Nearest-neighbor distances at an imperfect trap in two dimensions

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The distance between the nearest diffusing particle to a single trap has been shown to be a useful characterization of self-segregation in low-dimensional reaction kinetics. Recent studies in two dimensions show that the average of this distance increases asymptotically as $(\ln t)^{1/2}$. In this paper we study a two-dimensional system in which the trap is an imperfect one, modeled in terms of the radiation boundary condition. Our exact solution shows that there exists a spatial and temporal dependence on the trap absorptivity, but the asymptotic time dependence remains unchanged. These results enable us to follow the crossover between the two limiting cases, namely, perfect trapping and total reflection. Analytical expressions are also given for the concentration profile and the reaction rate at the trap.

I. INTRODUCTION

A number of recent papers[1–7] have been devoted to the problem of nearest-neighbor distances at a single trap. The trapping reaction, which is one of the simplest models for chemical reactions, can be formulated as a reaction of the form $A+B\rightarrow B$ where A is a particle and B is a trap. This corresponds to the original Smoluchowski work on coagulation,[8] a process involving the trapping of mobile particles (A) by stationary aggregates (B). It has recently become evident that in low dimensions the kinetic properties can differ significantly from classical results.[9–15] It has been shown that the anomalous diffusion laws are related to the self-organization of the reactants. In particular, the $A-B$ reactions in $A+B\rightarrow B$ result in a depletion zone around the trap. This phenomenon of self-segregation can be characterized quantitatively by statistical properties of the distance between the trap and the nearest unreacted A particle.[1] A second possible measure is the distance from the trap to a point where the concentration of A's is equal to a given fraction θ of its bulk value, hereafter referred to as the θ distance.[6]

In one dimension, the average distance from the static trap to its nearest diffusing neighbor, $\langle L(t)\rangle$, has been shown[1] to increase asymptotically as $t^{1/4}$, whereas the θ distance goes like $t^{1/2}$. In three dimensions, the analogous results are time independent, suggesting that self-segregation plays a negligible role in determining the kinetic behavior.

Very recently attention has been given to the two-dimensional case,[6,7] in which the trap is assumed to have a circular shape. Havlin *et al.*[6] found that $\langle L(t)\rangle$ is asymptotically proportional to $(\ln t)^{1/2}$, and that the concentration profile in the neighborhood of the trap goes like $(\ln r/\ln t)$, yielding a nonuniversal scaling for the θ distance. Similar results have been derived by Redner and Ben-Avraham[7] in the course of developing an approximate scheme for calculating nearest-neighbor distances.

All the above-mentioned works, including Smoluchowski's, assumed a perfectly absorbing trap, an assumption which requires an inevitable reaction at each encounter between particles (A) and the trap (B). Obviously, this is not the most realistic case. A more physical treatment must be based on defining the trap absorptivity as a parameter, ranging between perfect trapping and total reflection (without reaction). The mathematical distinction between a perfect and imperfect trap is made by replacing the absorption boundary conditon by the radiation boundary condition.[16,17] Collins and Kimball[16] showed that this kind of modification of Smoluchowski's model eliminates a transient and unphysical infinity in the expression for the rate constant. In the present context, we are interested in the effect of the partial trapping on the statistical properties of nearest-neighbor distances.

In an earlier work,[3] we studied the case of the imperfect trap in one and three dimensions, showing that the detailed physical description does have an effect on the kinetic parameters in the neighborhood of the trap, although the asymptotic expressions remain unchanged. Our solution enabled one to follow the transition in the shape of the probability density of the nearest-neighbor distance from a skewed-Gaussian function for perfect reaction, to the exponential Hertz distribution for total reflection in one dimension. Analogous results have been obtained in three dimensions. In this work we are studying the more complicated case of the imperfect trap in two dimensions.

II. ANALYSIS

Let the imperfect trap be a circle of radius a, centered at the origin. Mobile A particles are assumed to be initially uniformly distributed throughout the plane with concentration c_0. The diffusion equation governing the diffusion of A particles in the infinite two-dimensional region bounded internally by the circle $r=a$ is

$$\frac{\partial p}{\partial t}=D\nabla^2 p=D\left[\frac{\partial^2 p}{\partial r^2}+\frac{1}{r}\frac{\partial p}{\partial r}\right],\quad r\geq a \tag{1a}$$

subject to the initial condition

$$p(r,0)=c_0 \tag{1b}$$

and the radiation boundary condition

$$\left.\frac{\partial p}{\partial r}\right|_{r=a}=\kappa p|_{r=a} \ . \tag{1c}$$

The parameter κ is a measure of the reaction strength at the interface $r=a$. The value $\kappa=\infty$ corresponds to a perfectly absorbing trap, while $\kappa=0$ corresponds to complete reflection. The exact solution of Eq. (1) is given by the integral expression[17]

$$p(r,t)=-\frac{2\kappa c_0}{\pi}\int_0^\infty e^{-Dtu^2}\frac{J_0(ru)[uY_1(au)+\kappa Y_0(au)]-Y_0(ru)[uJ_1(au)+\kappa J_0(au)]}{[uY_1(au)+\kappa Y_0(au)]^2+[uJ_1(au)+\kappa J_0(au)]^2}u^{-1}du \ , \tag{2}$$

where $J_0(z)$, $J_1(z)$, $Y_0(z)$, and $Y_1(z)$ are Bessel functions. Since we are primarily interested in the long-time limit ($r^2 \ll Dt$), we shall follow Refs. 17 and 18 to obtain

$$p(r,t)\simeq 2c_0\left[\ln\left[\frac{r}{a}\right]+\frac{1}{\kappa a}\right]\left[\frac{1}{\ln(4T)-2\gamma+2/\kappa a}-\frac{\gamma}{[\ln(4T)-2\gamma+2/\kappa a]^2}+\cdots\right], \tag{3}$$

where $T\equiv Dt/a^2$ is the dimensionless time parameter and $\gamma=0.577\,22\ldots$ is Euler's constant. Further mathematical details are given in the Appendix. It can be seen from Eq. (3) that in the long-time limit $p(r,t)$ is separable in the sense that

$$p(r,t)\simeq 2c_0A(r)B(t) \ , \tag{4}$$

where each function contains a dependence on κ, the partial trapping parameter. This result reproduces the correct limits for $\kappa=\infty$ (Ref. 6) and for $\kappa=0$ $[p(r,t)=c_0]$.

Next we study the statistical properties of nearest-neighbor distances. Following the analysis of Ref. 1, let $Q(L,t)$ be the probability that the nearest-neighboring particle is located at a radial distance greater or equal to L. Then the corresponding probability density $f(L,t)$ is given by $f(L,t)=-\partial Q/\partial L$. The expression for $Q(L,t)$ in our two-dimensional system with cylindrical symmetry is

$$Q(L,t)=\exp\left[-2\pi\int_a^L p(r,t)\,r\,dr\right] . \tag{5}$$

Inserting $p(r,t)$ from Eq. (3), then taking the derivative with respect to L, one obtains

$$f(L,t)\simeq 4\pi c_0B(t)L\left[\ln\left[\frac{L}{a}\right]+\frac{1}{\kappa a}\right]\exp\left\{-2\pi c_0B(t)\left[L^2\ln\left[\frac{L}{a}\right]-\frac{1}{2}(L^2-a^2)\left[1-\frac{2}{\kappa a}\right]\right]\right\}, \tag{6}$$

where $B(t)$ is proportional to $[\ln(4T)-2\gamma+2/\kappa a]^{-1}$ in the long-time limit. Equation (6) reduces to the result found in Refs. 6 and 7 for the perfect trapping case ($\kappa=\infty$). Figure 1 shows typical plots of $f(L,t)$ in the $\kappa=\infty$ limit, and Fig. 2 shows similar plots for the imperfect trap case, with a finite value of κ, which has been set equal to $\frac{1}{7}$. One can see that with partial reflection, the probability density of the nearest-neighbor distance is larger in the immediate neighborhood of the trap, due to the possibility of having reflected particles. If we consider $f(L,t)$ in Eq. (6) as a "skewed-Gaussian"-like function, then it is shown that the effect of the imperfect trapping is to shift this function towards the trap, where the corrections involved are proportional to $1/(\kappa a)$. Thus, the slope of $f(L,t)$ at $L=a$ can be either negative (for short times) or positive (for longer times). The crossover from a negative to a positive slope occurs at a characteristic time, which depends on κ in a nontrivial manner. If we keep only the leading term in $B(t)$, then this characteristic time is given by

$$t_c=\frac{a^2}{4D}\exp\left[\frac{4\pi c_0}{\kappa^2(1+1/\kappa a)}+2\gamma-\frac{2}{\kappa a}\right] . \tag{7}$$

For a given time, there exists an analogous crossover at a characteristic κ (Fig. 3), which to the same approximation is given by

$$\kappa_c=\frac{1}{a}\left[\frac{4\pi c_0a^2-2}{\ln(4T)-2\gamma}\right] . \tag{8}$$

Hence for small κ the slope is negative as is typical for total reflection ($\kappa=0$), but for larger κ's it becomes positive, approaching the perfect absorption limit ($\kappa=\infty$). It should be noted from Fig. 3 that significant effects of the imperfect trap are expected only for very small values of κ, say $0<\kappa<1$.

The average of the nearest-neighbor distance is formally given by

$$\langle L(t)\rangle=\int_0^\infty Lf(L,t)dL=\int_0^\infty Q(L,t)dL \ . \tag{9}$$

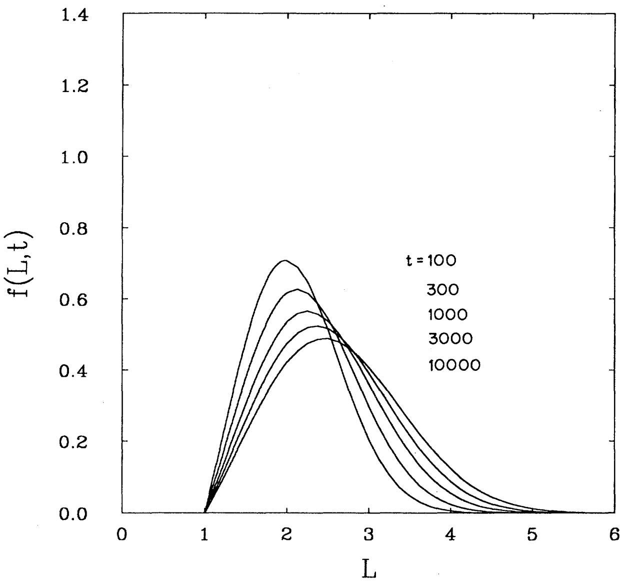

FIG. 1. Perfect trap ($\kappa=\infty$). Some typical curves of $f(L,t)$ as a function of L, the radial distance, for different values of time. The initial concentration is $c_0=0.25$ and the radius of the trap is $a=1$. The time values are indicated on the figure, where $t=100$ corresponds to the highest curve.

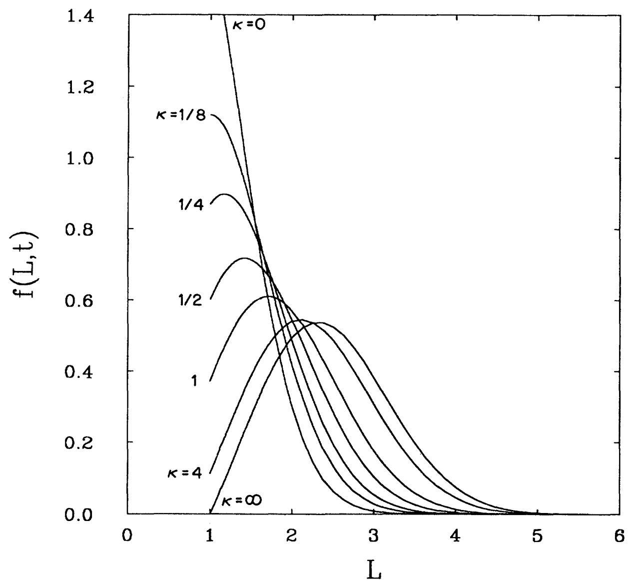

FIG. 3. Imperfect trap at a given time $t=2000$. Plots of $f(L,t)$ as a function of L, for various values of κ, and $c_0=0.25$. The crossover of the slope at the interface $a=1$ agrees with Eq. (8), and occurs at small κ.

The asymptotic dependence of $\langle L(t)\rangle$ comes from the exponential in Eq. (6), which requires a solution of a transcendental equation.[7] But as is evident from the figures, L is typically not larger than 5, so that $\ln(L/a)$ is in the order of unity, and the behavior is determined by the L^2 in the exponent. This scaling analysis thus yields

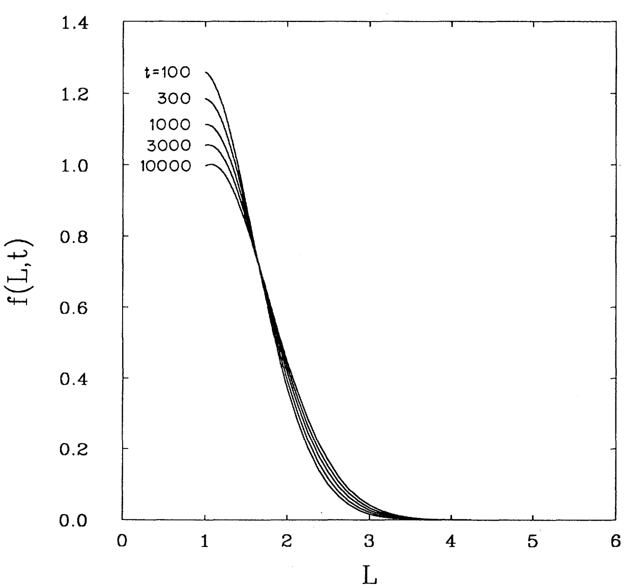

FIG. 2. Imperfect trap with $\kappa=\frac{1}{7}$. Plots of $f(L,t)$ as a function of L, for the same parameter values of Fig. 1. The crossover of the slope at $L=a=1$ agrees with Eq. (7).

$$\langle L(t)\rangle \sim \left|1-\frac{2}{\kappa a}\right|^{-1/2}\left[\ln(4T)+\frac{2}{\kappa a}\right]^{1/2}, \tag{10}$$

which shows that the asymptotic time dependence is the same as for a perfect trap, but the coefficient may be significantly different, especially for small values of κ, where it becomes very small. Indeed, in Fig. 2 we can observe that the nearest-neighbor distance increases with time much slower than for the perfect trap of Fig. 1. For large κ ($\kappa a \gg 2$), the dominant term in (10) is independent of κ, and $\langle L(t)\rangle$ is practically the same as for the $\kappa=\infty$ limit, namely proportional to $(\ln t)^{1/2}$.

Next we shall study the θ distance, which is the distance from the trap to a circle where the concentration profile equals to an arbitrary fraction θ of its bulk value. This is given by the equation

$$p(r_\theta,t)=\theta c_0 . \tag{11}$$

Inserting $p(r,t)$ from Eq. (3), but taking only the leading term, one obtains

$$r_\theta \simeq a(4T)^{\theta/2}\exp\left[-\frac{1}{\kappa a}(1-\theta)\right]. \tag{12}$$

For $\kappa\to\infty$ this reduces to the result found by Havlin *et al.*[6] They were the first to observe that r_θ has no universal scaling, but rather depends on the chosen value of θ. The exponential factor containing κ indicates that the partial reflection ($\kappa\to 0$) effect is to dramatically decrease the θ distance, again with a dependence on the value of θ. For $\kappa=0$ the θ distance is equal to zero, as it should be, except for $\theta=1$ where it is undefined since in the total reflection limit $p(r,t)=c_0$ for every radial distance r.

The quantity of greatest practical importance is the reaction rate, which is calculated from the flux $J(t)$ into the circle. Using the exact form of $p(r,t)$ from Eq. (2), we obtain the exact integral expression for the flux

$$J(t)=D\frac{\partial p}{\partial r}\bigg|_{r=a}$$
$$=\frac{4\kappa^2 c_0 D}{a\pi^2}\int_0^\infty e^{-Dtu^2}\frac{1}{[uY_1(au)+\kappa Y_0(au)]^2+[uJ_1(au)+\kappa J_0(au)]^2}u^{-1}du\ , \tag{13}$$

which reduces to the result of Ref. 17 in the $\kappa=\infty$ limit. For the long-time limit we can use $p(r,t)$ from Eq. (3) to get

$$J(t)\simeq\frac{2c_0 D}{a}\left[\frac{1}{\ln(4T)-2\gamma+2/\kappa a}-\frac{\gamma}{[\ln(4T)-2\gamma+2/\kappa a]^2}+\cdots\right], \tag{14}$$

which shows that the flux is proportional to $[\ln(4T)-2\gamma+2/\kappa a]^{-1}$. As is intuitively clear, the effect of the partial reflection is to decrease the flux. For $\kappa\to\infty$ we recover the result of Ref. 6.

III. THE SHORT-TIME LIMIT

Since self-segregation is relevant only in the long-time limit, we shall study the short-time limit only for the flux at the surface $r=a$. For this purpose we need first the form of the short-time limit of $p(r,t)$ for both the perfect and imperfect trap. Following Ref. 17, Sec. 13.3, we find that to first approximation

$$p(r,t)\simeq c_0\left[1-\left[\frac{a}{r}\right]^{1/2}\operatorname{erfc}\left[\frac{r-a}{\sqrt{4Dt}}\right]+\cdots\right] \tag{15}$$

for the perfect trap, and

$$p(r,t)\simeq c_0\left[1+\kappa\left[\frac{a}{r}\right]^{1/2}(r-a)\operatorname{erfc}\left[\frac{r-a}{\sqrt{4Dt}}\right]-\kappa\left[\frac{a}{r}\right]^{1/2}\left[\frac{4Dt}{\pi}\right]^{1/2}\exp\left[-\frac{(r-a)^2}{4Dt}\right]+\cdots\right] \tag{16}$$

for the imperfect trap, where erfc(z) is the complementary error function. Further approximation of these results requires a knowledge of the relation between $(r-a)$=distance from the surface, and $\sqrt{4Dt}$ (which was already considered small in obtaining these expressions). Note that the short-time limit is formally $\kappa\sqrt{Dt}\to 0$, so that the perfect-trap case ($\kappa\to\infty$) *cannot* be obtained as a limit of Eq. (16). But for $\kappa\to 0$, Eq. (16) does reduce to the proper limit for total reflection.

The flux at the short-time limit is actually calculated from extended forms of Eqs. (15) and (16), and is found to be

$$J(t)\simeq\frac{c_0 D}{a}\left[\frac{1}{(\pi T)^{1/2}}+\frac{1}{2}-\frac{1}{4}\left[\frac{T}{\pi}\right]^{1/2}+\frac{1}{8}T+\cdots\right] \tag{17}$$

for a perfect trap,[17] and

$$J(t)\simeq c_0 D\kappa\left[1-2\kappa a\left[\frac{T}{\pi}\right]^{1/2}-\frac{1}{2}\left[\frac{3}{4}+\kappa a\right]T+\cdots\right] \tag{18}$$

for an imperfect trap. Hence, in the short-time limit, the flux decreases as $T^{-1/2}$ for perfect absorption, whereas for partial absorption it is a constant proportional to κ. As before, $J(t)$ of Eq. (18) does give the correct limit for total reflection ($\kappa\to 0$), but *not* for perfect reaction ($\kappa\to\infty$).

IV. SUMMARY

We have analyzed the effect of an imperfect, rather than perfect, trap, on the statistical properties of nearest-neighbor distances in two dimensions. We found that this generalization does not introduce any new time dependence into the kinetic behavior. However, there are corrections as a function of κ, the measure of the trapping strength. Most of the corrections are additional terms proportional to $1/(\kappa a)$, which may be very large in the limit of small κ. Indeed, we have shown that the significant deviations from the perfect trap results[6,7] do occur for small values of κ, allowing us to follow the crossover between the limit of perfect trapping to the limit of total reflection.

Further aspects of the nearest-neighbor distance theory are of current interest. For example, Ref. 2 contains an analysis of the opposite case, in which a mobile trap diffuses in the presence of uniform density of static particles. Reference 5 presents predictions based on numerical results, for the intermediate case, where both particles and trap are allowed to diffuse. The question of diffusion subject to an external potential has been studied in Ref. 4, where it was shown that the result $\langle L(t)\rangle \sim t^{1/4}$, derived in one dimension for noninteracting particles,[1] is valid asymptotically also for particles interacting by means of a hard-core potential. Motion in the presence of other forms of external potentials is the subject of our present research.

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APPENDIX

The solution of Eq. (1) in the Laplace space is

$$\hat{p}(r,s)=\frac{c_0}{s}\left[1-\frac{\kappa K_0(qr)}{qK_1(qa)+\kappa K_0(qa)}\right], \quad q=\sqrt{s/D} \tag{A1}$$

where $K_0(z)$, $K_1(z)$ are modified Bessel functions. Following Ref. 17 (Sec. 13-6) and Ref. 18 (Appendix), the inverse will have the form

$$p(r,t)=\frac{c_0}{2\pi i}\int_{-\infty}^{(0+)}\frac{1}{\lambda}\left[1-\frac{\kappa K_0(\mu r)}{\mu K_1(\mu a)+\kappa K_0(\mu a)}\right]e^{\lambda t}d\lambda \ , \tag{A2}$$

where $\lambda=s$, $\mu=q=\sqrt{\lambda/D}$.

Substituting expressions of $K_0(z)$, $K_1(z)$ for small values of z (which corresponds to the long-time limit), one obtains

$$p(r,t)\simeq -2c_0\ln\left[\frac{r}{a}e^{1/(\kappa a)}\right]I_0^{-1}(x) \ , \tag{A3}$$

where $x\equiv(4T/2\gamma)e^{2/(\kappa a)}$, and, according to the notation of Ritchie and Sakakura,[18]

$$I_\nu^{-l}(x)\equiv\frac{1}{2\pi i}\int_{-\infty}^{(0+)}e^{xz}z^{\nu-1}(\ln z)^{-l}dz \ . \tag{A4}$$

In the limit of large x this integral is approximated by

$$I_\nu^{-l}(x)\sim(-1)^l x^{-\nu}\sum_{j=0}^{N}B_j^{\nu,-l}(\ln x)^{-(j+l)} \ , \tag{A5}$$

where $B_0^{0,-1}=1$, $B_1^{0,-1}=-\gamma$, $B_2^{0,-1}=-1.311\,76\ldots$, etc. Equation (A5) leads directly to Eq. (3) above.

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