Chapter 2

RANDOM WALK/DIFFUSION

Because the random walk and its continuum diffusion limit underlie so many fundamental processes in non-equilibrium statistical physics, we give a brief introduction to this central topic. There are several complementary ways to describe random walks and diffusion, each with their own advantages.

2.1 Langevin Equation

We begin with the phenomenological Langevin equation that represents a minimalist description for the stochastic motion of a random walk. We mostly restrict ourselves to one dimension, but the generalization to higher dimensions is straightforward. Random walk motion arises, for example, when a microscopic bacterium is placed in a fluid. The bacterium is constantly buffeted on a very short time scale by the random collisions with fluid molecules. In the Langevin approach the effect of these rapid collisions is represented by an effective, but stochastic, external force $\eta(t)$. On the other hand, if the bacterium had a non-zero velocity in the fluid, there would be a systematic frictional force proportional to the velocity that would bring the bacterium to rest. Under the influence of these two forces, Newton's second law for the motion of the bacterium leads to the Langevin equation

$$m\frac{dv}{dt} = -\gamma v + \eta(t). \tag{2.1}$$

This equation is very different from the deterministic equation of motion that one normally encounters in mechanics. Because the stochastic force is so rapidly changing with time, the actual trajectory of the particle contains too much information. The velocity changes every time there is a collision between the bacterium and a fluid molecule; for a particle of linear dimension 1μm, there are of the order of 10^{20} collisions per second and it is pointless to follow the motion on such a short time scale. For this reason, it is more meaningful physically to study the trajectory that is averaged over longer times. To this end, we need to specify the statistical properties of the random force. Because the force is a result of molecular collisions, it is natural to assume that the force $\eta(t)$ is a random function of time with zero mean, $\langle\eta(t)\rangle = 0$. Here the angle brackets denote the time average. Because of the rapidly fluctuating nature of the force, we also assume that there is no correlation between the force at two different times, so that $\langle\eta(t)\eta(t')\rangle = 2D\gamma^2\delta(t-t')$. As a result, the product of the forces at two different times has a mean value of zero. However, the *mean-square* force at any time has the value D. This statement merely states that the average *magnitude* of the force is well-defined.

In the limit where the mass of the bacterium is sufficiently small that it may be neglected, we obtain an even simpler equation for the position of the bacterium:

$$\frac{dx}{dt} = \frac{1}{\gamma}\eta(t) \equiv \xi(t). \tag{2.2}$$

In this limit of no inertia ($m = 0$) the instantaneous velocity equals the force. In spite of this strange feature, Eq. (2.2) has a simple interpretation—the change in position is a randomly fluctuating variable. This corresponds to a naive view of what a random walk actually does; at each step the position changes by a random amount.

One of the advantages of the Langevin equation description is that average values of the moments of the position can be obtained quite simply. Thus formally integrating Eq. (2.1), we obtain

$$x(t) = \int_0^t \xi(t')\, dt'. \tag{2.3}$$

Because $\langle \xi(t) \rangle = 0$, then $\langle x(t) \rangle = 0$. However, the mean-square displacement is non-trivial. Formally,

$$\langle x(t)^2 \rangle = \int_0^t \int_0^t \langle \xi(t')\xi(t'') \rangle\, dt'\, dt''. \tag{2.4}$$

Using $\langle \xi(t)\xi(t') \rangle = 2D\delta(t-t')$, it immediately follows that $\langle x(t)^2 \rangle = 2Dt$. Thus we recover the classical result that the mean-square displacement grows linearly in time. Furthermore, we can identify D as the diffusion coefficient. The dependence of the mean-square displacement can also be obtained by dimensional analysis of the Langevin equation. Because the delta function $\delta(t)$ has units of $1/t$ (since the integral $\int \delta(t)\, dt = 1$), the statement $\langle \xi(t)\xi(t') \rangle = 2D\delta(t-t')$ means that ξ has the units $\sqrt{D/t}$. Thus from Eq. (2.3), $x(t)$ must have units of $\sqrt{Dt}$.

The Langevin equation has the great advantage of simplicity. With a bit more work, it is possible to determine higher moments of the position. Furthermore there is a standard prescription to determine the underlying and more fundamental probability distribution of positions. This prescription involves writing a continuum Fokker-Planck equation for the evolution of this probability distribution. The Fokker-Planck equation is in the form of a convection-diffusion equation, namely, the diffusion equation augmented by a term that accounts for a global bias in the stochastic motion. The coefficients in this Fokker-Planck equation are directly related to the parameters in the original Langevin equation. The Fokker-Planck equation can be naturally viewed as the continuum limit of the *master equation*, which represents perhaps the most fundamental way to describe a stochastic process. We will not pursue this conventional approach because we are generally more interested in developing direct approaches to write the master equation.

2.2 Master Equation for the Probability Distribution

Discrete space and time

Consider a random walker on a one-dimensional lattice that hops to the right with probability p or to the left with probability $q = 1 - p$ in a single step. Let $P(x, N)$ be the probability that the particle is at site x at the Nth time step. Then evolution of this occupation probability is described by the master equation

$$P(x, N+1) = p\, P(x-1, N) + q\, P(x+1, N). \tag{2.5}$$

Because of translational invariance in both space and time, it is expedient to solve this equation by transform techniques. One strategy is to Fourier transform in space *and* write the generating function (sometimes called the z-transform). Thus multiplying the master equation by $z^{N+1}\, e^{ikx}$ and summing over all N and x gives

$$\sum_{N=0}^{\infty} \sum_{x=-\infty}^{\infty} z^{N+1} e^{ikx} \left[P(x, N+1) = p\, P(x-1, N) + q\, P(x+1, N) \right]. \tag{2.6}$$

We now define the joint transform—the Fourier transform of the generating function

$$P(k, z) = \sum_{N=0}^{\infty} z^N \sum_{x=-\infty}^{\infty} e^{ikx}\, P(x, N).$$

In what follows, either the arguments of a function or the context (when obvious) will be used to distinguish transforms from the function itself. The left-hand side of (2.6) is just the joint transform $P(k, z)$, except that the term $P(x, N = 0)$ is missing. Similarly, on the right-hand side the two factors are just the generating

function at $x-1$ and at $x+1$ times an extra factor of z. The Fourier transform then converts these shifts of ± 1 in the spatial argument to the phase factors $e^{\pm ik}$, respectively. Thus

$$P(k,z) - \sum_{x=-\infty}^{\infty} P(x, N=0) e^{ikx} = z u(k) P(k,z), \tag{2.7}$$

where $u(k) = p\, e^{ik} + q\, e^{-ik}$ is the Fourier transform of the single-step hopping probability. For the initial condition of a particle initially at the origin, $P(x, N=0) = \delta_{x,0}$, the joint transform becomes

$$P(k,z) = \frac{1}{1 - z u(k)}. \tag{2.8}$$

We now invert the transform to reconstruct the probability distribution. Expanding $P(k,z)$ in a Taylor series, the Fourier transform of the generating function is simply $P(k,N) = u(k)^N$. Then the inverse Fourier transform is

$$P(x,N) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{-ikx}\, u(k)^N\, dk, \tag{2.9}$$

To evaluate the integral, we write $u(k)^N = (p\, e^{ik} + q\, e^{-ik})^N$ in a binomial series. This gives

$$P(x,N) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{-ikx} \sum_{m=0}^{N} \binom{N}{m} p^m\, e^{ikm}\, q^{N-m}\, e^{-ik(N-m)}\, dk. \tag{2.10}$$

The only non-zero term is the one with $m = (N+x)/2$ in which all the phase factors cancel. This leads to the classical binomial probability distribution of a discrete random walk

$$P(x,N) = \frac{N!}{(\frac{N+x}{2})!(\frac{N-x}{2})!}\, p^{\frac{N+x}{2}}\, q^{\frac{N-x}{2}}. \tag{2.11}$$

Finally, using Stirling's approximation, the binomial approaches the Gaussian probability distribution in the long-time limit,

$$P(x,N) \to \frac{1}{\sqrt{2\pi N p q}} e^{-[x-N(p-q)]^2/2Npq}. \tag{2.12}$$

This result is a particular realization of the *central-limit theorem*—namely, that the asymptotic probability distribution of an N-step random walk is *independent* of the form of the single step distribution, as long as the mean displacement $\langle x \rangle$ and the mean-square displacement $\langle x^2 \rangle$ in a single step are finite; we will present the central limit theorem in Sec. 2.3.

Continuous time

Alternatively, we can treat the random walk in continuous time by replacing N by continuous time t, the increment $N \to N+1$ with $t \to t + \delta t$, and finally Taylor expanding the master equation (2.5) to first order in δt. These steps give

$$\frac{\partial P(x,t)}{\partial t} = w_+ P(x-1,t) + w_- P(x+1,t) - w_0 P(x,t) \tag{2.13}$$

where $w_+ = p/\delta t$ and $w_- = q/\delta t$ are the hopping rates to the right and to the left, respectively, and $w_0 = 1/\delta t$ is the total hopping rate from each site. This hopping process satisfies detailed balance, as the total hopping rates *to* a site equal the total hopping rate *from* the same site.

Again, the simple structure of Eq. (2.13) calls out for applying the Fourier transform. After doing so, the master equation becomes

$$\frac{dP(k,t)}{dt} = (w_+ e^{ik} + w_- e^{-ik} - w_0)\, P(k,t) \equiv w(k)\, P(k,t). \tag{2.14}$$

For the initial condition $P(x, t=0) = \delta_{x,0}$, the corresponding Fourier transform is $P(k, t=0) = 1$, and the solution to Eq. (2.14) is $P(k,t) = e^{w(k)t}$. To invert this Fourier transform, let's consider the symmetric case

where $w_\pm = 1/2$ and $w_0 = 1$. Then $w(k) = w_0(\cos k - 1)$, and we use the generating function representation for the modified Bessel function of the first kind of order x, $e^{z\cos k} = \sum_{x=-\infty}^{\infty} e^{ikx} I_x(z)$ (10), to give

$$P(k,t) = e^{-t} \sum_{x=-\infty}^{\infty} e^{ikx} I_x(t), \tag{2.15}$$

from which we immediately obtain

$$P(x,t) = e^{-t} I_x(t). \tag{2.16}$$

To determine the probability distribution in the scaling limit where x and t both diverge but x^2/t remains finite, it is more useful to Laplace transform the master equation (2.13) to give

$$sP(x,s) - P(x,t=0) = \frac{1}{2}P(x+1,s) + \frac{1}{2}P(x-1,s) - P(x,s). \tag{2.17}$$

For $x \neq 0$, we solve the resulting difference equation, $P(x,s) = a[P(x+1,s)+P(x-1,s)]$, with $a = 1/2(s+1)$, by assuming the exponential solution $P(x,s) = A\lambda^x$ for $x > 0$; by symmetry $P(x,s) = A\lambda^{-x}$ for $x < 0$. Substituting $P(x,s) = A\lambda^{-x}$ into the recursion for $P(x,s)$ gives a quadratic characteristic equation for λ whose solution is $\lambda_\pm = (1 \pm \sqrt{1-4a^2})/2a$. For all $s > 0$, $\lambda_\pm$ are both real and positive, with $\lambda_+ > 1$ and $\lambda_- < 1$. We reject the solution that grows exponentially with x, thus giving $P_x = A\lambda_-^x$. Finally, we obtain the constant A from the $x = 0$ boundary master equation

$$sP(0,s) - 1 = \frac{1}{2}P(1,s) + \frac{1}{2}P(-1,s) - P(0,s) = P(1,s) - P(0,s). \tag{2.18}$$

The -1 on the left-hand side arises from the initial condition, and the second equality follows by spatial symmetry. Substituting $P(n,s) = A\lambda_-^x$ into Eq. (2.18) gives A, from which we finally obtain

$$P(x,s) = \frac{1}{s+1-\lambda_-}\,\lambda_-^x. \tag{2.19}$$

This Laplace transform diverges at $s = 0$; consequently, we may easily obtain the interesting asymptotic behavior by considering the limiting form of $P(x,s)$ as $s \to 0$. Since $\lambda_- \approx 1 - \sqrt{2s}$ as $s \to 0$, we find

$$P(x,s) \approx \frac{(1-\sqrt{2s})^x}{\sqrt{2s}+s} \sim \frac{e^{-x\sqrt{2s}}}{\sqrt{2s}}. \tag{2.20}$$

We now invert the Laplace transform $P(x,t) = \int_{s_0-i\infty}^{s_0+i\infty} P(x,s)\, e^{st}\, ds$ by using the integration variable $u = \sqrt{s}$. This immediately leads to the Gaussian probability distribution quoted in Eq. (2.26) for the case $\langle x \rangle = 0$ and $\langle x^2 \rangle = 1$.

Continuous space and time

When both space and time are continuous, we expand the master equation (2.5) in a Taylor series to lowest non-vanishing order—second order in space x and first order in time t—we obtain the fundamental *convection-diffusion equation*,

$$\frac{\partial P(x,t)}{\partial t} + v\frac{\partial P(x,t)}{\partial x} = D\,\frac{\partial^2 P(x,t)}{\partial x^2}, \tag{2.21}$$

for the concentration $P(x,t)$. Here $v = (p-q)\delta x/\delta t$ is the bias velocity and $D = \delta x^2/2\delta t$ is the diffusion coefficient. Notice that the factor v/D diverges as $1/\delta x$ in the continuum limit. Therefore the convective term $\frac{\partial P}{\partial x}$ invariably dominates over the diffusion term $\frac{\partial^2 P}{\partial x^2}$. To construct a non-pathological continuum limit, the bias $p-q$ must be proportional to δx as $\delta x \to 0$ so that both the first- and second-order spatial derivative terms are simultaneously finite. For the diffusion equation, we obtain a non-singular continuum limit merely by ensuring that the ratio $\delta x^2/\delta t$ remains finite as both δx and δt approach zero.

To solve the convection-diffusion equation, we introduce the Fourier transform $P(k,t) = \int P(x,t)\, e^{ikx}\, dx$ to simplify the convection-diffusion equation to $\dot{P}(k,t) = (ikv - Dk^2)P(k,t)$, with solution

$$P(k,t) = P(k,0)e^{(ikv-Dk^2)t} = e^{(ikv-Dk^2)t}, \tag{2.22}$$

for the initial condition $P(x, t = 0) = \delta(x)$. We then obtain the probability distribution by inverting the Fourier transform to give, by completing the square in the exponential,

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\, e^{-(x-vt)^2/4Dt}. \tag{2.23}$$

Alternatively, we may first Laplace transform in the time domain. For the convection-diffusion equation, this yields the ordinary differential equation

$$sP(x,s) - \delta(x) + vP(x,s) = DP''(x,s), \tag{2.24}$$

where the delta function reflects the initial condition. This equation may be solved separately in the half-spaces $x > 0$ and $x < 0$. In each subdomain Eq. (2.24) reduces to a homogeneous constant-coefficient equation that has exponential solutions. The corresponding solution for the entire line has the form $c_+(x,s) = A_+ e^{-\alpha_- x}$ for $x > 0$ and $c_-(x,s) = A_- e^{\alpha_+ x}$ for $x < 0$, where $\alpha_\pm = \left(v \pm \sqrt{v^2 + 4Ds}\right)/2D$ are the roots of the characteristic polynomial. We join these two solutions at the origin by applying the joining conditions of continuity of $P(x,s)$ at $x = 0$, and a discontinuity in $\frac{\partial c}{\partial x}$ at $x = 0$ whose magnitude is determined by integrating Eq. (2.24) over an infinitesimal domain which includes the origin. The continuity condition trivially gives $A_+ = A_- \equiv A$, and the condition for the discontinuity in $P(x,s)$ is $D\left(P'_+|_{x=0} - P'_-|_{x=0}\right) = -1$. This gives $A = 1/\sqrt{v^2 + 4Ds}$. Thus the Laplace transform of the probability distribution is

$$c_\pm(x,s) = \frac{1}{\sqrt{v^2 + 4Ds}}\, e^{-\alpha_\mp |x|}. \tag{2.25}$$

For zero bias, this coincides with Eq. (2.20) and thus recovers the Gaussian probability distribution.

2.3 Central Limit Theorem

The central limit theorem states that the asymptotic $N \to \infty$ probability distribution of an N-step random walk is the universal Gaussian function

$$P(x,N) \to \frac{1}{\sqrt{2\pi N\sigma^2}}\; e^{-(x-\langle x\rangle)^2/2N\sigma^2}, \tag{2.26}$$

where $\langle x\rangle$ and $\langle x^2\rangle$ are respectively the mean and the mean-square displacement for a single step of the walk, and $\sigma^2 = \langle x^2\rangle - \langle x\rangle^2$. A necessary condition for the central limit theorem to hold is that each step of the walk is an independent identically distributed random variable that is drawn from a distribution $p(x)$ such that $\langle x\rangle$ and $\langle x^2\rangle$ are both finite. We now give a simple derivation of this fundamental result. For simplicity we give the derivation for a one-dimensional system, but this derivation can immediately be extended to any dimension.

When the steps of the random walk are independent, the probability distribution after N steps is related to the probability after $N-1$ steps by the recursion (also known as the Chapman-Kolmogorov equation)

$$P_N(x) = \int P_{N-1}(x')p(x' \to x)\, dx'. \tag{2.27}$$

This equation merely states that to reach x in N steps, the walk first reaches an arbitrary point x' in $N-1$ steps and then makes a transition from x' to x with probability $p(x' \to x)$. It is now useful to introduce the Fourier transforms

$$f(k) = \int_{-\infty}^{\infty} f(x)e^{ikx}\, dx \qquad f(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(k)e^{-ikx}\, dk$$

to transform Eq. (2.27) to the algebraic equation $P_N(k) = P_{N-1}(k)p(k)$ that we iterate to give $P_N(k) = P_0(k)p(k)^N$. At this stage, there is another mild condition for the central limit theorem to hold—the initial condition cannot be too long range in space. The natural condition is for the random walk to start at the origin, $P_0(x) = \delta x, 0$ for which the Fourier transform of the initial probability distribution is simply $P_0(k) = 1$. Then the Fourier transform of the probability distribution is simply

$$P_N(k) = p(k)^N, \tag{2.28}$$

so that

$$P_N(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} p(k)^N\, e^{-ikx}\, dk. \tag{2.29}$$

To invert the Fourier transform, we now use the fact that the first two moments of $p(x)$ are finite to write the Fourier transform $p(k)$ as

$$\begin{aligned} p(k) &= \int_{-\infty}^{\infty} p(x)\, e^{ikx}\, dx \\ &= \int_{-\infty}^{\infty} p(x)\left[1 + ikx - \frac{1}{2}k^2x^2 + \ldots\right] dx \\ &= 1 + ik\langle x\rangle - \frac{1}{2}k^2\langle x^2\rangle + \ldots \end{aligned}$$

Now the probability distribution is

$$\begin{aligned} P_N(x) &\sim \frac{1}{2\pi}\int_{-\infty}^{\infty} [1 + ik\langle x\rangle - \frac{1}{2}k^2\langle x^2\rangle]^N\, e^{-ikx}\, dx \\ &\sim \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{N\ln[1+ik\langle x\rangle - \frac{1}{2}k^2\langle x^2\rangle]}\, e^{-ikx}\, dx \\ &\sim \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{N[1+ik\langle x\rangle - \frac{k^2}{2}(\langle x^2\rangle - \langle x\rangle^2)]}\, e^{-ikx}\, dx \end{aligned} \tag{2.30}$$

We now complete the square in the exponent and perform the resulting Gaussian integral to arrive at the fundamental result

$$P_N(x) \sim \frac{1}{\sqrt{2\pi N\sigma^2}}\, e^{-(x-N\langle x\rangle)^2/2N\sigma^2}. \tag{2.31}$$

2.4 Connection to First-Passage Properties

An intriguing property of random walks is the transition between *recurrence* and *transience* as a function of the spatial dimension d. Recurrence means that a random walk is certain to return to its starting point; this occurs for $d \le 2$. Conversely, $d > 2$ the random walk is transient in that there is positive probability for a random walk to never return to its starting point. It is striking that the spatial dimension—and not any other features of a random walk—is the only parameter that determines this transition.

The qualitative explanation for this transition is quite simple. Consider the trajectory of a typical random walk. After a time t a random walk explores a roughly spherical domain of radius $\sqrt{Dt}$ while the total number of sites visited during this walk equals to t. Therefore the density of visited sites within an exploration sphere is $\rho \propto t/t^{d/2} \propto t^{1-d/2}$ in d dimensions. For $d < 2$ this density grows with time; thus a random walk visits each site within the sphere infinitely often and is certain to return to its starting point. On the other hand, for $d > 2$, the density decreases with time and so some points within the exploration sphere never get visited. The case $d = 2$ is more delicate but turns out to be barely recurrent.

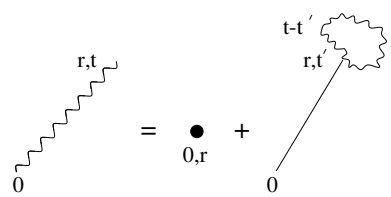

Figure 2.1: Diagrammatic relation between the occupation probability of a random walk (propagation is represented by a wavy line) and the first-passage probability (straight line).

We now present a simple-minded approach to understand this transition between recurrence and transience. Let $P(\mathbf{r},t)$ be probability that a random walk is at $\mathbf{r}$ at time t when it starts at the origin. Similarly, let $F(\mathbf{r},t)$ be the *first-passage probability*, namely, the probability that the random walk visits $\mathbf{r}$ *for the first time* at time t with the same initial condition.

For a random walk to be at $\mathbf{r}$ at time t, the walk must *first* reach $\mathbf{r}$ at some earlier time step t' and then return to $\mathbf{r}$ after $t-t'$ (Fig. 2.1). This connection between $F(\mathbf{r},t)$ and $P(\mathbf{r},t)$ may therefore be expressed as the convolution

$$P(\mathbf{r},t) = \delta_{\mathbf{r},0}\,\delta_{t,0} + \int_0^t F(\mathbf{r},t')\,P(0,t-t')\,dt'. \tag{2.32}$$

The delta function term accounts for the initial condition. The second term accounts for the ways that a walk can be at $\mathbf{r}$ at time t. To reach r at time t, the walk must first reach r at some time $t' \le t$. Once a first passage has occurred, the walk must return to r exactly at time t (and the walk can also return to r at earlier times, so long as the walk is also at r at time t). Because of the possibility of multiple visits to $\mathbf{r}$ between time t' and t, the return factor involves P rather than F. This convolution equation is most conveniently solved in terms of the Laplace transform to give $P(\mathbf{r},s) = \delta_{\mathbf{r},0} + F(\mathbf{r},s)P(0,s)$. Thus we obtain the fundamental connection

$$F(\mathbf{r},s) = \begin{cases} \dfrac{P(\mathbf{r},s)}{P(0,s)}, & \mathbf{r} \neq 0 \\ 1 - \dfrac{1}{P(0,s)}, & \mathbf{r} = 0, \end{cases} \tag{2.33}$$

in which the Laplace transform of the first-passage probability is determined by the corresponding transform of the probability distribution of diffusion $P(\mathbf{r},t)$.

We now use the techniques of Section A.2 to determine the time dependence of the first-passage probability in terms of the Laplace transform for the occupation probability. For isotropic diffusion, $P(\mathbf{r}=0,t) = (4\pi Dt)^{-d/2}$ in d dimensions and the Laplace transform is $P(0,s) = \int_0^\infty P(0,t)\,e^{-st}\,dt$. As discussed in Section A.2, this integral has two fundamentally different behaviors, depending on whether $\int^\infty P(0,t)\,dt$ diverges or converges. In the former case, we apply the last step in Eq. (A.6) to obtain

$$P(0,s) \propto \int^{t^*=1/s} (4\pi Dt)^{-d/2}\,dt \sim \begin{cases} \mathcal{A}_d (t^*)^{1-d/2} = \mathcal{A}_d s^{d/2-1}, & d<2 \\ \mathcal{A}_2 \ln t^* = -\mathcal{A}_2 \ln s, & d=2, \end{cases} \tag{2.34}$$

where the dimension-dependent prefactor $\mathcal{A}_d$ is of the order of 1 and does not play any role in the asymptotic behavior.

For $d>2$, the integral $\int^\infty P(0,t)\,dt$ converges and one has to be more careful to extract the asymptotic behavior by studying $P(0,1) - P(0,s)$. By such an approach, it is possible to show that $P(0,s)$ has the asymptotic behavior

$$P(0,s) \sim (1-\mathcal{R})^{-1} + B_d s^{d/2-1} + \ldots, \qquad d>2, \tag{2.35}$$

where $\mathcal{R}$ is the *eventual return* probability, namely, the probability that a diffusing particle random walk ultimately reaches the origin, and B_d is another dimension-dependent constant of the order of 1. Using these results in Eq. (2.33), we infer that the Laplace transform for the first-passage probability has the asymptotic behaviors

$$F(0,s) \sim \begin{cases} 1 - A_d s^{1-d/2}, & d<2 \\ 1 + A_2 (\ln s)^{-1}, & d=2 \\ \mathcal{R} + B_d (1-\mathcal{R})^2 s^{d/2-1}, & d>2, \end{cases} \tag{2.36}$$

From this Laplace transform, we determine the time dependence of the survival probability by approximation (A.9); that is,

$$F(0, s = 1 - 1/t^*) \sim \int_0^{t^*} F(0,t)\,dt \equiv T(t^*), \tag{2.37}$$

where $T(t)$ is the probability that the particle gets trapped (reaches the origin) by time t. For what follows, we also define the survival probability $S(t) = 1 - T(t)$, which is simply the probability that the particle has

not reached the origin by time t. Here the trick of replacing an exponential cutoff by a sharp cutoff provides an extremely easy way to invert the Laplace transform. From Eqs. (2.36) and (2.37) we thus find

$$S(t) \sim \begin{cases} A_d t^{d/2-1}, & d<2 \\ A_2 (\ln t)^{-1}, & d=2 \\ (1-\mathcal{R}) + C_d\,(1-\mathcal{R})^2\, t^{1-d/2}, & d>2. \end{cases} \tag{2.38}$$

where C_d is another d-dependent constant of the order of 1. Finally, the time dependence of the first-passage probability may be obtained from the basic relation $1 - S(t) \sim \int^t F(0,t)\,dt$ to give

$$F(0,t) = -\frac{\partial S(t)}{\partial t} \propto \begin{cases} t^{d/2-2,} & d<2 \\ t^{-1}(\ln t)^{-2}, & d=2 \\ t^{-d/2}, & d>2. \end{cases} \tag{2.39}$$

It is worth emphasizing several important physical ramifications of the above first-passage properties. First, the asymptotic behavior is determined by the spatial dimension only and that there is a dramatic change in behavior when $d = 2$. For $d \le 2$, the survival probability $S(t)$ ultimately decays to zero. This means that a random walk is *recurrent* and is certain to eventually return to its starting point, and indeed visit *any* site of an infinite lattice. Finally, because a random walk has no memory, it is "renewed" every time a specific lattice site is reached. Thus recurrence also implies that every lattice site is visited infinitely often.

We can give is a simple physical explanation for this efficient visitation of sites. After a time t a random walk explores a roughly spherical domain of radius $\sqrt{Dt}$. The total number of sites visited during this exploration is also proportional to t. Consequently in d dimensions, the density of visited sites within this exploration sphere is $\rho \propto t/t^{d/2} \propto t^{1-d/2}$. For $d < 2$, ρ diverges as $t \to \infty$ and a random walk visits each site within the sphere infinitely often. This feature is termed *compact exploration.* Paradoxically, although every site is visited with certainty, these visitations take forever because the mean time to return to the origin, $\langle t \rangle = \int t\, F(0,t)\,dt$, diverges for all $d \le 2$.

Finally, we outline a useful technique to compute *where* on a boundary is a diffusing particle absorbed and *when* does this absorption occur. This method will provide helpful in understanding finite-size effect in reaction kinetics. For simplicity, consider a symmetric nearest-neighbor random walk in the finite interval $[0,1]$. Let $\mathcal{E}_+(x)$ be the probability that a particle, which starts at x, eventually hits $x = 1$ *without* hitting $x = 0$. This eventual hitting probability $\mathcal{E}_+(x)$ is obtained by summing the probabilities for all paths that start at x and reach 1 without touching 0. Thus

$$\mathcal{E}_+(x) = \sum_p \mathcal{P}_p(x), \tag{2.40}$$

where $\mathcal{P}_p(x)$ denotes the probability of a path from x to 1 that does not touch 0. The sum over all such paths can be decomposed into the outcome after one step (the factors of 1/2 below) and the sum over all path remainders from the location after one step to 1. This gives

$$\mathcal{E}_+(x) = \sum_p \left[\frac{1}{2}\,\mathcal{P}_p(x+\delta x) + \frac{1}{2}\,\mathcal{P}_p(x-\delta x)\right] = \frac{1}{2}[\mathcal{E}_+(x+\delta x) + \mathcal{E}_+(x-\delta x)]. \tag{2.41}$$

By a simple rearrangement, this equation is equivalent to

$$\Delta^{(2)}\mathcal{E}_+(x) = 0, \tag{2.42}$$

where $\Delta^{(2)}$ is the second-difference operator. Notice the opposite sense of this recursion formula compared to the master equation Eq. (2.5) for the probability distribution. Here $\mathcal{E}_+(x)$ is expressed in terms of *output from* x, while in the master equation, the occupation probability at x is expressed in terms of *input to* x. For this reason, Eq. (2.41) is sometimes referred to as a backward master equation. This backward equation is just the Laplace equation and gives a hint of the deep relation between first-passage properties, such as the exit probability, and electrostatics. Equation (2.42) is subject to the boundary conditions $\mathcal{E}_+(0) = 0$

and $\mathcal{E}_+(1) = 1$; namely if the walk starts at 1 it surely exits at 1 and if the walk starts at 0 it has no chance to exit at 1. In the continuum limit, Eq. (2.42) becomes the Laplace equation $\mathcal{E}'' = 0$, subject to appropriate boundary conditions. We can now transcribe well-known results from electrostatics to solve the exit probability. For the one dimensional interval, the result is remarkably simple: $\mathcal{E}_+(x) = x$!

This exit probability also represents the solution to the classic "gambler's ruin" problem: let x represent your wealth that changes by a small amount dx with equal probability in a single bet with a Casino. You continue to bet as long as you have money. You lose if your wealth hits zero, while you break the Casino if your wealth reaches 1. The exit probability to $x = 1$ is the same as the probability that you break the Casino.

Let's now determine the mean time for a random walk to exit a domain. We focus on the *unconditional* exit time, namely, the time for a particle to reach *any* point on the absorbing boundary of this domain. For the symmetric random walk, let the time increment between successive steps be δt, and let $t(x)$ denote the average exit time from the interval $[0, 1]$ when a particle starts at x. The exit time is simply the time for each exit path times the probability of the path, averaged over all trajectories, and leads to the analog of Eq. (2.40)

$$t(x) = \sum_p \mathcal{P}_p(x)\, t_p(x), \tag{2.43}$$

where $t_p(x)$ is the exit time of a specific path to the boundary that starts at x.

In analogy with Eq. (2.41), this mean exit time obeys the recursion

$$t(x) = \frac{1}{2}\left[(t(x+\delta x)+\delta t) + (t(x-\delta x)+\delta t)\right], \tag{2.44}$$

This recursion expresses the mean exit time starting at x in terms of the outcome one step in the future, for which the initial walk can be viewed as restarting at either $x+\delta x$ or $x-\delta x$, each with probability 1/2, but also with the time incremented by δt. This equation is subject to the boundary conditions $t(0) = t(1) = 0$; the exit time equals zero if the particle starts at the boundary. In the continuum limit, this recursion formula reduces to the Poisson equation $Dt''(x) = -1$. For diffusion in a d-dimensional domain with absorption on a boundary B, the corresponding Poisson equation for the exit time is $D\nabla^2 t(\mathbf{r}) = -1$, subject to the boundary condition $t(\mathbf{r}) = 0$ for $\mathbf{r} \in B$. Thus the determination of the mean exit time has been recast as a time-independent electrostatic problem! For the example of the unit interval, the solution to the Laplace equation is just a second-order polynomial in x. Imposing the boundary conditions immediately leads to the classic result

$$t(x) = \frac{1}{2D}\, x(1-x). \tag{2.45}$$

First passage probability and the gambler's ruin problem

Consider a random walk in a finite interval of length N. The two boundary sites are absorbing, *i.e.*, the random walker immediately disappears upon reaching these sites. Suppose that the starting position of the random walk is n, with $0 \le n \le N$. What is F_n, the probability that the walker first reaches the boundary at site N? We can write a simple recursion formula for the first-passage probability. With probability 1/2, the walk steps to site $n-1$, at which point the exit probability to site N is F_{n-1}. Similarly, the walk steps to site $n+1$ with probability 1/2, where the exit probability is F_{n+1}. Thus the first passage probability satisfies the discrete Poisson equation

$$F_n = \frac{1}{2}(F_{n-1} + F_{n+1}), \tag{2.46}$$

with the boundary conditions $F_0 = 0$ and $F_N = 1$. The solution is simple:

$$F_n = \frac{n}{N}. \tag{2.47}$$

This first passage probability also solves a neat probability theory problem. In a fair coin-toss game, the probability that a gambler ruins a Casino equals the wealth of the gambler divided by the combined wealth of the gambler and casino. Gambling is most definitely a bad idea...

2.5 The Reaction Rate

Suppose that you wanted to hit the side of a barn using an ensemble of blind riflemen that fire bullets in random directions as your incident beam. What is the rate at which the barn is hit? Theorists that we are, let's model the barn as a sphere of radius R. A patently obvious fact is that if the radius of the barn is increased, the number of bullets that hit our theoretical barn increases as its cross-sectional area. In d spatial dimensions, the cross section therefore scales as R^{d-1}. Now suppose that we take away the rifles from our blind marksmen and give them the task of hitting the barn simply by wandering around. Surprisingly, the rate at which the blind riflemen diffuse to the barn is proportional to R^{d-2} for $d > 2$. Thus in the physical case of 3 dimensions, the absorption rate is proportional to the sphere radius rather than to its cross section! Even more striking— for $d \leq 2$ the absorption rate no longer depends on the radius of the absorbing sphere. The rate at which diffusing particles hit an absorbing sphere is the underlying mechanism of diffusion-controlled reactions. Because of the centrality of this topic to reaction kinetics and because it represents a nice application of first-passage ideas, we now determine this reaction rate.

As in the original Smoluchowski theory for the reaction rate, we fix a spherical absorbing particle of mass m_i radius R_i at the origin, while a gas of non-interacting particles each of mass m_j and radii R_j freely diffuses outside the sphere. The separation between the absorbing sphere and a background particle diffuses with diffusion coefficient $D_i + D_j$, where D_i is the diffusion coefficient of a droplet of radius R_i. When the separation first reaches $a = R_i + R_j$, reaction occurs. The reaction rate is then identified as the flux to an absorbing sphere of radius a by an effective particle with diffusivity $D = D_i + D_j$.

The concentration of background particles around the absorbing sphere thus obeys the diffusion equation

$$\frac{\partial c(\vec{r},t)}{\partial t} = D\nabla^2 c(\vec{r},t), \tag{2.48}$$

subject to the initial condition $c(\vec{r}, t = 0) = 1$ for $r > a$ and the boundary conditions $c(r = a, t) = 0$ and $c(r \to \infty, t) = 1$. The reaction rate is then identified with the integral of the flux over the sphere surface

$$K(t) = -D \int_S \Big| \frac{\partial c(\vec{r},t)}{\partial r} \Big|_{r=a} d\Omega. \tag{2.49}$$

There are two regimes of behavior as a function of the spatial dimension. For $d > 2$, the loss of reactants at the absorbing sphere is sufficiently slow that it is replenished by the re-supply from larger distances. A steady state is thus reached and the reaction rate K is finite. In this case, the reaction rate can be determined more simply by solving the time-independent Laplace equation, rather than the diffusion equation (2.48).

The solution to the Laplace equation with the above initial and boundary conditions is

$$c(r) = 1 - \left(\frac{a}{r}\right)^{d-2}.$$

The flux is then $-D\frac{\partial c}{\partial r}|_{r=a} = D(d-2)/a$ and the total current is the integral of this flux over the surface of the sphere $K = (d-2)\Omega_d\, Da^{d-2}$, where $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the area of a unit sphere in d dimensions. We translate this flux into the reaction kernel for aggregation by expressing a and D in terms of the parameters of the constituent reactants to give

$$K_{ij} = (d-2)\Omega_d\, (D_i + D_j)(R_i + R_j)^{d-2}. \tag{2.50}$$

We can express this result as a function of reactant masses only for the physical case of three dimension by using $R_i \propto i^{1/3}$, while for the diffusion coefficient, we use the Einstein-Stokes relation $D_i = kT/(6\pi\eta R_i) \propto i^{-1/3}$, where kT is the thermal energy and η is the viscosity coefficient to obtain

$$K_{ij} \propto \frac{2kT}{3\eta}\, (R_i^{-1} + R_j^{-1})(R_i + R_j). \tag{2.51}$$

What happens for $d < 2$? We could solve the diffusion equation with the absorbing boundary condition and the unit initial condition, from which the time-dependent flux and thereby a time-dependent reaction rate

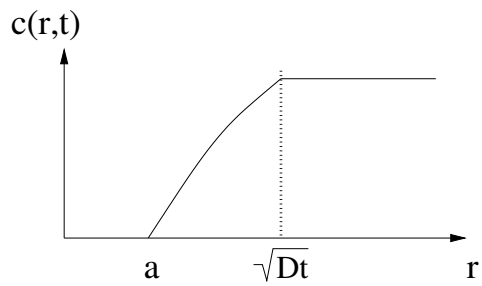

Figure 2.2: Sketch of the concentration about an absorbing sphere according to the quasi-static approximation. The near- and far-zone concentrations match at $r = \sqrt{Dt}$.

can be deduced. However, it is simpler and more revealing to apply the general *quasi-static* approximation. Because of its simplicity and general utility, we now present the quasi-static calculation of the reaction rate. The basis of the quasi-static approximation is that the region exterior to the absorbing sphere naturally divides into "near" and "far" zones. In the near zone, which extends to a distance $\sqrt{Dt}$ from the sphere, diffusing particles have ample time to explore this near zone thoroughly and the concentration is nearly time independent. In the complementary far zone there is negligible depletion because diffusing particles that are more distant than $\sqrt{Dt}$ typically will not hit the sphere in a time t. Thus in the far zone the concentration $c(r) = 1$ for $r > \sqrt{Dt}$.

Based on this picture, we merely solve the Laplace equation in the near zone $a < r < \sqrt{Dt}$ with the *time-dependent* boundary conditions $c(r = \sqrt{Dt}) = 1$, to match to the static far-zone solution, and $c(a) = 0$. The general solution is $c(r) = A + Br^{2-d}$, and matching to the boundary conditions gives

$$c(r,t) = \frac{1-(a/r)^{d-2}}{1-(a/\sqrt{Dt})^{d-2}} \to \left(\frac{\sqrt{Dt}}{r}\right)^{d-2} \qquad t \to \infty \qquad \text{for } d = 1. \tag{2.52a}$$

For $d = 2$, we can still apply the same quasi-static approach because diffusion is still recurrent, so that a qualitatively similar depletion layer builds up around the absorbing sphere. Now, however, the general solution to the Laplace equation is $c(r) = A + B \ln r$. Apply the boundary conditions at $r = a$ and $r = \sqrt{Dt}$ leads to

$$c(r,t) = \frac{\ln(r/a)}{\ln(\sqrt{Dt}/a)} \to \frac{\ln r}{\ln t} \qquad t \to \infty \qquad \text{for } d = 2. \tag{2.52b}$$

Finally, we substitute the above expressions for the concentration into the definition of the time-dependent reaction rate from Eq. (2.49) to obtain the reaction rate.

$$K(t) \propto \begin{cases} D \times (Dt)^{(d-2)/2} & d < 2; \\ \dfrac{4\pi D}{\ln\left(Dt/a^2\right)} & d = 2; \\ Da^{d-2} & d > 2. \end{cases} \tag{2.53}$$

Notice that the rate does not depend on the cluster radius for $d \leq 2$. This surprising fact arises because of the recurrence of diffusion in $d \leq 2$ so that two diffusing particles are guaranteed to eventually meet independent of their radii.

Problems

Section 2.2

1. Find the generating function for the Fibonacci sequence, $F_n = F_{n-1} + F_{n-2}$, with the initial condition $F_0 = F_1 = 1$; that is, determine $F(z) = \sum_0^\infty F_n z^n$. Invert the generating function to find a closed form expression for F_n.

2. Consider a random walk in one dimension in which a step to the right of length 2 occurs with probability 1/3 and a step to the left of length 1 occurs with probability 2/3. Investigate the corrections to the isotropic Gaussian that characterizes the probability distribution in the long-time limit. *Hint:* Consider the behavior of moments beyond second order, $\langle x^k \rangle$ with $k > 2$.

3. Solve the gambler's ruin problem when the probability of winning in a single bet is p. The betting game is repeated until either you are broke or the casino is broken. Take the total amount of capital to be $\$N$ and you start with $\$n$. What is the probability that you will break the casino? Also determine the mean time until the betting is over (either you are broke or the Casino is broken). *More advanced:* Determine the mean time until betting is over with the condition that: (i) you are broke, and (ii) you break the Casino. Solve this problem both for fair betting and biased betting.

4. Consider the gambler's ruin problem under the assumptions that you win each bet with probability $p \neq 1/2$, but that the casino has an infinite reserve of money. What is the probability that you break the casino as a function of p? For those values of p where you break the casino, what is the average time for this event to occur?

Section 2.4

5. For $\mathbf{r} \neq 0$ and $t > 0$, explicitly verify Eq. (2.32) in one dimension.

   Solution.

Notes

The field of random walks, diffusion, and first-passage processes are classic areas of applied probability theory and there is a corresponding large literature. For the more probabilistic aspects of random walks and probability theory in general, we recommend 15; 3; 11; 9. For the theory of random walks and diffusion from a physicist's perspective, we recommend 12; 13; 14. For first-passage properties, please consult 8; 9.