Statistical properties of nearest-neighbor distances at an imperfect trap

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There have been a number of recent investigations of statistical properties of the nearest-neighbor distance of the closest diffusing particle in the presence of a trap. These have been shown to be useful characterizations of self-organizing properties of simple binary reactions of the form $A+A\rightarrow A$ or $A+A\rightarrow 0$. In this paper we extend our results to diffusion in the presence of an imperfect trap in one and three dimensions. The imperfect trap is modeled in terms of a radiation boundary condition. Our exact solution permits one to follow the transition in the shape of the probability density for the nearest-neighbor distance from the exponential in one dimension corresponding to total reflection, to the skewed Gaussian form for perfect reaction. Similar results are given for the case of a reactive sphere in the presence of mobile particles in three dimensions.

I. INTRODUCTION

The trapping reaction $A+T\rightarrow T$ is one of the simplest elementary reactions in chemistry and physics. Chemical catalysis often requires the reacting species to be trapped at the catalytic site. This is true for some industrial chemical reactions, requiring an active surface site as well as for some biochemical reactions that involve an enzyme site and a mobile substrate. Similarly, in condensed state physics there are defect traps for electrons, holes, solitons, excitons, etc. Traps and supertraps also play an especially important role in the context of energy (excitation) transport, from crystals to polymers, to photosynthetic antennae (where the supertrap is the reaction center). The kinetics of trapping have therefore played a central role in the theoretical treatment of reaction kinetics, starting from the classical work of Smoluchowski[1] on coagulation, a process involving the trapping of mobile particles by stationary aggregates (colloids). Recent reviews[2-6] deal with solid-state, chemical, and biological diffusion-limited trapping. Indeed, the trapping reaction was probably the first one in which the role of fluctuations was taken into account,[7] where low-dimensional and fractal media were considered,[8] and where the chemical rate coefficient was related to the random-walk efficiency.[9-11] Very recently it has become evident that the anomalous diffusion of the single mobile particle is directly related to the self-organization of the ensemble of mobile particles.[12,13] This self-organization expresses itself in a *depletion zone* formed around the trap which is analogous to the depletion of A particles near B particles and *vice versa* in an $A+B$ reaction,[4,5,14] leading to self-segregation,[15] and to the depletion of A particles with respect to other A particles in an $A+A$ reaction.[16-19] We also note, in passing, the historical connection between the Smoluchowski trapping (coagulation) reaction and a problem arising in astrophysics.[20]

A measure of the self-organization of reactants around traps, in low dimensions, and its relation to anomalous reaction kinetics was very recently expressed in terms of statistical properties of the distance from a stationary trap (T) embedded in a sea of mobile (A) particles to the nearest unbound A particle.[21] In this paper we derive results for nearest-neighbor distances in the important transition regime between the original Smoluchowski model, which requires inevitable reaction at every encounter between an A and a T, and the case in which no reaction occurs at an encounter. Real reactions exist along the entire domain between these two limits (which may depend on the temperature and other relevant parameters). The mathematical distinction between the different models is contained in the boundary conditions. The Smoluchowski model corresponds to an absorbing boundary condition and the present calculation uses a radiation boundary condition.

A number of earlier papers[21–23] have been devoted to the calculation of statistical properties of the spacing between particles undergoing both reaction and diffusion. The distribution of this spacing may be regarded as a generalization of the Hertz density[20] originally proposed in the context of astronomy. Reference 21 models the reaction in terms of an initial uniform density of particles diffusing in the presence of a single static trap, corresponding to the original Smoluchowski model. Reference 22 contains an analysis of the opposite limiting case in which a single mobile trap diffuses in the presence of a uniform density of particles. The intermediate case, which would provide a more realistic model for reacting species, allows for both the single trap and the remaining particles to diffuse. The analysis of this case poses a considerably more challenging mathematical problem, although some partial results have recently appeared in the literature.[23]

The Smoluchowski model[1] for calculating reaction rates falls short of being a realistic model for chemical reactions in a number of respects. The most glaring omission is that of many-body effects. However, in spite of the work of Waite,[24] it would appear that a full many-body analysis presents extraordinary difficulties. Hence most theoretical work in the area has concentrated on modifying the Smoluchowski model in various ways, because, in spite of its simplicity, it does reproduce a number of features of reaction kinetics. One of the earliest modifications to the theory was that of Collins and Kimball,[25] who analyzed the original Smoluchowski model. In this context they pointed out that changing the boundary condition on the static particle from a trapping condition to the so-called radiation boundary condition (i.e., not every encounter between an A and B particle results in a reaction) eliminates at least a transient and unphysical infinity in the calculated rate constant. In the present paper we calculate the probability density for the distance between a static partial reflector and the nearest particle to it (which may or may not have collided with it) under the assumption that the mobile particles are initially uniformly distributed throughout the space. Results will be presented for diffusion along an infinite line, and for the three-dimensional problem with spherical symmetry.

II. ONE DIMENSION

The single static trap will be located at $x=0$, and mobile particles are assumed to be initially randomly distributed on the line with a uniform density equal to c. Once one finds the probability that the nearest-neighboring particle is located at a distance $\geq L$ from the trap at time t, $Q_0(L,t)$, it is possible to calculate the corresponding probability density $f(L,t)$ from the relation $f(L,t)=-\partial Q_0(L,t)/\partial L$. A first step in the calculation of $Q_0(L,t)$ is to find the probability density of displacement of a single diffusing particle, initially at x_0, in the presence of a point characterized by the partial reflection coefficient κ, which measures the strength of the reaction. The value $\kappa=\infty$ corresponds to a perfect trap and $\kappa=0$ corresponds to complete reflection. This required probability density will be denoted by $q(x,t|x_0)$ and is the solution to the diffusion equation

$$\frac{\partial q}{\partial t}=D\frac{\partial^2 q}{\partial x^2}\ , \tag{1}$$

subject to the initial condition $q(x,0)=\delta(x-x_0)$ and the radiation boundary condition

$$\left.\frac{\partial q}{\partial x}\right|_{x=0}=\kappa q(0,t|x_0)\ . \tag{2}$$

The solution of the problem with the radiation boundary condition in Eq. (2) is known to be[26]

$$q(x,t|x_0)=\frac{1}{\sqrt{4\pi Dt}}\left[\exp\left[-\frac{(x-x_0)^2}{4Dt}\right]+\exp\left[-\frac{(x+x_0)^2}{4Dt}\right]\right]-\kappa\exp[\kappa^2Dt+\kappa(x+x_0)]\operatorname{erfc}\left[\frac{x+x_0}{\sqrt{4Dt}}+\kappa\sqrt{Dt}\right]\ , \tag{3}$$

where

$$\operatorname{erfc}(x)=1-\operatorname{erf}(x),\quad \operatorname{erf}(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}dy\ . \tag{4}$$

Thus the expression for $Q_0(L,t)$ can be written in terms of the functions

$$\theta=\frac{L}{\sqrt{4Dt}},\quad F(x)=e^{x^2}\operatorname{erfc}(x) \tag{5}$$

as

$$\begin{aligned}Q_0(L,t)&=\exp\left[-2c\int_0^L dx\int_0^\infty q(x,t|x_0)dx_0\right]\\&=\exp\left\{-2c\left[L\operatorname{erf}(\theta)-2\left[\frac{Dt}{\pi}\right]^{1/2}(1-e^{-\theta^2})+\frac{1}{\kappa}[e^{-\theta^2}F(\theta+\kappa\sqrt{Dt})-F(\kappa\sqrt{Dt})+\operatorname{erf}(\theta)]\right]\right\}\ .\end{aligned} \tag{6}$$

The behavior of $Q_0(L,t)$ in the double limit $Dt \gg L^2$ and $\kappa\sqrt{Dt} \gg 1$ is found to have a Gaussian form with a peak at $L=-1/\kappa$,

$$Q_0(L,t) \sim \exp\left\{-\frac{c}{\sqrt{\pi Dt}}\left[\left[L+\frac{1}{\kappa}\right]^2-\frac{1}{\kappa^2}\right]\right\} . \quad (7)$$

This form implies the intuitively obvious result that with partial reflection the distance from the trap to the nearest-neighboring particle is decreased over the case in which there is perfect trapping. The asymptotic value of the average of this distance is found from Eq. (7) to be

$$\begin{aligned}\langle L(t)\rangle &= \int_0^\infty Q_0(L,t)dL \\ &= \frac{\pi^{3/4}(Dt)^{1/4}}{2c^{1/2}} \exp\left[\frac{c}{\kappa^2\sqrt{\pi Dt}}\right] \\ &\quad \times \operatorname{erfc}\left[\frac{c^{1/2}}{\kappa(\pi Dt)^{1/4}}\right] , \end{aligned} \quad (8)$$

which at sufficiently long times approaches proportionality to $(Dt)^{1/4}/c^{1/2}$ independent of the parameter κ. Thus the asymptotic result is independent of whether there is perfect or partial trapping. In the same limits required for the derivation of $Q_0(L,t)$ given in Eq. (7), the corresponding probability density function $f(L,t)$ has the form

$$f(L,t) \sim \frac{2c}{\sqrt{\pi Dt}}\left[L+\frac{1}{\kappa}\right]Q_0(L,t) . \quad (9)$$

Some typical plots of this function as a function of L are shown in Fig. 1. From these it is evident that the slope of $f(L,t)$ at $L=0$ can be either positive or negative. The condition for the slope to be positive is that

$$Dt > \frac{4c^2}{\pi\kappa^4} . \quad (10)$$

Hence we expect that at early times the slope of $f(L,t)$ at $L=0$ is negative, while at sufficiently late times the slope shifts to a positive value as is characteristic of the situation in which there is a perfect trap at the origin. Figure 2 shows some curves of $f(L,t)$ when t is fixed and κ is allowed to vary. The crossover point in the slope is found from Eq. (10) to occur at $\kappa_c=[4c^2/(\pi Dt)]^{1/4}$. It is readily shown that the short-time limit of Eq. (6) is just the exponential, $Q_0(L,t\to 0)\sim\exp(-2cL)$.

The reaction rate is calculated from the flux $J(t)$ at the partial trap. This is given by

$$\begin{aligned} J(t) &= -2Dc\int_0^\infty \left.\frac{\partial q}{\partial x}\right|_{x=0} dx_0 = -2Dc\kappa\int_0^\infty q(0,t|x_0)dx_0 \\ &= D\kappa \left.\frac{d\ln Q_0}{dL}\right|_{L=0} = -2Dc\kappa F(\kappa\sqrt{Dt}) . \end{aligned} \quad (11)$$

This expression has the asymptotic behavior $J(t)\sim -2c[D/(\pi t)]^{1/2}$, which is independent of κ. Hence, just as in the case of $\langle L(t)\rangle$, the asymptotic time dependence is unchanged from that predicted by the perfect trapping case.

III. THREE DIMENSIONS

We discuss only one of the many three-dimensional analogues of the problem discussed in the previous section, namely that of diffusion of an initially uniformly (and therefore spherically symmetrically) distributed set of particles in the presence of a sphere of radius r_0 with a partially reflecting surface. Let the initial density of par-

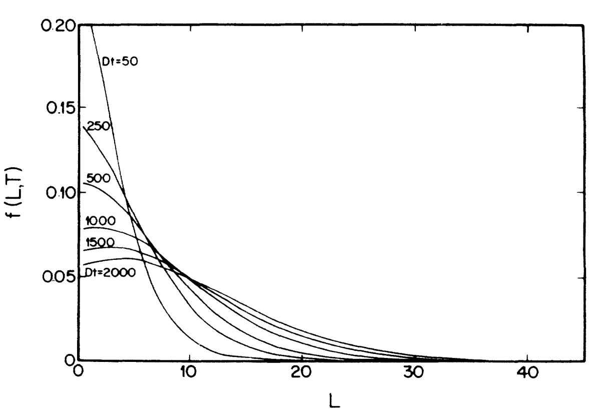

FIG. 1. Typical curves of $f(L,t)$ plotted as a function of L, for different values of Dt. The parameter values used to generate these curves are $\kappa=\frac{1}{9}$ and $c=0.25$.

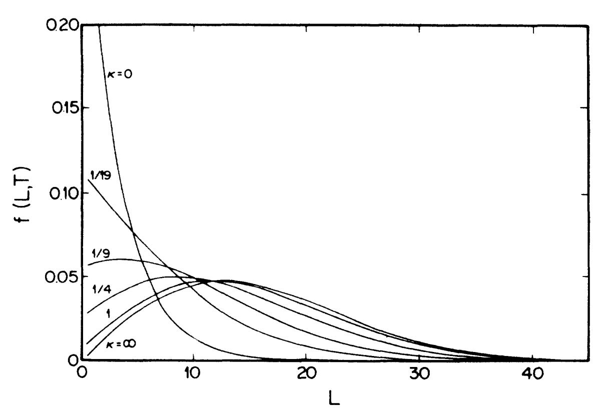

FIG. 2. Curves of $f(L,t)$ as a function of L for different values of the parameter κ. The value $\kappa=\infty$ corresponds to the case of a pure trap, and $\kappa=0$ to total reflection. The fixed parameters are $Dt=2000$ and $c=0.25$.

ticles per unit volume be denoted by c, and define the dimensionless distance from the center of the sphere to be $\rho \equiv r/r_0$, the dimensionless initial concentration $\sigma_0 = cr_0^3$, and the dimensionless time $\tau = Dt/r_0^2$. The probability density for radial position at time τ will be denoted by $q(\rho,\tau|\rho_0)$, which is the solution to a spherically symmetric diffusion equation subject to a radiation boundary condition at $\rho = 1$ characterized by the dimensionless parameter $\kappa_0 \equiv \kappa r_0$. The function of interest in the present investigation is not the density $q(\rho,\tau|\rho_0)$ itself, but rather this function averaged with respect to the initial density, i.e., $p(\rho,\tau) \equiv 4\pi\sigma_0 \int_1^\infty \rho_0^2 q(\rho,\tau|\rho_0) d\rho_0$. An expression for $q(\rho,\tau|\rho_0)$ is given in Ref. 26. We cite the result for $p(\rho,\tau)$,

$$p(\rho,\tau) = \sigma_0 \left\{ 1 - \frac{\kappa_0}{\rho(\kappa_0+1)} \left[\operatorname{erfc}\left[\frac{\rho-1}{\sqrt{4\tau}} \right] - \exp\left[-\frac{(\rho-1)^2}{4\tau} \right] F\left[\frac{\rho-1}{\sqrt{4\tau}} + (\kappa_0+1)\sqrt{\tau} \right] \right] \right\} . \tag{12}$$

Because of the spherical symmetry the expression for $Q_1(\Omega,\tau)$, the probability that the nearest diffusing particle is at a (dimensionless) distance $\geq \Omega$ from the surface of the sphere is

$$Q_1(\Omega,\tau) = \exp\left[-4\pi \int_1^\Omega \rho^2 p(\rho,\tau) d\rho \right] . \tag{13}$$

An exact evaluation of the integral with the integrand in Eq. (12) leads to a complicated result, but in the limit of large τ the expression for $Q_1(\Omega,\tau)$ becomes

$$Q_1(\Omega,\tau) \sim \exp\left\{ -4\pi\sigma_0 \left[\frac{\Omega^3-1}{3} - \frac{\kappa_0}{\kappa_0+1} \left[\frac{\Omega^2-1}{2} \right] \right] \right\} , \tag{14}$$

which reduces to the Hertz distribution[20] in the limit of perfect reflection ($\kappa_0 \to 0$) and to the result given as Eq. (12) of Ref. 21 when $\kappa_0 \to \infty$. Far from the surface of the sphere $\Omega \to \infty$, $Q_1(\Omega,\infty)$ has the Hertz form independent of the value of κ_0, while close to the surface ($\Omega \sim 1$), $Q_1(\Omega,\infty)$ can be approximated by

$$Q_1(\Omega,\infty) \sim \exp\left[-\frac{4\pi\sigma_0}{\kappa_0+1} \left[\Omega - 1 + \frac{\kappa_0+2}{2}(\Omega-1)^2 \right] \right] , \tag{15}$$

which reduces to the Gaussian form found in Ref. 21 when $\kappa_0 = \infty$. The asymptotic flux is constant.

We therefore see that the replacement of a trapping boundary condition by a radiation boundary condition gives rise to no new time dependence of reaction rates, although there are local effects in the neighborhood of the boundary. However, one might expect a different time dependence of the reaction rate to appear if the so-called back reaction boundary condition[27] is used (equivalent to reversible trapping) or non-Markovian generalizations of this type of boundary condition,[28–30] which correspond to the inclusion of memory effects in the interactions between the two types of particles.

IV. DISCUSSION

Equation (11) indicates that the flux is asymptotically proportional to $ct^{-1/2}$ in one dimension, as is the case when a perfect trapping boundary conditions is used. This implies the same dependence on concentration and time for the reaction (trapping) rate. In the limit of complete reflection ($\kappa = 0$) both the flux and the rate are asymptotically proportional to c and independent of the time. On the other hand, in three dimensions the rate is independent of time in both limits of complete reflection and complete absorption. It is intuitively obvious that for a "reaction-limited reaction," in contrast to a diffusion-limited reaction, one should obtain for the rate the result familiar from classical kinetics $R = kc$, where k is the traditional time-independent rate constant which depends on the absorption (reaction) efficiency at the surface. We note that in this limit k is independent of the diffusion constant D as the diffusion process is efficient enough, in comparison to absorption, to maintain a random (Hertz) particle density. The same result is found by using the *ad hoc* assumption[5,17,21] that the time dependence of the reaction probability is proportional to $cf(L,t)$ in the limit $L \to 0$. The same assumption also leads to the classical result for all values of the parameter κ_0 in three dimensions.

We have noted in Ref. 21 the similarity between our model of reaction as a trapping event and the homobinary reaction $A + A \to$product, where $R \sim c^2 t^{-1/2}$ in one dimension and $R \sim c^2$ in three dimensions, in the limit $\kappa \to \infty$, which is equivalent to the perfectly efficient trap. Very recent simulations for a lattice system show that, when the probability of reaction on collision is equal to $\alpha \leq 1$, there is a similar pattern in one dimension, i.e., a crossover to classical behavior for $\alpha \to 0$ accompanied by a crossover in the shape of the probability density of the nearest-neighbor distance from a skewed-Gaussian form to an exponential-like one.

The experimental results for exciton heterofusion cited in Ref. 21 can now be seen to be consistent with both the total and partial absorption cases, but obviously not with results obtained for perfect reflection. We can therefore easily distinguish between diffusion-limited and reaction-limited reactions in one-dimensional wires and pores.[17] No such easy distinction is possible in three dimensions.

In two dimensions, there are presumably logarithmic corrections to the results which would pose serious problems in any practical attempt to classify the type of reaction.

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