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Trapping rate dependence on the trap size in one dimension

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The one-dimensional trapping problem is revisited with emphasis on the role of the size of the traps. It is discovered that the process rate is dependent on the trap size whenever the traps are correlated. Qualitatively, the effect is manifested as slowdown or acceleration of trapping with enlargement of traps, according to whether there is trap attraction or repulsion, respectively. The dependence is studied in detail for a particular model.

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The problem of survival of a diffusing particle among randomly located static traps is widely used for the theoretical description of a variety of diffusion-controlled processes in physics and chemistry such as fluorescence quenching, fast chemical reactions in liquids, migration of excitations in solids, etc. [1]. As usual, most extensively studied is the one-dimensional (1D) case, which yields to explicit analysis thanks to restricted topology of the line [2]. The experimental significance of this case is discussed in the literature [3,4]. In this paper we revisit the 1D problem with emphasis on the role of the trap size b. Note that in higher dimensions the dependence of the trapping rate on this parameter is primarily due to the fact that the absorbing surface of a trap varies with b whereas in 1D, where such a "surface" is represented by points, this is not the case. Perhaps, this could have been a motivation for a seemingly widespread opinion that in 1D the trapping kinetics is *independent* of the trap size. At least, the 1D problem has been considered so far within the point-trap setting only (see Refs. [3–5], and references therein).

In the present work, we show that this opinion is generally not valid. We have discovered that dependence of the trapping rate on the trap size b does exist whenever the traps are distributed in a *correlated* fashion. The origin of this effect is as follows. In 1D the problem can actually be reduced to that with *point* traps; however, the distribution of such effective traps turns out to be dependent on b (in particular, the effective trap concentration is different from the original one). In turn, the dependence on b shows up in the trapping kinetics. Only in the case of uncorrelated traps does the effective ensemble prove to be equivalent to the original one and hence the parameter b drops out from the kinetics.

Consider a point Brownian particle moving on a line in the presence of randomly distributed static traps of size b. The traps are supposed to be perfect, that is, the particle is instantaneously absorbed upon hitting a trap. The distribution of traps is characterized by the probability density $\varphi(\ell)$ for random distances between the centers of adjacent traps. The trap concentration c is equal to the inverse of the mean value of such distance:

$$c = \left(\int_0^\infty \ell\, \varphi(\ell)\, d\ell \right)^{-1} . \tag{1}$$

The quantity of interest is the survival probability $P(t;b)$, defined as the probability for the particle to be untrapped up to time t (we introduce b in the notation in order to emphasize the presence of this parameter). It is assumed that the particle's starting point occurs in the trap-free part of the line, so that $P(0;b) = 1$.

Note that unlike higher dimensions, in 1D the absorbing "surface" of traps is represented by points. This observation allows one to reduce the original problem to one with *point* traps. To do this, let us cut out those parts of the line which are covered by at least one trap, paste together the remaining intervals, and put a point trap at each sticking point. As a result of such "cutting procedure" we arrive at an effective ensemble of point traps. To find the effective probability density, $\tilde{\varphi}(\ell)$, note that a distance ℓ between the neighboring effective traps corresponds to the distance $\ell + b$ between the former trap centers. Taking into account normalization to unity, we get

$$\tilde{\varphi}(\ell) = \frac{\varphi(\ell + b)}{\int_0^\infty \varphi(\ell + b)\, d\ell} . \tag{2}$$

The effective trap concentration is given by

$$\tilde{c} = \left(\int_0^\infty \ell\, \tilde{\varphi}(\ell)\, d\ell \right)^{-1} = \frac{\int_0^\infty \varphi(\ell + b)\, d\ell}{\int_0^\infty \ell\, \varphi(\ell + b)\, d\ell} . \tag{3}$$

Equations (2) and (3) involving b indicate that the statistical properties of the effective ensemble depend on the trap size.

After the reduction to the case of point traps, one can easily calculate the trapping kinetics using that in 1D a particle dies only on one of the two nearest (left and right) traps. Note that the probability density of the particle birth at intertrap interval of length ℓ equals $\tilde{c}\, \ell\, \tilde{\varphi}(\ell)$ [6]. Let $S_\ell(t)$ be the probability of survival for such a particle during time t averaged over its starting positions. Then the desired survival probability $P(t;b)$ can be expressed as

$$P(t;b) = \int_0^\infty S_\ell(t)\,\tilde{c}\,\ell\,\tilde{\varphi}(\ell)\,d\ell\,. \qquad (4)$$

Substitution of Eqs. (2) and (3) into Eq. (4) yields

$$P(t;b) = \frac{\int_0^\infty S_\ell(t)\,\ell\,\varphi(\ell+b)\,d\ell}{\int_0^\infty \ell\,\varphi(\ell+b)\,d\ell}\,. \qquad (5)$$

The explicit form of the function $S_\ell(t)$ is well known [4]

$$S_\ell(t) = \frac{8}{\pi^2}\sum_{n=0}^{\infty}(2n+1)^{-2}\exp\left(-\pi^2(2n+1)^2\,\frac{Dt}{\ell^2}\right), \qquad (6)$$

where D is the diffusion coefficient; for small t, another expression is more convenient:

$$S_\ell(t) = 1 - \frac{4\sqrt{Dt}}{\sqrt{\pi}\,\ell}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n\exp\left(-\frac{n^2\ell^2}{4Dt}\right)\right] + 4\sum_{n=1}^{\infty}(-1)^n\,n\,\mathrm{erfc}\left(\frac{n\ell}{2\sqrt{Dt}}\right), \qquad (7)$$

where $\mathrm{erfc}\,(z) = (2/\sqrt{\pi})\int_z^\infty \exp(-x^2)\,dx$ is the complementary error function. Thus, Eqs. (5)–(7) give the solution to the problem.

From Eq. (5) it is clearly seen that the trap size affects the trapping kinetics. However, in the particular case of *noncorrelated* traps, the process rate is in fact independent of b. Indeed, in this case the (Poisson) ensemble of traps is described by the probability density

$$\varphi_{\rm nc}(\ell) = c\,e^{-c\ell}. \qquad (8)$$

Inserting Eq. (8) into Eq. (5), one can check that the parameter b is “canceled,” that is, $P_{\rm nc}(t;b) = P_{\rm nc}(t;0)$. It follows that for noncorrelated traps of *arbitrary* size, the process is described by the well-known Balagurov-Vaks formula [5]

$$P_{\rm nc}(t;0) = \frac{4}{\pi^2}\int_0^\infty \exp\left(-\frac{\pi^2c^2Dt}{x^2}\right)\frac{x}{\sinh x}\,dx\,. \qquad (9)$$

Note that such a remarkable feature of the noncorrelated case is actually due to the fact that a Poisson ensemble stays *invariant* with respect to the cutting procedure described above [since the effective probability density $\tilde{\varphi}_{\rm nc}(\ell)$ calculated from Eq. (2) coincides with $\varphi_{\rm nc}(\ell)$]. Moreover, the Poisson ensemble is the only one to have such a property, as can be shown by analyzing Eq. (2).

So, the trap correlations “induce” dependence of the kinetics on the trap size. To analyze the effect from the qualitative point of view, let us first discuss the b dependence of the effective trap concentration $\tilde{c}$. Consider a large interval of length L containing $N \simeq cL$ finite-size traps. Under the cutting procedure, such an interval is transformed into one, say, of length $\tilde{L}$ with $\tilde{N}$ point traps. Obviously, $\tilde{L} < L$ and $\tilde{N} < N$, whereas the ratio $\tilde{N}/\tilde{L} \simeq \tilde{c}$ may turn out to be either greater or smaller than $N/L \simeq c$. On the other hand, for noncorrelated traps $\tilde{c} = c$.

Proceeding from the latter remark, introduce a “reference” Poisson ensemble of traps, with the *same* values of c and b. If the traps are attractive, their overlapping is more intensive as compared to the reference ensemble, so that $\tilde{L} > \tilde{L}_{\rm nc}$ and $\tilde{N} < \tilde{N}_{\rm nc}$. Hence, $\tilde{N}/\tilde{L} < \tilde{N}_{\rm nc}/\tilde{L}_{\rm nc}$, that is, $\tilde{c} < c$. If the traps are repulsive, they are distributed along the line more uniformly than in the reference ensemble and, analogously as above, one is led to the opposite inequality, $\tilde{c} > c$. Thus, for attractive (repulsive) traps, the point trap ensemble generated by the cutting procedure is more sparse (dense) than the original one. Moreover, this effect is strengthened with the increase of the trap size, that is, the ratio $\tilde{c}/c$ monotonically decreases or increases with b, according to whether there is attraction or repulsion between the traps.

This observation suggests that the b dependence of the kinetics is qualitatively characterized as follows: with enlargement of traps, the trapping becomes less (more) intensive, provided there is trap attraction (repulsion). At the initial stage of the process, this hypothesis can be proved rigorously. Indeed, from Eqs. (4) and (7) under the condition $\tilde{c}^2Dt \ll 1$ it follows that

$$P(t;b) \simeq \exp\left[-\frac{4}{\sqrt{\pi}}\left(\tilde{c}^2Dt\right)^{1/2}\right]. \qquad (10)$$

Note that this formula is of Smoluchowski type, which is obviously due to the fact that at small times one can neglect the competition between the traps [1]. It should be stressed that the effective concentration is the single characteristic of the trap distribution entering Eq. (10) and hence the specific form of the probability density $\tilde{\varphi}(\ell)$ is unimportant here. In view of the monotonic character of the b dependence of $\tilde{c}$ discussed above, from Eq. (10) it is seen that finiteness of the trap size inhibits or promotes the process as compared to the case $b = 0$, according to whether the traps be attractive or repulsive. Note that by the conclusions of Refs. [7,8], trap attraction (repulsion) generally leads to the slowdown (acceleration) of trapping. Thus, manifestation of trap correlations in the reaction kinetics is enhanced due to the finiteness of the trap size, at least at the initial stage of the process. Moreover, with the growth of b such an effect becomes more pronounced. In particular, in the case of attractive traps, the *increase* of the trap size results in the *slowdown* of trapping. This rather unexpected fact is striking evidence that the nature of the b dependence of the trapping rate in 1D is different from that known in higher dimensions where the surface of a trap is growing with b.

For intermediate and large times, $\tilde{c}^2Dt \gtrsim 1$, the analysis of the b influence on the kinetics is much more complicated. The reason is that the process rate is no longer determined by the (effective) concentration only and more detailed information of the probability density $\varphi(\ell)$ is required. Nevertheless, one general remark about the trapping rate at *asymptotically* large times, $t \to \infty$, can still be made. The crucial point here is that at such times, the kinetics is controlled by the particle's survival in very large “voids” free of traps [5,9]. So, the (logarithmic) asymptotics of the survival probability Eq. (4) is determined by the tail of $\tilde{\varphi}(\ell)$. Now, from Eq. (5) it is seen that if the decay of $\varphi(\ell)$ is not anomalously fast, the difference between $\varphi(\ell+b)$ and $\varphi(\ell)$ can be neglected and hence $P(t;b)$ is reduced to $P(t;0)$. In other words, one can expect that in the long-time regime, the trapping rate is independent of b (in the main term of the asymptotics).

To illustrate our general statements, consider a particular model. Let the probability density $\varphi(\ell)$ be of the form

$$\varphi_\alpha(\ell) = \frac{\alpha c}{\Gamma(\alpha)}\,(\alpha c\ell)^{\alpha-1}e^{-\alpha c\ell}, \qquad (11)$$

where $\alpha > 0$ is a dimensionless parameter, $\Gamma(\alpha) = \int_0^\infty x^{\alpha-1}e^{-x}\,dx$ is the gamma function, and c is the trap concentration [cf. Eq. (1)]. By varying α one can imitate different qualitative types of trap correlations. Namely, the case $\alpha = 1$ is that of noncorrelated (Poisson) traps since Eq. (11) is reduced to Eq. (8). For $\alpha > 1$, small intervals between adjacent traps are less probable as compared to the case of noncorrelated traps, which may be interpreted as a manifestation of trap repulsion. In particular, in the limit $\alpha \to \infty$ one has $\varphi_\alpha(\ell) \to \delta(\ell - 1/c)$, which corresponds to a regular lattice of period $1/c$. In contrast, for $0 < \alpha < 1$ small values of ℓ are more probable, which can be thought of as a trap attraction tendency. In the limit $\alpha \to 0$, the traps are gathered in small, dense clusters separated by very long void intervals (which is typical of *intermittency* phenomenon [10]).

Substitution of Eq. (11) into Eq. (2) after some transformations yields

$$\tilde{\varphi}_\alpha(\ell) = \frac{\alpha c}{\Gamma(\alpha,\alpha bc)}\,[\alpha c(\ell+b)]^{\alpha-1}\,e^{-\alpha c(\ell+b)}, \qquad (12)$$

where $\Gamma(\alpha,z) = \int_z^\infty x^{\alpha-1}e^{-x}dx$ is the incomplete gamma function. Correspondingly, from Eq. (3) the effective concentration is found as

$$\tilde{c}_\alpha = c\left\{1 - \rho\left[1 - \frac{(\alpha\rho)^{\alpha-1}e^{-\alpha\rho}}{\Gamma(\alpha,\alpha\rho)}\right]\right\}^{-1}, \qquad (13)$$

where $\rho = bc$ is the "volume" fraction of traps. Using Eq. (13), one can check that $\tilde{c}_\alpha \to 0$ as $\alpha \to 0$ (infinitely strong attraction), whereas in the opposite limit, $\alpha \to \infty$ (infinitely strong repulsion), one has $\tilde{c}_\alpha \to c(1-\rho)^{-1}$ (for $\rho < 1$). Moreover, the analysis of Eq. (13) shows that for fixed b, $\tilde{c}_\alpha$ is an increasing function of α (Fig. 1). On the other hand, with α fixed and b increasing, $\tilde{c}_\alpha$ grows if $\alpha > 1$ and decreases if $\alpha < 1$ (Fig. 1). Note that this is in agreement with the above qualitative discussion.

By means of Eqs. (12) and (13) the survival probability Eq. (5) takes the form

$$P_\alpha(t;b) = \frac{\tilde{c}\int_0^\infty S_{x/\alpha c}(t)\,x\,(x+\alpha\rho)^{\alpha-1}e^{-x}\,dx}{\alpha\rho\,e^{\alpha\rho}\,\Gamma(\alpha,\alpha\rho)}. \qquad (14)$$

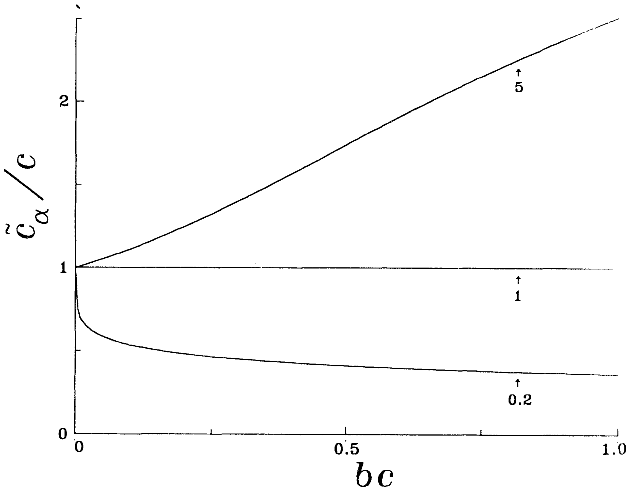

FIG. 1. The ratio $\tilde{c}_\alpha/c$ as a function of the "volume" fraction of traps, $\rho = bc$. Numbers indicate the values of α.

The time dependence of $P_\alpha(t;b)$ calculated from Eq. (14) is presented in Fig. 2. The small-time behavior of $P_\alpha(t;b)$ is described by Eq. (10) with $\tilde{c}$ given by Eq. (13). At asymptotically long times, $t \to \infty$, from Eqs. (6) and (14) it follows

$$-\ln P_\alpha(t;b) \simeq 3\,(\pi/2)^{2/3}\,(\alpha^2c^2Dt)^{1/3}. \qquad (15)$$

Equation (15) shows that the long-time survival depends on the character of trap correlations rather than on the trap size. On the other hand, in the limiting case $\alpha = \infty$ where a trap lattice is formed, the long-time decay of the survival probability is b dependent:

$$-\ln P_\infty(t;b) \simeq \pi^2c^2Dt/(1-\rho)^2. \qquad (16)$$

As is seen from Fig. 2 and can also be proven analytically, for a fixed b the probability $P_\alpha(t;b)$ is a decreasing function of parameter α. This means that trap repulsion ($\alpha > 1$) leads to the increase of the trapping rate as compared to the case of noncorrelated traps ($\alpha = 1$), whereas trap attraction ($\alpha < 1$) results in the process slowdown. Let us note that in the case of point traps ($b = 0$) this

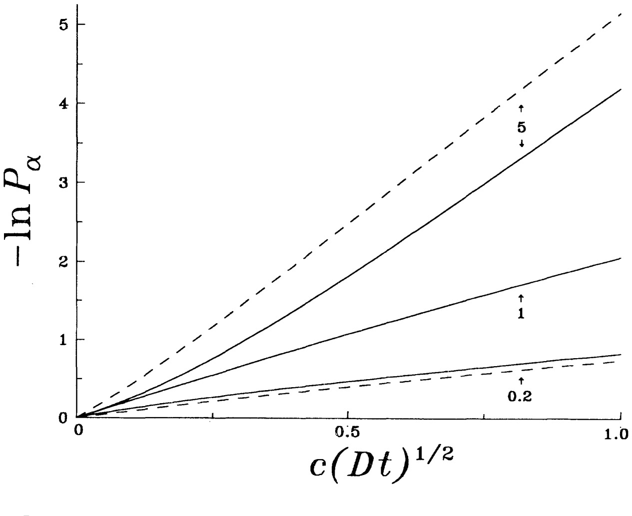

FIG. 2. Plot of the function $-\ln P_\alpha(t;b)$ as calculated from Eq. (14) for $\rho = 0$ (solid curves) and $\rho = 0.5$ (dashed curves). Numbers indicate the values of α.

effect was observed in [7]. Figure 2 also demonstrates that for $\alpha = 1$ the kinetics is independent of the trap size. At fixed $\alpha \neq 1$, the survival probability $P_\alpha(t;b)$ monotonically increases or decreases with the growth of b according to whether $\alpha < 1$ or $\alpha > 1$. This means that the trap correlation influence on the trapping kinetics is more pronounced due to a finite trap size, which supports the qualitative picture discussed above.

In summary, we have demonstrated that the trapping rate dependence upon the trap size does exist in 1D. The only case where the trap size does not affect the kinetics is that of noncorrelated traps. We have also shown that the finiteness of traps either inhibits or promotes the trapping process according to whether the traps are attractive or repulsive, thereby strengthening the manifestation of trap correlations. This effect may appear useful in detecting and studying trap correlations in real 1D systems. It should be emphasized that the dependence discovered is due to the presence of trap correlations and hence its origin is essentially different from that in higher dimensions. This is strikingly demonstrated by the fact that in the case of attractive traps the increase of the size parameter b leads to the slowdown rather than the acceleration of trapping. Our final remark is that the assumption of trap perfectness is not critical for the results obtained, which in fact can be easily extended to the case of *impenetrable* traps.

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[1] S. A. Rice, *Diffusion-Limited Reactions* (Elsevier, Amsterdam, 1985); A. A. Ovchinnikov, S. F. Timashev, and A. A. Belyi, *Kinetics of Diffusion-Controlled Chemical Processes* (Khimiya, Moscow, 1986); A. Blumen, J. Klafter, and G. Zumofen, in *Optical Spectroscopy of Glasses,* edited by I. Zschokke (Reidel, Dordrecht, 1986), p. 199.

[2] F. den Hollander and G. H. Weiss, in *Contemporary Problems in Statistical Physics*, edited by G. H. Weiss (SIAM, Philadelphia, 1994), p. 1.

[3] B. Movaghar, G. W. Sauer, D. Würtz, and D. L. Huber, Solid State Commun. **39**, 1179 (1981); G. H. Weiss and S. Havlin, J. Stat. Phys. **37**, 17 (1984).

[4] N. Agmon, J. Stat. Phys. **43**, 537 (1986).

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

[6] D. R. Cox, *Renewal Theory* (Wiley, New York, 1962).

[7] A. M. Berezhkovskii, Yu. A. Makhnovskii, R. A. Suris, L. V. Bogachev, and S. A. Molchanov, Phys. Lett. A **161**, 114 (1991).

[8] A. M. Berezhkovskii, Yu. A. Makhnovskii, R. A. Suris, L. V. Bogachev, and S. A. Molchanov, Chem. Phys. Lett. **193**, 211 (1992); Phys. Rev. A **45**, 6119 (1992).

[9] A. A. Ovchinnikov and Ya. B. Zel'dovich, Chem. Phys. **28**, 215 (1978); P. Grassberger and I. Procaccia, J. Chem. Phys. **77**, 6281 (1982); R. F. Kayser and J. B. Hubbard, Phys. Rev. Lett. **51**, 79 (1983); J. Chem. Phys. **80**, 1127 (1984).

[10] Ya. B. Zel'dovich, S. A. Molchanov, A. A. Ruzmaikin, and D. D. Sokoloff, Sov. Sci. Rev. C. Math. Phys. **7**, 1 (1988).