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Density of nearest-neighbor distances in diffusion-controlled reactions at a single trap

George H. Weiss
Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Health, Bethesda, Maryland 20892

Raoul Kopelman
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

Shlomo Havlin
Department of Physics, Bar-Ilan University, Ramat-Gan, Israel 52100
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We derive the probability density function for the nearest-neighbor distance of the closest Brownian particle to an isolated trap in one and three dimensions. The asymptotic (in time) density of the nearest-neighbor distance in one dimension is a time-dependent skewed Gaussian function and the mean value of this distance increases asymptotically as $t^{1/4}$. The large-distance form of this function is a simple exponential. In three dimensions the analogous result in the presence of an absorbing sphere is shown to resemble the Hertz density closely at large distances. The asymptotic reaction rate goes as c (density) in three dimensions but as $ct^{-1/2}$ in one dimension. The results are related to exciton fusion and reaction kinetics.

Diffusion-controlled reactions play an important role in various branches of biology, chemistry, and physics.[1-5] There has been considerable recent interest in the theory of reacting systems in low and/or fractal dimensions. In these, the global kinetics laws will differ from ones traditionally used in physical chemistry. It has been conjectured that deviations from classical kinetics result from the fact that the density in space of the reacting particles is not uniform. Quite recently,[6] calculations have been published that establish and quantify the macroscopic segregation of A and B particles for the reaction $A+B \rightarrow 0$. Nonuniform densities have also been found by simulation for nearest-neighbor distances between particles for the simplest binary reactions $A+A \rightarrow 0$ and $A+A \rightarrow A$ in one dimension[7,8] which is of interest for the description of exciton homofusion ($A+A \rightarrow A$) experiments. The probability density function (PDF) for the nearest-neighbor distance x, at time t, as found from simulations[7,8] of the $A+A \rightarrow A$ reaction (transient) are well described by the skewed-Gaussian form $f_G(x,t) = 2\alpha c^2 x e^{-\alpha c^2 x^2}$ where c is the (time-dependent) instantaneous density and α is a constant, rather than the Hertzian density $f_H(x,t) = 2ce^{-2cx}$. Similarly, for the reaction $A+A \rightarrow 0$ it is found[7,8] that the PDF of nearest-neighbor distances at time t has the form $f(x,t) = (\lambda c)^2 x e^{-\lambda c x}$ in steady state, where again c is the instantaneous concentration and λ is a constant. The density $f_G(x,t)$ is consistent[8] with an anomalous[9-11] reaction rate, k, that varies with density as $k \sim c^3$, in contrast to the classical dependence[1] $k \sim c^2$ which implies a Hertz-like density[2] (or the equivalent radial, or pair-correlation distributions) for nearest-neighbor distances. The Hertz density is the probability density for the distance from an arbitrary point in an infinite space to the closest of an infinite set of points uniformly distributed throughout space with a density equal to c. Thus, in one dimension the Hertz density is given by the negative exponential density, $f_H(x,t)$, that was mentioned earlier, while in three dimensions the Hertz density is known[2] to have the form $f_H(r,t) - 4\pi c r^2 \exp(-4\pi c r^3/3)$, where r is the distance from the point. In the original formulation of this problem there are no time-dependent processes taking place so that the Hertz densities are independent of the time.

In this paper we derive the probability density function for the distance to the nearest particle from a static isolated trap located at the origin in one dimension. Our calculation will be partially extended to three dimensions for which we calculate the PDF of the distance to the nearest particle to a sphere with an absorbing surface. This constitutes a generalization of the Hertz density which has found explicit application in astrophysics[2] and implicit application to the study of the kinetics of trapping problems,[1,3,5] but differs from it due to the trapping process.

The classical trapping problem, in the language of chemical kinetics, can be characterized as the reaction $A+B \rightarrow B$ where A represents a random walker and B a trap. We solve for the PDF of nearest-neighborhood distances for an initially randomly distributed ensemble of Brownian particles (A) diffusing in a uniform field in the presence of a single trap (B). The function of specific interest in the analysis of reacting particles is the PDF, $f(L,t)$ of the nearest-neighbor distance, L, to a trap at time t. We find that in three dimensions the average distance from the surface of the trapping sphere to the nearest-neighboring particle is asymptotically constant as is the trapping rate. In one dimension, the average distance from the trap to the nearest neighbor will be seen to increase as $t^{1/4}$ and the trapping rate to decrease as $t^{-1/2}$.

The PDF of the nearest-neighbor distance from the trap is not a pure exponential as is the Hertz form of the PDF in the absence of a trap but rather has the form of a skewed Gaussian density. There is, however, a transition to the exponential form if one calculates the PDF of nearest-neighbor distance from a point sufficiently far removed from the trap.

Consider first Brownian motion in one dimension in the presence of a trap. Let $q(x,t\,|\,x_0)$ be the PDF for the position of a particle initially at x_0, and let $Q_y(L,t)$ be the probability that at time t the nearest neighbor to a point, y, is to be found at some distance $\geq L$ from that point. We will assume that the initial probability that a diffusing particle is found in the interval (x_0,x_0+dx_0) is equal to $c\,dx_0$, where c is a constant density. The PDF of the nearest-neighbor distance from an arbitrary point is therefore equal to $2c\exp(-2cx)$ at $t=0$ which is just the one-dimensional Hertz density. Let us find the PDF of the nearest-neighbor distance of a particle from a trap at the origin, $f(L,t)$, by calculating $Q_0(L,t)$ and making use of the relation $f(L,t)=-\partial Q_0/\partial L$. It is possible to derive the form of $Q_0(L,t)$ by restricting our attention to Brownian particles on one side of the origin, say $x>0$, since particles do not cross the origin. Let $q(x,t\,|\,x_0)$ be the PDF for the position, x, of a particle at time t, given its initial position, x_0. The two-sided $Q_0(L,t)$ is then

$$Q_0(L,t)=\exp\left[-2c\int_0^L dx\int_0^\infty q(x,t\,|\,x_0)dx_0\right], \quad (1)$$

where

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

The double integral in Eq. (1) is readily evaluated, leading to the result

$$Q_0(L,t)=\exp\left[-2c\left\{L\left[2\Phi\left[\frac{L}{\sqrt{2Dt}}\right]-1\right]-2\left[\frac{Dt}{\pi}\right]^{1/2}(1-e^{-L^2/4Dt})\right\}\right] \quad (3)$$

in which $\Phi(x)$ is the error function

$$\Phi(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{x}e^{-v^2/2}dv\,. \quad (4)$$

The long-time limit $(Dt\gg L^2)$ of $Q_0(L,t)$ is found to be

$$Q_0(L,t)\approx\exp\left[-\frac{cL^2}{\sqrt{\pi Dt}}\right] \quad (5)$$

from which it follows that the asymptotic value of the mean distance to the nearest neighbor is

$$\langle L\rangle=\int_0^\infty Lf(L,t)dL=\int_0^\infty Q_0(L,t)dL=\frac{\pi^{3/4}}{2}\left[\frac{Dt}{c^2}\right]^{1/4}. \quad (6)$$

Thus, the effect of the trap in one dimension is to slowly repel the Brownian particles. A similar calculation suffices to show that the standard deviation of this nearest-neighbor distance also has the same order of magnitude as the result in Eq. (6). Figure 1 shows the time-dependent development of the function $f(L,t)$ plotted as a function of L. The asymptotic (in time) PDF of L, $f(L,t)$, to the same approximation can be expressed as

$$f(L,t)\approx\frac{2cL}{\sqrt{\pi Dt}}\exp\left[-\frac{cL^2}{\sqrt{\pi Dt}}\right]. \quad (7)$$

In consequence, the most likely value of L, i.e., the value of L that maximizes $f(L,t)$ also varies as $(Dt)^{1/4}$. Notice that when $L^2\gg Dt$ the tail of $Q_0(L,t)$ is not described by the Gaussian shown in Eq. (5) but rather by the exponential $Q_0(L,t)\approx\exp(-2cL)$. A somewhat more involved calculation can be made to find approximations for the more general distribution $Q_y(L,t)$. These serve to confirm that, in the limit $y\rightarrow\infty$, $Q_y(L,t)$ is approximately given by $Q_y(L,t)\approx\exp(-2cL)$ which is just the Hertz distribution in one dimension.

The three-dimensional density for nearest-neighbor distances differs from that in one dimension because of the restricted geometry in the lower dimension. To define the three-dimensional problem we assume that a sphere of ra-

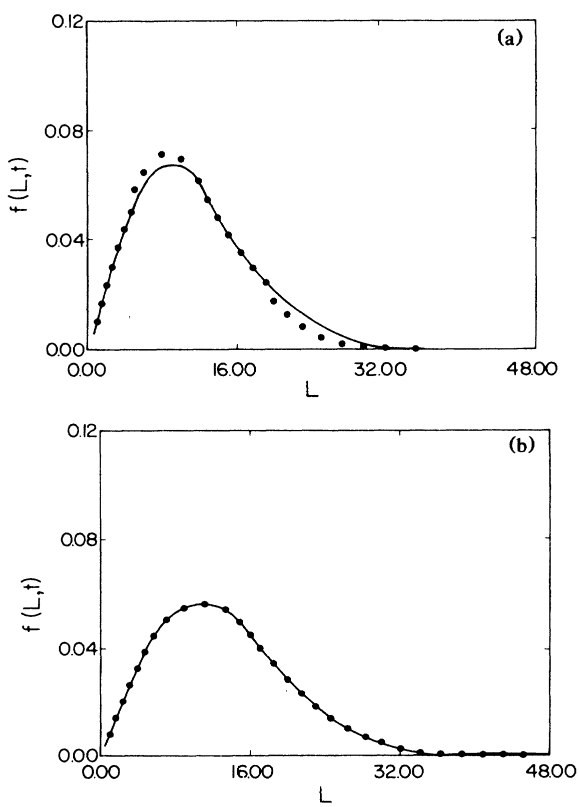

FIG. 1. Comparison of the exact result (line) for $f(L,t)$ calculated from Eq. (3) with the asymptotic skewed Gaussian form in Eq. (7), plotted as a function of the dimensionless parameter $L/\langle L\rangle$. The two cases are (a) $Dt=1000$, $c=0.5$; (b) $Dt=2000$, $c=0.5$. Notice the improved fit at the longer time.

dius r_0 centered at the origin has an absorbing surface and that the diffusion of point particles in the space external to the sphere is radially symmetric. In analogy to the one-dimensional case we examine the form taken by the PDF of the distance to the nearest particle in the neighborhood of the surface of the sphere. If we define dimensionless variables $\rho = r/r_0$ and $\tau = Dt/r_0^2$, the diffusion equation whose solution is required in our calculation of the PDF of nearest-neighbor distances can be written as

$$\frac{\partial p}{\partial \tau} = \frac{1}{\rho^2}\frac{\partial}{\partial \rho}\left[\rho^2 \frac{\partial p}{\partial \rho}\right] \tag{8}$$

which is to be solved subject to the initial and boundary conditions

$$p(\rho,0) = \sigma_0 = c r_0^3, \quad p(1,\tau) = 0\,, \tag{9}$$

c being the initial concentration of Brownian particles and $\rho = 1$ being the surface of the sphere. Notice that the density is expressed in terms of a dimensionless initial density, σ_0, to insure that $4\pi\rho^2 p(\rho,\tau)d\rho$ represents the probability that there be a particle at a distance between ρ and $\rho + d\rho$ from the origin. Standard techniques can be used to show that the solution for $p(\rho,\tau)$ is

$$p(\rho,\tau) = \frac{\sigma_0}{\rho}\left[\rho + 2\Phi\left[\frac{\rho-1}{\sqrt{2\tau}}\right]\right]. \tag{10}$$

Let Ω be a dimensionless radial coordinate measured from the origin. The probability that at time τ all particles are at a distance greater than Ω from the origin, $Q_1(\Omega,\tau)$, is equal to

$$Q_1(\Omega,\tau) = \exp\left[-4\pi \int_1^{\Omega} \rho^2 p(\rho,\tau)d\rho\right]. \tag{11}$$

An evaluation of the integral with $p(\rho,\tau)$ given in Eq. (10) leads to a quite complicated expression for $Q_1(\Omega,\tau)$, but it is relatively simple to examine the form of $Q_1(\Omega,\tau)$ in the limit of large τ. In this regime one finds that

$$Q_1(\Omega,\tau) \approx \exp\left[-4\pi\sigma_0\left\{1 + \frac{1}{\sqrt{\pi\tau}}\right\}\left\{\frac{\Omega^3-1}{3} - \frac{\Omega^2-1}{2}\right\}\right] \tag{12}$$

which reduces to the Hertz form without trapping only at large distances, i.e., when $\Omega \gg 1$. Notice that since the factor $(\pi\tau)^{-1/2}$ is negligible in the present approximation, $Q_1(\Omega,\tau)$ can be regarded as being asymptotically independent of time. In the immediate neighborhood of the absorbing sphere, i.e., for Ω slightly greater than 1, we have

$$Q_1(\Omega,\tau) \approx \exp[-4\pi\sigma_0(\Omega-1)^2] \tag{13}$$

which resembles the Hertz distribution in two dimensions.

The asymptotic form of the PDF of nearest-neighbor distance is found in the approximation of Eq. (12) to be expressible as

$$f(\Omega,\tau) \approx 4\pi\sigma_0\{\Omega^2 - \Omega\}\exp\left[-4\sigma_0\left\{\frac{\Omega^3-1}{3} - \frac{\Omega^2-1}{2}\right\}\right]. \tag{14}$$

The important feature of this result is that it is independent of time. We conjecture that in two dimensions the repulsion due to the presence of the trap will lead to a result like $\langle\Omega(\tau)\rangle \sim \ln\tau$.

The one-dimensional nearest-neighbor density, $f(L,t)$, in the long-time limit given in Eq. (7) has a skewed-Gaussian functional form similar to the conjectured density for the nearest-neighbor distance for the reaction $A + A \rightarrow$ product. The analogy goes even further. For the reaction (or trapping) rate, R, one can show, by calculating the flux, J, at the trap,

$$J = -2Dc\int_0^{\infty} \left.\frac{\partial q}{\partial x}\right|_{x=0} dx_0 \tag{15}$$

that $R \sim ct^{-1/2}$ at long times. In three dimensions, on the other hand, $R \sim c$ at long times, which is the classical result. This explains results on exciton heterofusion $(A + B \rightarrow B)$ in ultrathin naphthalene wires. With an empirical formula[12] $R \sim t^{-h}c$ the experimental results have been found to give the value $h = 0.49$ while for thick wires $h = 0.02$, in agreement with the theoretical results. The analogous results for the reaction $A + A \rightarrow$ product are $R \sim c^2 t^{-1/2}$ in one dimension[9-15] and $R \sim c^2$ in three dimensions.[1] All of these results can also be found by making the *ad hoc* assumption[7,8] that the time dependence of the reaction probability is proportional to $cf(L,t)$ in the limit $L \rightarrow 0$, where $f(L,t)$ is the probability density defined earlier. In the simple trapping model of this paper this assumption leads to an asymptotic time dependence proportional to $t^{-1/2}$ in one dimension and to a constant in three dimensions.

In summary, we have shown that the probability density function for the nearest-neighbor distance to the trap is asymptotically independent of time in three dimensions, but not in one dimension where both the average and the most probable nearest-neighbor distances increase as $t^{1/4}$. Concomitantly, the global trapping rate reaches a stable long-time limit in three dimensions but decreases as $t^{-1/2}$ in one dimension. These results have been shown to mimic aspects of the kinetic behavior of the diffusion-limited $A + A \rightarrow A$ reaction in one and three dimensions and also to account for experimental reactions with dilute traps.

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