Four Lectures on Non-Equilibrium Statistical Physics

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Contents

Chapter 3

FIRST-PASSAGE PROPERTIES

Here we focus on two basic questions: *when* does a random walk *first* reach a given point? More generally, what is the *first-passage probability* $F(\mathbf{r}, t)$ for a random walk to *first* reach $\mathbf{r}$ at time t? First-passage phenomena underlie a wide range of phenomena where a stochastic variable first reaches a specified value. Examples include the evolution of chemical reactions, the firing of neurons in the brain, or the triggering of stock options. This section outlines several basic ideas of first-passage processes.

3.1 Transience and Recurrence

Suppose that a random walk begins at the origin of an infinite lattice at $t = 0$. Does the random walker *eventually* return to its starting point? Remarkably, the answer depends only the spatial dimension d:

- For $d \leq 2$, a random walk surely returns to the origin — the walk is *recurrent*.
- For $d > 2$, there is a nonzero probability that the walk never returns — the walk is *transient*.

Moreover, if a random walk is recurrent it returns infinitely often, but the average return time is infinite!

To understand the criterion for transience and recurrence, consider a typical trajectory of a random walk. After time t the walk explores a spheroidal domain of radius $L \sim \sqrt{Dt}$, while the number of sites visited grows linearly in t. The density of visited sites is therefore $\rho \sim t/L^d \sim t^{1-d/2}$. For $d > 2$, ρ decreases as t increases so that some points in the domain of exploration may never be visited — transience. For $d < 2$, the density is an increasing function of t so that every site within the domain is surely visited — recurrence. The marginal case of $d = 2$ is barely recurrent, as we discuss below.

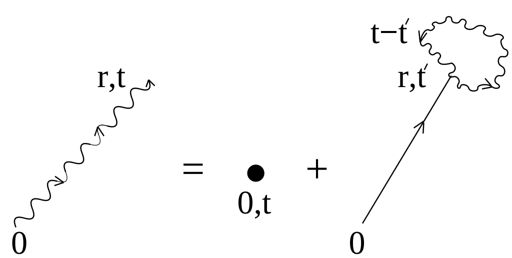

Figure 3.1: Diagrammatic representation of the relation between the occupation probability of a random walk (whose propagation is represented by a wavy line) and the first-passage probability (straight line).

We now calculate the first-passage probability, from which the criterion for transience and recurrence can be inferred. The first-passage probability is related to the familiar occupation probability $P(\mathbf{r}, t)$ by

$$P(\mathbf{r}, t) = \int_0^t F(\mathbf{r}, t')\, P(\mathbf{0}, t - t')\, dt' + \delta_{\mathbf{r},\mathbf{0}}\, \delta_{t,0}\,. \tag{3.1}$$

This equation accounts for a walk that reaches $(\mathbf{r},t)$ by a first passage to $\mathbf{r}$ at a time $t'\leq t$ and then a return to r in the remaining time $t-t'$ (Fig. 3.1). Because the walk may also return to $\mathbf{r}$ at intermediate times between t' and t, the return factor involves the occupation probability P rather than F. In terms of the Laplace transform $P(\mathbf{r},s)=\int_0^\infty P(\mathbf{r},t)\,e^{-st}\,dt$ and similarly for $F(\mathbf{r},s)$, the convolution (3.1) becomes the algebraic equation $P(\mathbf{r},s)=F(\mathbf{r},s)P(\mathbf{0},s)+\delta_{\mathbf{r},\mathbf{0}}$, from which

$$F(\mathbf{r},s)=\frac{P(\mathbf{r},s)-\delta_{\mathbf{r},\mathbf{0}}}{P(\mathbf{0},s)}\ . \tag{3.2}$$

The transience or recurrence of a random walk is determined by the *eventual* return probability to the origin

$$\mathcal{R}=F(\mathbf{0},s)=\int_0^\infty F(\mathbf{0},t)\,dt\,;$$

$\mathcal{R}=1$ means that the walk is recurrent, while for $\mathcal{R}<1$ the walk is transient. Since we only consider return to the origin, we drop the spatial argument in the following discussion.

Connection between a power-law function and its Laplace transform

Suppose that $f(t)$ has an algebraic tail, $f(t)\sim t^{-\mu}$ when $t\gg 1$, with $\mu<1$, so that the integral $\int_0^\infty f(t)\,dt$ diverges. What is the Laplace transform $f(s)$? The answer obviously depends on the entire function $f(t)$, but the small-s asymptotic of the Laplace transform is governed by the large-t asymptotic of $f(t)$. Therefore consider $f(t)=t^{-\mu}$. By the definition of the Laplace transform,

$$f(s)=\int_0^\infty t^{-\mu}\,e^{-st}\,dt\,.$$

We now make the substitution $x=st$ to write the Laplace transform in the dimensionless form

$$f(s)=s^{\mu-1}\int_0^\infty x^{-\mu}\,e^{-x}\,dx=\Gamma(1-\mu)\,s^{\mu-1}\ , \tag{3.3}$$

where we have used the definition of the gamma function,

$$\Gamma(z)=\int_0^\infty x^{z-1}e^{-x}\,dx\,.$$

Thus we obtain the handy relation between a sufficiently singular function of time and its Laplace transform:

$$t^{-\mu}\quad\text{with }\mu<1\qquad\longleftrightarrow\qquad\Gamma(1-\mu)\,s^{\mu-1}\ , \tag{3.4}$$

which we will use extensively in this section and throughout this book.

To compute the first-passage probability for the continuous-time random walk, we start with the occupation probability at the origin on a d-dimensional hypercubic lattice:

$$P(t)=\left[I_0(2t)\,e^{-2t}\right]^d\simeq\frac{1}{(4\pi t)^{d/2}}\quad\text{when}\quad t\to\infty. \tag{3.5}$$

We use this basic result to compute the first-passage and eventual return probabilities for $d=1$, 2, and 3.

$\mathbf{d=1}$. From Eqs. (3.5) and (3.4), the Laplace transform of the occupation probability at the origin is $P(s)\simeq 1/\sqrt{4s}$. Then Eq. (3.2) gives, for the Laplace transform of the first-passage probability to the origin,

$$F(s)\simeq 1-\sqrt{4s}\,. \tag{3.6}$$

Thus a random walk in one dimension is recurrent because the eventual return probability $\mathcal{R}=F(s=0)=1$. However, because $F(s)$ does not diverge for small s, it is not convenient to invert this Laplace transform directly. Instead, we consider the derivative of Eq. (3.6):

$$-\frac{dF(s)}{ds}=-\frac{d}{ds}\int_0^\infty F(t)\,e^{-st}\,dt=\int_0^\infty t\,F(t)\,e^{-st}\,dt=\frac{1}{\sqrt{s}}\ .$$

The point of this trick is that the Laplace transform of $tF(t)$ is more singular than the Laplace transform of $F(t)$ for small s, and we can then directly apply Eq. (3.4) to find that $t\,F(t) \simeq (\pi t)^{-1/2}$. Thus

$$F(t) \simeq \frac{1}{\sqrt{\pi}}\frac{1}{t^{3/2}} \quad \text{when} \quad t \to \infty. \tag{3.7}$$

d = 2. This case is subtle because the time integral of $P(t)$ diverges only weakly as $t \to \infty$. We must also cut off the integral for $t < 1$ to eliminate the spurious singularity that arises from using the large-time form of $P(t)$ for short times. With these caveats, we have

$$P(s) \simeq \int_1^\infty \frac{1}{4\pi t}\, e^{-st}\, dt = \frac{1}{4\pi}\int_s^\infty \frac{dx}{x}\, e^{-x} \simeq -\frac{1}{4\pi}\ln s\,. \tag{3.8}$$

The exponential factor in the integrand leads to a subdominant correction in small-s limit, and we may ignore it to obtain the leading contribution to the integral. Using (3.8) in (3.2) we find

$$F(s) \simeq 1 + \frac{4\pi}{\ln s} \quad \text{when} \quad s \to 0. \tag{3.9}$$

A random walk is again recurrent in two dimensions because $F(s=0) = \mathcal{R} = 1$. To solve for $F(t)$, we again apply $-\frac{d}{ds}$ to both sides of Eq. (3.9) to give

$$\int_0^\infty t\,F(t)\,e^{-st}\,dt \simeq \frac{4\pi}{s(\ln s)^2} \quad \text{when} \quad s \to 0. \tag{3.10}$$

Since the Laplace transform of a constant function equals $1/s$, the function $tF(t)$ must vary weakly in time to give the extra factor of $(\ln s)^{-2}$; namely

$$F(t) \simeq \frac{4\pi}{t[\ln t]^2} \quad \text{when} \quad t \to \infty. \tag{3.11}$$

d = 3. This case is different from $d \leq 2$ because

$$P(s) \simeq \int_1^\infty \frac{1}{(4\pi t)^{3/2}}\, e^{-st}\, dt \tag{3.12}$$

converges as $s \to 0$. Notice that the integral is again cut off for $t < 1$ to avoid the spurious singularity that arises from using the large-t form of $P(t)$ for all t. To determine $P(s)$ it is again useful to apply $-\frac{d}{ds}$ to both sides of Eq. (3.12) to give

$$-\frac{dP(s)}{ds} = \int_0^\infty \frac{1}{(4\pi)^{3/2}}\frac{1}{t^{1/2}}\, e^{-st} dt = \frac{1}{8\pi\sqrt{s}}\ ,$$

where we use Eq. (3.4) to evaluate the integral. Consequently $P(s)$ itself is given by

$$P(s) \simeq P(0) - \frac{\sqrt{s}}{4\pi}\ . \tag{3.13}$$

Then from Eq. (3.2), the Laplace transform of the first-passage probability is

$$F(s) \simeq [1 - P(0)^{-1}] - \frac{\sqrt{s}}{4\pi P(0)^2} = \mathcal{R} - \frac{(1-\mathcal{R})^2\sqrt{s}}{4\pi}\ .$$

Because $P(s=0) < \infty$, we conclude that $\mathcal{R} = [1 - P(0)^{-1}] < 1$ and the random walk is transient. Finally by comparing with Eq. (3.6), the asymptotic form of $F(t)$ is

$$F(t) \simeq \frac{(1-\mathcal{R})^2}{8\pi^{3/2}}\frac{1}{t^{3/2}}\ . \tag{3.14}$$

3.2 Exit Probabilities and Exit Times

Two of the most important first-passage properties are the *exit probability* and the *exit time*. Namely, for a diffusing particle that starts at a point $\mathbf{r}$ within a domain $\mathcal{B}$, what is the probability that the particle eventually reaches the boundary and how long does it take for this event to occur? In this section, we present some basic features of these two quantities.

Exit probability

For the exit probability, it is natural to partition the boundary of some domain $\partial\mathcal{B}$ into two disjoint subsets $\partial\mathcal{B}_+$ and $\partial\mathcal{B}_-$, with $\partial\mathcal{B}_+ \cup \partial\mathcal{B}_- = \partial\mathcal{B}$, and ask for the probability $\mathcal{E}(\mathbf{r})$ that the particle exits the domain via $\partial\mathcal{B}_+$ before touching the boundary $\partial\mathcal{B}_-$. For example in a finite one-dimensional interval $[0, N]$, $\partial\mathcal{B}_-$ would represent the point $x = 0$ and $\partial\mathcal{B}_+$ the point $x = N$, and we are interested, for example, in the probability that the walk eventually reaches $x = N$ without ever touching $x = 0$ in this sojourn.

Consider a discrete random walk that starts at site n on the interval $[0, N]$ and let $\mathcal{E}_n$ be the probability that the walk reaches N without visiting 0. This quantity satisfies the recurrence

$$\mathcal{E}_n = \frac{1}{2}(\mathcal{E}_{n-1} + \mathcal{E}_{n+1}), \tag{3.15a}$$

or, equivalently,

$$\Delta^{(2)}\mathcal{E} = 0, \tag{3.15a}$$

where $\Delta^{(2)}$ is the discrete Laplace, or second difference, operator defined by $\Delta^{(2)} f_n \equiv f_{n+1} - 2f_n + f_{n-1}$. Eq. (3.15) expresses the fact that to exit starting from n, the walk either steps to the left with probability $\frac{1}{2}$, after which exit from $n-1$ occurs, or steps to the right with probability $\frac{1}{2}$, after which exit from $n+1$ occurs. The boundary conditions are $\mathcal{E}_0 = 0$ and $\mathcal{E}_N = 1$; *i.e.*, the the walker starts at 0 it cannot exit at N, while it exits at N if it starts at this point. The general solution to Eq. (3.15b) is linear in the spatial variable, $An + B$, and invoking the boundary conditions gives

$$\mathcal{E}_n = \frac{n}{N}. \tag{3.16}$$

The reasoning that led to Eq. (3.15) applies to an arbitrary domain, and the exit probability again satisfies the Laplace equation

$$\nabla^2\mathcal{E}(\mathbf{r}) = 0\,, \tag{3.17}$$

subject to the boundary conditions $\mathcal{E}(\mathbf{r} \in \partial\mathcal{B}_+) = 1$ and $\mathcal{E}(\mathbf{r} \in \partial\mathcal{B}_-) = 0$. If $d > 2$ and the domain $\mathcal{B}$ is unbounded, the exit probability through the entire boundary is non-trivial. Mathematically we still need to solve the Laplace equation (3.17) subject to the boundary condition $\mathcal{E}(\mathbf{r} \in \partial\mathcal{B}) = 1$.

By this mapping of the exit probability into electrostatics, we can easily treat a variety of geometries. Consider, for instance, a diffusing particle, which starts at a distance r from the center of a sphere of radius $R < r$. What is the probability that it will eventually hit the sphere? In one and two dimensions, the solution to Laplace's equation that satisfies $\mathcal{E} = 1$ for $r = R$ is indeed $\mathcal{E}(r) = 1$. This result merely reflects the recurrence of diffusion for $d \le 2$. For $d > 2$, the solution to Eq. (3.17) gives the exit probability $\mathcal{E}(r) = (R/r)^{d-2}$.

Exit time

Let us begin by returning to a puzzling feature of the random walk in one dimension — the walker certainly visits the origin, yet the average time for the first visit is infinite. For concreteness, consider a random walk that is continuous in space and time with diffusion coefficient D. Let the walker start at $x = \ell > 0$. At a certain time T the walker will hit the origin for the first time; we call T the exit time. The exit time is the random quantity with infinite average, $\langle T\rangle = \infty$, yet the *typical* exit time is finite — it can depend only on D and ℓ, and dimensional analysis tells us that $T_{\rm typ} \sim \ell^2/D$.

To resolve this dichotomy, we compute the probability distribution $\Pi(T, \ell)$ of the exit time. A straightforward approach is to first calculate the probability density $P(x, t\,|\,\ell)$ that the walker starts at $x = \ell$, is at position x at time t, and has not reached the origin during the time interval $(0, t)$. To determine $P(x, t\,|\,\ell)$ we solve the diffusion equation subject to the initial condition $P(x, t = 0\,|\,\ell) = \delta(x - \ell)$ and the boundary condition $P(x = 0, t\,|\,\ell) = 0$, that assures that the walker has not reached the origin. The solution can be found using the image method, that is, by putting a fictitious "sink" at $x = -\ell$ so that the initial condition becomes

$$P(x, t = 0\,|\,\ell) = \delta(x - \ell) - \delta(x + \ell). \tag{3.18}$$

With this initial condition, the boundary condition $P(x=0,t\,|\,\ell)=0$ is manifestly obeyed. Due to the linearity of the diffusion equation, the solution is just a combination of the two Gaussian distributions

$$P(x,t\,|\,\ell)=\frac{1}{\sqrt{4\pi Dt}}\left[e^{-(x-\ell)^2/4Dt}-e^{-(x+\ell)^2/4Dt}\right] \tag{3.19}$$

corresponding to the source at $x=\ell$ and sink at $x=-\ell$. Now the flux to the origin $D\frac{\partial P}{\partial x}\Big|_{x=0}$ is precisely the exit time probability distribution $\Pi(t,\ell)$. Thus

$$\Pi(T,\ell)=\frac{\ell}{\sqrt{4\pi DT^3}}\;e^{-\ell^2/4DT}\;. \tag{3.20}$$

As a formal definition of the typical time we use the quantity $\langle T^\alpha\rangle^{1/\alpha}$ where $\langle T^\alpha\rangle$ is the $\alpha^{\rm th}$ moment of the exit time

$$\langle T^\alpha\rangle=\int_0^\infty T^\alpha\,\Pi(T\,|\,\ell)\;dT$$

Using (3.20) we obtain

$$\langle T^\alpha\rangle^{1/\alpha}=\frac{\ell^2}{4D}\left[\frac{\Gamma(\frac{1}{2}-\alpha)}{\Gamma(\frac{1}{2})}\right]^{1/\alpha} \tag{3.21}$$

Typical times defined according to (3.21) are finite when $\alpha<1/2$ and infinite otherwise; in particular, the average time $\langle T\rangle$ is infinite!. However, when $\alpha<1/2$, the moments $\langle T^\alpha\rangle^{1/\alpha}$ indeed scale as ℓ^2/D.

Consider now a diffusing particle in a finite domain. In such a domain, the average exit time is finite[1] and we can in principle compute the exit time distribution by employing the same scheme as in the case of the half-line. That is, we solve the diffusion equation

$$\frac{\partial P}{\partial t}=\nabla^2 P \tag{3.22}$$

inside domain $\mathcal{B}$ subject to the initial and the "adsorption" boundary conditions

$$\begin{cases}P(\mathbf{x},t=0\,|\,\mathbf{r})=\delta(\mathbf{x}-\mathbf{r})\\ P(\mathbf{x}\in\partial\mathcal{B},t\,|\,\mathbf{r})=0.\end{cases} \tag{3.23}$$

The exit time distribution is given by the surface integral

$$\Pi(T,\mathbf{r})=-D\int_{\partial\mathcal{B}}\nabla P(\mathbf{x},T\,|\,\mathbf{r})\cdot d\boldsymbol{\sigma} \tag{3.24}$$

and hence the average exit time (which is finite when the domain is bounded) is

$$t(\mathbf{r})=\langle T(\mathbf{r})\rangle=\int_0^\infty T\;\Pi(T,\mathbf{r})\,dT. \tag{3.25}$$

The implementation of the above procedure is laborious[2] whereas the final answers are often remarkably simple. If we are interested only in the average exit time, the above method for computing this time-*independent* quantity is especially cumbersome because it requires (i) solving the time-dependent problem (3.22)–(3.23); (ii) computing the exit time distribution (3.24); (iii) performing the averaging (3.25).

There is, however, a more clever procedure that does not require analysis of time-dependent equations and usage of auxiliary quantities. We illustrate this approach for the random walk on a one-dimensional lattice. By construction, in an infinitesimal time interval dt the exit time changes according to

$$T(x)=dt+\begin{cases}T(x) & \text{probability} \quad 1-2dt;\\ T(x+1) & \text{probability} \quad dt;\\ T(x-1) & \text{probability} \quad dt.\end{cases} \tag{3.26}$$

[1] All other moments, *e.g.*, $\langle T^2\rangle,\langle T^3\rangle$, *etc.*, are also finite.

[2] For instance, when the domain is a finite interval $(0,L)$, this approach gives the probability density of exit times in the form of an infinite series. However, the average exit time for a particle that starts at $x\in(0,L)$ can be expressed in the simple form $t(x)=x(L-x)/2D$.

Averaging equation (3.26) yields

$$t(x) = dt + (1 - 2dt)t(x) + dt[t(x+1) + t(x-1)]$$

which simplifies to

$$t(x+1) - 2t(x) + t(x-1) = -1. \tag{3.27}$$

We now take the continuum limit of Eq. (3.27) by replacing the second difference by second derivative, $t(x+1) - 2t(x) + t(x-1) \to d^2t/dx^2$, and write $1/D$ instead of one on the right-hand side. Thus the average exit time satisfies

$$D\,\frac{d^2t}{dx^2} = -1 \tag{3.28}$$

in one dimension. Generally, the average exit time from an arbitrary domain obeys the Poisson equation

$$D\nabla^2 t(\mathbf{r}) = -1 \tag{3.29}$$

subject to the boundary condition $t(\mathbf{r} \in \partial\mathcal{B}) = 0$ that the exit time is zero if the diffusing particle starts on the domain boundary. As an example, consider the exit time to the surface of an absorbing sphere of radius R. Since all that matters is the radial distance, we only need the radial part of the Poisson equation

$$\frac{d^2t}{dr^2} + \frac{d-1}{r}\frac{dt}{dr} = -\frac{1}{D}\ ,$$

with solution

$$t(r) = \frac{R^2 - r^2}{2dD}\,. \tag{3.30}$$

The procedure for computing the exit time distribution is formidable, in principle, as it involves solving Eqs. (3.22)–(3.23) for the density $P(\mathbf{x}, t\,|\,\mathbf{r})$, and then computing the spatial integral (3.24). The use of the Laplace transform allows us to avoid dealing with the probability density $P(\mathbf{x}, t\,|\,\mathbf{r})$, and instead work directly with the exit time distribution. Instead of giving a formal derivation, we derive the exit time distribution for the lattice problem defined by Eq. (3.26) and then take the continuum limit. The Laplace transform of the exit time distribution is

$$\Pi(s,x) = \int_0^\infty e^{-sT}\,\Pi(T,x)\,dT = \left\langle e^{-sT(x)}\right\rangle \tag{3.31}$$

Now we apply the process defined by Eq. (3.26) to write the evolution equation for $\langle e^{-sT(x)}\rangle$ as

$$\left\langle e^{-sT(x)}\right\rangle = e^{-sdt}\left\{(1-2dt)\left\langle e^{-sT(x)}\right\rangle + dt\left\langle e^{-sT(x+1)}\right\rangle + dt\left\langle e^{-sT(x-1)}\right\rangle\right\} \tag{3.32}$$

Expanding in powers of dt and taking the $dt \to 0$ limit we obtain

$$s\Pi(s,x) = \Pi(s,x+1) - 2\Pi(s,x) + \Pi(s,x-1)$$

from which we get

$$s\Pi(s,x) = D\,\frac{d^2\Pi(s,x)}{dx^2} \tag{3.33}$$

in the continuum limit, and more generally

$$s\Pi(s,\mathbf{x}) = D\nabla^2\Pi(s,\mathbf{x}) \tag{3.34}$$

in higher dimensions. The exit time is equal to zero if the particle starts on the boundary, $\Pi(T, \mathbf{x} \in \partial\mathcal{B}) = \delta(T)$. Hence Eq. (3.34) should be supplemented by the boundary condition for the Laplace transform, $\Pi(s, \mathbf{x} \in \partial\mathcal{B}) = 1$.

Taken together, Eqs. (3.17) and (3.34) provide a convenient and powerful approach to determine the exit probabilities and exit times for diffusing particles in arbitrary domains.

Application to vicious random walks

A natural application of first-passage processes is to the dynamics of mutually annihilating, or "vicious", random walks. What is their survival probability? We restrict ourselves to one dimension because the most interesting behavior occurs in this case. Let's start with the problem of two diffusing particles at x_1 and $x_2 > x_1$, with the same diffusion coefficient D, that both die when they meet. To find the survival probability, we first map this two-particle problem onto a single-particle problem by treating the coordinates x_1 and x_2 on the line as the position (x_1, x_2) of a single effective diffusing particle in two dimensions, subject to the constraint $x_2 > x_1$ (Fig. 3.2). If the effective particle hits the line $x_2 = x_1$ it dies. Because only the perpendicular distance to the line $x_2 = x_1$ matters, we have thus mapped the 2-particle problem to that of a single diffusing particle at $y = x_2 - x_1$, with diffusion coefficient $2D$, and with an absorbing boundary at the origin.

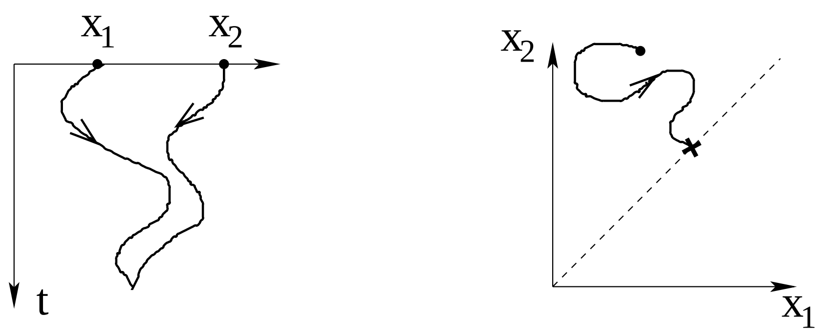

Figure 3.2: Schematic illustration of the equivalence of two diffusing particles on the line (left) and a single diffusing particle in the region $x_2 > x_1$ (right). The former shows a space-time plot of the particle trajectories, while the right shows (not to scale) the trajectory of the equivalent particle in the plane.

This single-particle problem can be solved by the image method. We want the probability density for a diffusing particle on the line that starts at $y_0 > 0$, so that $c(y, t = 0) = \delta(y - y_0)$, and the particle dies if it reaches the origin. Here y_0 is the initial separation of the two particles on the line. The probability density is [see also (3.19)]

$$c(y,t) = \frac{1}{\sqrt{8\pi Dt}}\left[e^{-(y-y_0)^2/8Dt} - e^{-(y+y_0)^2/8Dt}\right] . \tag{3.35}$$

Since the initial condition is normalized, the first-passage probability to the origin at time t is just the flux to this point:

$$F(0,t) = +2D\frac{\partial c(y,t)}{\partial y}\bigg|_{y=0} = \frac{y_0}{\sqrt{8\pi Dt^3}}\, e^{-y_0^2/8Dt} \propto t^{-3/2} \tag{3.36}$$

as $t \to \infty$, in agreement with the time dependence in Eq. (3.7). The survival probability $S(t)$ of the two particles may be found from $S(t) = 1 - \int_0^t F(0,t')\,dt'$. Introducing the variable $u^2 = y_0^2/8Dt'$ leads to

$$S(t) = 1 - \frac{2}{\sqrt{\pi}}\int_{y_0/\sqrt{8Dt}}^{\infty} e^{-u^2}\,du = \mathrm{erf}\left(\frac{y_0}{\sqrt{8Dt}}\right) \to \frac{y_0}{\sqrt{2\pi Dt}} \tag{3.37}$$

as $t \to \infty$. As expected by the recurrence of diffusion, the survival probability ultimately decays to zero. The two particles certainly annihilate; however, the average annihilation time, $\langle t\rangle \equiv \int_0^\infty t\,F(0,t)\,dt$, is infinite.

What happens with three particles at x_1, $x_2 > x_1$, and $x_3 > x_2$ on the line? If they are mutually vicious, the probability that they all survive until time t equals the probability that they all maintain the ordering $x_3 > x_2 > x_1$ for all times $t' \le t$. It is again convenient to solve this problem by mapping to a single diffusing particle in three dimensions whose coordinates always satisfy $x_3 > x_2 > x_1$. The constraint $x_2 > x_1$ corresponds to the diffusing particle always remaining on one side of the plane $x_2 = x_1$. Similarly, the constraint $x_3 > x_2$ corresponds to the diffusing particle always remaining on one side of the plane $x_3 = x_2$.

To satisfy both constraints, the particle must remain within the infinite two-dimensional wedge of opening angle $\pi/3$ that is defined by these two constraints. The survival probability of a diffusing particle inside an infinite two-dimensional wedge of opening angle ϕ asymptotically decays as

$$S(t) \sim t^{-\pi/2\phi} \; . \tag{3.38}$$

Consequently, the survival probability of 3 mutually vicious walkers asymptotically decays as $t^{-3/2}$.

The 3-particle system contains more subtlety. Let's designate one of the particles as a "prey" and the other two as "predators" that do not interact with each other, but each kill the prey if they meet it. Assume that both species diffuse with the same diffusion coefficient. What is the prey survival probability? There are two distinct cases: (a) prey initially in the middle, and (b) prey at the end. These 3-particle problems can each be solved by mapping to a single diffusing particle in three dimensions subject to appropriate constraints. For the prey in the middle, the constraints $x_2 > x_1$ and $x_3 > x_2$ are the same as that for three mutually vicious walks and the prey survival probability asymptotically decays as $t^{-3/2}$. For the prey at x_1 at one end, the survival constraints are now: $x_1 < x_2$ and $x_1 < x_3$. By mapping to the equivalent three-dimensional problem, the opening angle of the wedge is now $2\pi/3$, so that the prey survival probability asymptotically decays as $t^{-3/4}$.

Notice the diminishing return of adding a second predator at the end: for one predator the survival probability decays as $t^{-1/2}$, while for two predators the survival probability decays slower than $(t^{-1/2})^2$. The nature next question is: what is the prey survival probability $S_N(t)$ for $N > 2$ predators on one side of the prey? The answer is unknown! Numerically, it appears that $S_N \sim t^{-\gamma_N}$ with $\gamma_3 \approx 0.91342$, $\gamma_4 \approx 1$, $\gamma_{10} \approx 1.4$; for $N \to \infty$, a qualitative argument gives $\gamma_N \sim \frac{1}{4}\ln 4N$.

3.3 Reaction-Rate Theory

What is the rate at which diffusing molecules react with an absorbing object? The answer to this question sheds light on diffusion-controlled reactions. In such processes, a reaction occurs as soon as two reactants approach to within an interaction radius — effectively, the reactants "meet". The evolution of the reaction is therefore limited by the rate at which diffusion brings reactants in proximity. The goal of reaction rate theory is to calculate this rate.

To provide context for reaction-rate theory, consider the much simpler example of the reaction rate when external particles move ballistically rather than diffusively. For a uniform beam of particles that is incident on an absorbing object, the reaction rate is clearly proportional to the cross-sectional area of this object. In stark contrast, when the background consists of diffusing particles, the reaction rate grows *more slowly* than the cross-sectional area, and the rate also has a non-trivial shape dependence. By employing the mathematical similarity between diffusion and electrostatics we will show how to determine the reaction rate of an object in terms of its electrical capacitance.

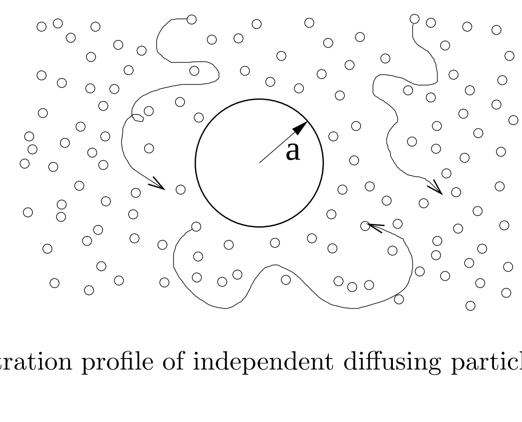

Figure 3.3: Schematic concentration profile of independent diffusing particles around an absorbing sphere.

We first study the reaction rate of an arbitrarily-shaped absorbing object in three dimensions ($d = 3$). The object is surrounded by a gas of non-interacting molecules, each of which is absorbed whenever it hits the surface of the object (Fig. 3.3). The reaction rate is defined as the steady-state diffusive flux to the object. An important simplifying feature for $d = 3$ is that the loss of molecules by absorption is balanced by replenishment from afar because diffusion is transient. Consequently, the density ultimately reaches a steady state profile for any reasonable initial distribution of background molecules. To find this profile, we need to solve the diffusion equation for the concentration $c(\mathbf{r}, t)$ exterior to the object $\mathcal{B}$, with absorption on its boundary $\partial\mathcal{B}$. It is conventional to choose a spatially uniform unit density for the initial condition. The problem that we need to solve is specified by:

$$\frac{\partial c}{\partial t} = D\nabla^2 c; \qquad c(\mathbf{r} \in \partial\mathcal{B}, t) = 0, \quad c(\mathbf{r}, t = 0) = 1. \tag{3.39}$$

Because $c(\mathbf{r}, t)$ approaches the steady-state value $c_\infty(\mathbf{r})$ for $d = 3$, we study the complementary function $\phi(\mathbf{r}) = 1 - c_\infty(\mathbf{r})$. The governing equations for $\phi(\mathbf{r})$ are

$$D\nabla^2\phi = 0, \quad \phi(\mathbf{r} \in \partial\mathcal{B}) = 1, \quad \phi(\mathbf{r} \to \infty) = 0. \tag{3.40}$$

Since $\phi = 1$ on the boundary and $\phi(\mathbf{r})$ satisfies the Laplace equation, ϕ is just the *electrostatic potential* generated by a perfectly conducting object $\mathcal{B}$ that is held at unit potential.

By definition, the reaction rate K is given by

$$K = D\int_{\partial\mathcal{B}} \nabla c \cdot d\boldsymbol{\sigma} = -D\int_{\partial\mathcal{B}} \nabla\phi \cdot d\boldsymbol{\sigma}\,. \tag{3.41}$$

On the other hand, according to electrostatics the total charge on the surface of the equivalent conductor in three dimensions is

$$Q = -\frac{1}{4\pi}\int_{\partial\mathcal{B}} \nabla\phi \cdot d\boldsymbol{\sigma}\,. \tag{3.42}$$

Moreover, the total charge on the conductor is related to its capacitance C by $Q = C\phi|_{\partial\mathcal{B}}$. Consequently, when the conductor is held at unit potential the reaction rate is given by

$$K = 4\pi DQ = 4\pi DC\,. \tag{3.43}$$

This fundamental equivalence allows us to find the reaction rate of various simple objects from known values of their capacitances:

- Sphere of radius R in three dimensions[3]:

$$C = R \qquad\qquad K = 4\pi DR. \tag{3.44a}$$

- Prolate ellipsoid of revolution with axes $a > b = c$:

$$C = \frac{\sqrt{a^2 - b^2}}{\cosh^{-1}(a/b)} \qquad\qquad K = 4\pi D\frac{\sqrt{a^2 - b^2}}{\cosh^{-1}(a/b)}. \tag{3.44b}$$

- Oblate ellipsoid of revolution with axes $a = b > c$:

$$C = \frac{\sqrt{a^2 - c^2}}{\cos^{-1}(c/a)} \qquad\qquad K = 4\pi D\frac{\sqrt{a^2 - c^2}}{\cos^{-1}(c/a)}. \tag{3.44c}$$

- Disk of radius R:

$$C = 2R/\pi \qquad\qquad K = 8DR. \tag{3.44d}$$

What about the reaction rate in low-dimensional systems $d \leq 2$? Because diffusion is recurrent, the absorber sweeps out a continuously growing depletion zone around it. Consequently, the absorbed flux monotonically decreases to zero as $t \to \infty$. While the reaction rate is, strictly speaking, zero, it is useful

[3] For the sphere in $d > 2$ dimensions, $C = (d-2)R^{d-2}$ and consequently $K = D\,(d-2)\,\Omega_d\,R^{d-2}$ where $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the surface area of a d-dimensional unit sphere.

to think of a *time-dependent* reaction rate. To obtain this reaction rate, we now have to solve the full time-dependent diffusion equation and then compute the flux to the absorber.

We can simplify this calculation considerably by the *quasi-static* approximation. The basis of this approximation is that the region exterior to the absorbing sphere naturally divides, for $d \le 2$, into a "near" zone that extends a distance $\sqrt{Dt}$ from the surface, and the complementary "far" zone. In the near zone, diffusing particles have ample time to explore this region thoroughly before being absorbed. Consequently, the concentration is nearly time independent. In the far zone, the probability of a particle being adsorbed is negligible; thus the concentration remains close to its initial value, $c(r) \approx 1$ for $r > R + \sqrt{Dt}$.

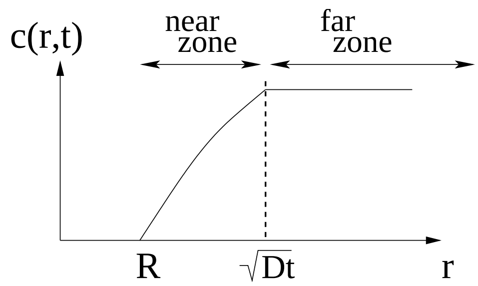

Figure 3.4: Sketch of the concentration about an absorbing sphere in the quasi-static approximation. The near- and far-zone concentrations match at $r = R + \sqrt{Dt}$.

Based on this intuition, we solve the Laplace equation in the near zone, but with the *time-dependent* boundary condition $c(r = R + \sqrt{Dt}) = 1$ to match to the static far-zone solution at $r = \sqrt{Dt}$. The general solution to the Laplace equation has the form $c(r) = A + Br^{2-d}$ for $d < 2$ and $c(r) = A + B \ln r$ for $d = 2$. Matching to the boundary conditions at $r = R$ and at $r = R + \sqrt{Dt} \approx \sqrt{Dt}$ for $t \to \infty$ gives

$$c(r,t) \simeq \begin{cases} \dfrac{1-(R/r)^{d-2}}{1-(R/\sqrt{Dt})^{d-2}} \to \left(\dfrac{\sqrt{Dt}}{r}\right)^{d-2} & d < 2 \\[3ex] \dfrac{\ln(r/R)}{\ln(\sqrt{Dt}/R)} & d = 2. \end{cases} \tag{3.45}$$

Finally, we compute the flux $D \int_{\partial\mathcal{B}} \nabla c \cdot d\boldsymbol{\sigma}$ to the surface, from which we obtain the dimension dependence of the reaction rate to a sphere is radius R:

$$K(t) \sim \begin{cases} D \times (Dt)^{(d-2)/2} & d < 2; \\[3ex] \dfrac{4\pi D}{\ln\left(Dt/R^2\right)} & d = 2; \\[3ex] DR^{d-2} & d > 2. \end{cases} \tag{3.46}$$

The rate is time independent and grows with radius as R^{d-2} for $d > 2$; for $d \le 2$ the rate is *independent* of the sphere radius and decreases as a power law in time when $d < 2$.