we shall discuss the case of spaces of arbitrary dimensions $d \geqslant 3$, using the method suggested in [11].

It is clear that the particle will not die during the time t if it spends all this time inside a region free from traps. Let us introduce a d-dimensional sphere of arbitrary radius R, surrounding the starting point of a particle and write down the evident inequality

$$P(t) > Q_1(R)Q_2(R, t)Q_3(R, t). \tag{3}$$

Here

$$Q_1(R) = \exp(-nv_dR^d) \tag{4}$$

is the probability of trap absence inside a sphere of radius R at the initial instant of time; $Q_2(R, t)$, defined by

$$Q_2(R, t) = \exp[-nv_d d(d-2)R^{d-2}D_B t] \tag{5}$$

is the probability of keeping a sphere of the radius R free from the traps during the time t; D_B is the coefficient of trap diffusion; $Q_3(R, t)$, defined by

$$Q_3(R, t) \simeq \exp\left(-\beta_d \frac{D_A t}{R^2}\right) \tag{6}$$

is the probability of a particle staying during the time t inside a sphere of radius R surrounding its starting point. The estimation (6) of the probability $Q_3(R, t)$ is true for times which satisfy the inequality $D_A t \gg R$.

Substituting the expressions (4)-(6) in the inequality (3) we obtain

$$P(t) > \exp\{-[nv_dR^d + nv_d d(d-2)R^{d-2}D_B t + \beta_d D_A t/R^2]\}. \tag{7}$$

Up to now, no restrictions have been imposed on the radius of the sphere R. Now we shall optimise our estimation choosing $R = R_t$ so that the right-hand side of the inequality (7) is maximal at a certain instant of time t. Substituting the value R_t, obtained in this way, into the inequality (7) we shall obtain the estimate we are interested in of the probability of particle survival:

$$P(t) > \begin{cases} \exp\left[-\dfrac{d+2}{2}\left(\dfrac{2\beta_d}{d}(nv_d)^{2/d}D_A t\right)^{d/(d+2)}\right] & t < t_c \\ \exp\left[-\dfrac{d\beta_d}{d-2}\left(\dfrac{d(d-2)^2}{2\beta_d}\right)^{2/d}(nv_d)^{2/d}D_A^{1-2/d}D_B^{2/d}t\right] & t > t_c \end{cases} \tag{8}$$

where

$$t_c = \frac{d+2}{d^2(d-2)}\left(1-\frac{4}{d^2}\right)^{d/2}\left(\frac{2\beta_d}{d(d-2)^2}\right)^{2/d}\frac{D_A^{2/d}}{D_B^{1+2/d}(nv_d)^{2/d}}.$$

This estimate is of a special interest if it predicts a higher probability of particle survival than the conventional expression having the form

$$P_{tr}(t) = \exp[-nv_d d(d-2)b^{d-2}(D_A + D_B)t]. \tag{9}$$

With $D_B = 0$ this expression passes into the expression (2).

Comparison of expressions (8) and (9) shows that the fluctuation slow-down of particle death takes place both with $D_B = 0$ and when $D_B \neq 0$, if the trap diffusion takes place slowly enough

$$\frac{D_B}{D_A} < \frac{2}{d}\left(\frac{(d-2)^2}{\beta_d}\rho\right)^{(d-2)/2} \tag{10}$$

where $\rho = nv_d b^d$ is the volume fraction of traps, which we take to be small, $\rho \ll 1$. With times which satisfy the condition

$$\begin{aligned} &\frac{d+2}{2}\left(\frac{\beta_d(d+2)}{d^2(d-2)}\right)^{d/2}\frac{1}{\rho^{(d-2)/2}} \\ &\qquad < \tau = nv_d d(d-2)b^{d-2}(D_A + D_B)t \\ &\qquad < \frac{d}{d-2}\left(\frac{2\beta_d}{d(d-2)^2}\right)^{2/d}\left(\frac{D_A}{D_B}\right)^{(d+2)/d}\rho^{(d-2)/d} \end{aligned} \tag{11}$$

the probability of particle survival is described by the expression (1). Here τ is the dimensionless time resulting from the reference of time t to the characteristic time $1/nv_d d(d-2)b^{d-2}(D_A + D_B)$, during which the probability of particle survival decreases by e times, according to the conventional formula (2).

With stationary traps, $D_B = 0$, the expression (1) is the asymptotic limit of the survival probability $P(t)$ as $t \to \infty$. If $D_B \neq 0$ the expression (1) is the intermediate asymptotic limit. With the times determined by the inequality

$$\tau > \frac{d}{d-2}\left(\frac{2\beta_d}{d(d-2)^2}\right)^{2/d}\left(\frac{D_A}{D_B}\right)^{(d+2)/d}\rho^{(d-2)/d} \tag{12}$$

it passes into the expression having the form

$$P(t) \propto \exp\left[-\frac{d\beta_d}{d-2}\left(\frac{d(d-2)^2}{2\beta_d}\right)^{2/d}(nv_d)^{2/d}D_A^{1-2/d}D_B^{2/d}t\right]. \tag{13}$$

This formula describes the fluctuation slow-down of particle death when $t \to \infty$ in the case of movable traps. We shall emphasise that although in the expression (13) the exponent is linear with time, as in the conventional expression (9), this expression, however, describes a slower particle death than that predicted by the conventional formula due to the small value of the parameter

$$\left[\frac{D_B}{D_A}\frac{d}{2}\left(\frac{(d-2)^2}{\beta_d}\rho\right)^{1-d/2}\right]^{2/d} \tag{14}$$

(see the inequality (10)).

Note that similar estimates of the trap diffusion influence on the fluctuation slow-down of particle death with $t \to \infty$ were made in [12, 13]. The estimates which were presented in [12, 13] of the particle survival probability with $D_B \neq 0$ in the case $d \geqslant 3$ have the form

$$P(t) > \exp(-\Lambda n t) \tag{15}$$

where Λ is a constant. Note the erroneous dependence of the coefficient with t in the exponent on the concentration of traps in this expression. According to (15) it is proportional to n whereas according to (8) it is proportional to $n^{2/d}$.

Let us now discuss the varying role of fluctuation slow-down in spaces of different dimensions. In accordance with the conventional expression (9), the survival probability depends on the mobility of particles and traps only via the sum of their coefficients of diffusion $D = D_A + D_B$ but not on each of these values taken separately. The formula (13) shows that this is not so. According to the inequality (10), the larger the space dimensionality the narrower the interval of values of the relationship D_B/D within which the fluctuation slow-down occurs. It will be recalled that with $d = 1$, 2 the fluctuation slow-down takes place with an arbitrary value of the relationship $D_B/D < 1$ [11].

Furthermore, an increase in the space dimensionality results in restricting the time interval where an intermediate asymptotic limit (1) is true. This happens at the expense of a shift in its lower boundary towards larger values of τ, while the upper limit of the interval with $d \gg 1$ does not depend on the space dimensionality. Indeed, with $d \gg 1$, $\beta_d \simeq d^2/4$ [14] and the inequality (11) takes the form

$$\frac{d}{2}\frac{1}{(4\rho)^{d/2}} < \tau < \frac{D_A}{D_B}\rho. \tag{16}$$

Thus, with an increase in the space dimensionality there is an extension of the interval where the conventional expression of particle survival probability (9) is valid.

References

[1] von Smoluchowsky M 1916 *Phys. Z.* **17** 557, 585

[2] Rice S A 1985 *Diffusion-limited Reactions* (Amsterdam: Elsevier)

[3] Ovchinnikov A A, Timashov S F and Belii A A 1986 *Kinetica Diffuzionno-Kontroliruemykh Khimitcheskikh Protsessov* (Moscow: Khimiya)

[4] Calef D F and Deutch J M 1983 *Ann. Rev. Phys. Chem.* **34** 493

[5] Weiss G H 1986 *J. Stat. Phys.* **42** 3

[6] Cukier R I 1986 *J. Stat. Phys.* **42** 69

[7] Balagurov B Ya and Vaks V G 1973 *Zh. Eksp. Teor. Fiz.* **65** 1939 (1974 *Sov. Phys.-JETP* **38** 968)

[8] Donsker M D and Varadhan S R S 1975 *Commun. Pure Appl. Math.* **28** 525

[9] Ovchinnikov A A and Zeldovich Ya B 1978 *Chem. Phys.* **28** 215

[10] Grassberger P and Procaccia I 1982 *J. Chem. Phys.* **77** 6281

[11] Berezhkovskii A M, Makhnovskii Yu A and Suris R A 1986 *Zh. Eksp. Teor. Fiz.* **91** 2190 (1986 *Sov. Phys.-JETP* **64** 1301)

[12] Bramson M and Lebowitz J L 1988 *Phys. Rev. Lett.* **61** 2397

[13] Redner S and Kang K 1984 *J. Phys. A: Math. Gen.* **17** 451

[14] Abramowitz M and Stegun I A 1964 *Handbook of Mathematical Functions* (New York: Dover)