Contents

1 APERITIFS 5
   1.1 Diffusion .......................................................... 5
   1.2 Single-Species Annihilation ..................................... 7
   1.3 Two-Species Annihilation ...................................... 10

2 RANDOM WALK/DIFFUSION 13
   2.1 Langevin Equation ............................................... 13
   2.2 Master Equation for the Probability Distribution .......... 14
   2.3 Connection to First-Passage Properties ..................... 17

3 AGGREGATION 21
   3.1 Exact Solutions .................................................. 22
   3.2 Theory of the Reaction Rate ................................... 31
   3.3 Scaling Theory ................................................... 34
   3.4 Extensions ......................................................... 35
      3.4.1 Exchange ...................................................... 35
      3.4.2 Aggregation with Input ................................... 37
      3.4.3 Finite Systems .............................................. 39

4 FRAGMENTATION 43
   4.1 Exact Solutions .................................................. 44
   4.2 Scaling Theory ................................................... 47
   4.3 The Shattering Transition ...................................... 50
   4.4 Fragmentation with Input ...................................... 51
   4.5 Geometrical Fragmentation ..................................... 53

5 ADSORPTION 57
   5.1 Random Sequential Adsorption .................................. 57
   5.2 Adsorption-diffusion and reaction equivalence .............. 72
   5.3 Adsorption-Desorption and slow dynamics .................... 73
   5.4 Cooperative sequential adsorption ............................. 76
   5.5 Nucleation and growth .......................................... 79

6 SPIN DYNAMICS 85
   6.1 Glauber Spin-Flip Dynamics .................................... 85
   6.2 Kawasaki spin-exchange dynamics .............................. 93
   6.3 Cluster dynamics ................................................ 95
   6.4 Extremal dynamics ............................................... 98
   6.5 Voter Model ....................................................... 102
   6.6 Disordered Spin Chains ......................................... 106
   6.7 Disordered Systems ............................................. 112
# CONTENTS

7 ANOMALOUS TRANSPORT
  7.1 The Asymmetric Exclusion Process .............................................. 115
  7.2 Random Walks in Random Environments ....................................... 120
  7.3 Random Walks in Random Velocity Fields .................................... 124

8 HYSTERESIS
  8.1 Homogeneous Ferromagnets ....................................................... 127
  8.2 Disordered Ferromagnets .......................................................... 135

9 REACTIONS
  9.1 Single-Species .............................................................................. 145
  9.2 Two Species Annihilation ............................................................ 153
  9.3 The Trapping Reaction
    9.3.1 Exact Solution in One Dimension ........................................... 158
    9.3.2 Lifshitz Argument for General Spatial Dimension .................... 160

10 COARSENING
  10.1 The Models .................................................................................. 165
  10.2 Scaling ....................................................................................... 168
  10.3 Non-conservative Dynamics ......................................................... 168

11 COLLISIONS
  11.1 Inelastic Gases .......................................................................... 175
  11.2 Lorentz Gas ................................................................................ 190
  11.3 Traffic Flows .............................................................................. 190
  11.4 Sticky Gases .............................................................................. 198
  11.5 Ballistic Annihilation .................................................................. 200

12 GROWING NETWORKS
  12.1 Models ....................................................................................... 203
  12.2 Structure of the Growing Network .............................................. 205
  12.3 Global Properties ....................................................................... 209

A MATTERS OF TECHNIQUE
  A.1 Transform Methods ....................................................................... 223
  A.2 Relation between Laplace Transforms and Real Time Quantities ....... 223
  A.3 Asymptotic Analysis .................................................................... 226
  A.4 Scaling Approaches ..................................................................... 227
  A.5 Differential Equations .................................................................. 227
  A.6 Partial Differential Equation ........................................................ 228
  A.7 Extreme Statistics ....................................................................... 229
  A.8 Probability theory ........................................................................ 230

B Formulas & Distributions
  B.1 Useful Formulas ........................................................................... 231
Preface

Statistical physics is an unusual branch of physics because it is not really a well-defined field in a formal sense, but rather, statistical physics is a viewpoint—indeed, the most appropriate viewpoint—to investigate systems with many degrees of freedom. Part of the appeal of statistical physics is that it can be applied to a disparate range of systems that are in the mainstream of physics, as well as to problems that might appear to be outside physics, such as econophysics, quantitative biology, and social organization phenomena. Many of the basic features of these systems involve fluctuations or explicit time evolution rather than equilibrium distributions. Thus the approaches of non-equilibrium statistical physics are needed to discuss such systems.

While the tools of equilibrium statistical physics are well-developed, the statistical description of systems that are out of equilibrium is still relatively primitive. In spite of more than a century of effort in constructing an over-arching approach for non-equilibrium phenomena, there still does not exist canonical formulations, such as the Boltzmann factor or the partition function in equilibrium statistical physics. At the present time, some of the most important theoretical approaches for non-equilibrium systems are either technical, such as deriving hydrodynamics from the Boltzmann equation, or somewhat removed from the underlying phenomena that are being described, such as non-equilibrium thermodynamics.

Because of this disconnect between fundamental theory and applications, our view is that it is more instructive to illustrate non-equilibrium statistical physics by presenting a number of current and paradigmatic examples of systems that are out of equilibrium, and to elucidate, as completely as possible, the range of techniques available to solve these systems. By this approach, we believe that readers can gain general insights more quickly compared to formal approaches, and, further, will be well-equipped to understand many other topics in non-equilibrium statistical physics. We have attempted to make our treatment as self-contained and user-friendly as possible, so that an interested reader can work through the book without encountering unresolved methodological mysteries or hidden calculational pitfalls. Thus while much of the material is mathematical in nature, we have tried to present it as pedagogically as possible. Our target audience is graduate students with a one-course background in equilibrium statistical physics. Each of the main chapters is intended to be self-contained. We also made an effort to supplement the chapters with research exercises and open questions, in the hopes of stimulating further research.

The specific examples presented in this book are primarily based on irreversible stochastic processes. This branch of statistical physics is in many ways the natural progression of kinetic theory that was initially used to describe dynamics of simple gases and fluids. We will discuss the development of basic kinetic approaches to more complex and contemporary systems. Among the large menu of stochastic and irreversible processes, we chose the ones that we consider to be among the most important and most instructive in leading to generic understanding. Our main emphasis is on exact analytical results, but we also spend time developing heuristic and scaling methods. We largely avoid presenting numerical simulation results because these are less definitive and instructive than analytical results. An appealing (at least to us) aspect of these examples is that they are broadly accessible. One needs little background to appreciate the systems being studied and the ideas underlying the methods of solution. Many of these systems naturally suggest new and non-trivial questions that an interested reader can easily pursue.

We begin our exposition with a few “aperitifs”—an abbreviated qualitative discussion of basic problems and a general hint at the approaches that are available to solve these systems. Chapter 2 provides a basic introduction to diffusion phenomena because of the central role played by diffusion in many non-equilibrium statistical systems. These preliminary chapters serve as an introduction to the rest of the book.

The main body of the book is then devoted to working out specific examples. In the next three chapters, we discuss the fundamental kinetic processes of aggregation, fragmentation, and adsorption (chapters 3–5).
Aggregation is the process by which two clusters irreversibly combine in a mass-conserving manner to form a larger cluster. This classic process that very nicely demonstrates the role of conservation laws, the utility of exact solutions, the emergence of scaling in cluster-size distributions, and the power of heuristic derivations. Many of these technical lessons will be applied throughout this book.

We then turn to the complementary process of fragmentation, which involves the repeated breakup of an element into smaller fragments. While this phenomenon again illustrates the utility of exact and scaling solutions, fragmentation also exposes important new concepts such as multiscaling, lack of self-averaging, and methods such as traveling waves and velocity selection. All of these are concepts that are used extensively in non-equilibrium statistical physics. We then discuss the phenomenon of irreversible adsorption where, again, the exact solutions of underlying master equations for the occupancy probability distributions provides a comprehensive picture of the basic phenomena.

The next two chapters (6 & 7) discuss the time evolution of systems that involve the competition between multiple phases. We first treat classical spin systems, in particular, the kinetic Ising model and the voter model. The kinetic Ising model occupies a central role in statistical physics because of its broad applicability to spins systems and many other dynamic critical phenomena. The voter model is perhaps not as well known in the physics literature, but it is an even simpler model of an evolving spin system that is exactly soluble in all dimensions. In chapter 7, we study phase ordering kinetics. Here the natural descriptions are in terms of continuum differential equations, rather than master equations.

In chapter 8, we discuss collision-driven phenomena. Our aim is to present the Boltzmann equation in the context of explicitly soluble examples. These include traffic models, and aggregation and annihilation processes in which the particles move at constant velocity between collisions. The final chapter (#9) presents several applications to contemporary problems, such as the structure of growing networks and models of self-organized criticality.

In an appendix, we present the fundamental techniques that are used throughout our book. These include various types of integral transforms, generating functions, asymptotic analysis, extreme statistics, and scaling approaches. Each of these methods is explain fully upon its first appearance in the book itself, and the appendix is a brief compendium of these methods that can be used either as a reference or a study guide, depending on one’s technical preparation.
Broadly speaking, non-equilibrium statistical physics describes the time-dependent evolution of many-particle systems. The individual particles are elemental interacting entities which, in some situations, can change in the process of interaction. In the most interesting cases, interactions between particles are strong and hence the deterministic description of even few-particle systems are beyond the reach of exact theoretical approaches. On the other hand, many-particle systems often admit an analytical statistical description when their number becomes large and in that sense they are simpler than few-particle systems. This feature has several different names—the law of large numbers, ergodicity, etc.—and it is one of the reasons for the spectacular successes of statistical physics and probability theory.

Non-equilibrium statistical physics is quite different from other branches of physics, such as the 'fundamental' fields of electrodynamics, gravity, and elementary-particle physics that involve a reductionist description of few-particle systems, and applied fields, such as hydrodynamics and elasticity that are primarily concerned with the consequences of fundamental governing equations. Some of the key and distinguishing features of non-equilibrium statistical physics include:

- no basic equations (like Maxwell equations in electrodynamics or Navier-Stokes equations in hydrodynamics) from which the rest follows;
- intermediate between fundamental applied physics;
- the existence of common underlying techniques and concepts in spite of the wide diversity of the field;
- non-equilibrium statistical physics naturally leads to the creation of methods that are quite useful in applications far removed from physics (for example the Monte Carlo method and simulated annealing).

Our guiding philosophy is that in the absence of underlying principles or governing equations, non-equilibrium statistical physics should be oriented toward explicit and illustrative examples rather than attempting to develop a theoretical formalism that is still incomplete.

Let’s start by looking briefly at the random walk to illustrate a few key ideas and to introduce several useful analysis tools that can be applied to more general problems.

## 1.1 Diffusion

For the symmetric diffusion on a line, the probability density

$$
\text{Prob} [\text{particle } \in (x, x + dx)] \equiv P(x, t) \, dx
$$

satisfies the diffusion equation

$$
\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2}.
$$

As we discuss soon, this equation describes the continuum limit of an unbiased random walk. The diffusion equation must be supplemented by an initial condition that we take to be $P(x, 0) = \delta(x)$, corresponding to a walk that starts at the origin.
Dimensional Analysis

Let’s pretend that we don’t know how to solve (1.1.2) and try to understand the behavior of the walker without explicit solution. What is the mean displacement? There is no bias, so clearly

$$\langle x \rangle = \int_{-\infty}^{\infty} dx \, x \, P(x, t) = 0.$$  

The next moment, the mean square displacement,

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} dx \, x^2 \, P(x, t)$$  

is non-trivial. Obviously, it should depend on the diffusion coefficient $D$ and time $t$. We now apply dimensional analysis to determine these dependences. If $L$ denotes the unit of length and $T$ denotes the time unit, then from (1.1.2) the dimensions of $\langle x^2 \rangle$, $D$, and $t$ are

$$[\langle x^2 \rangle] = L^2, \quad [D] = L^2/T, \quad [t] = T.$$  

The ratio $\langle x^2 \rangle / Dt$ is dimensionless and thus be constant, as a dimensionless quantity cannot depend on dimensional quantities. Hence

$$\langle x^2 \rangle = C \times Dt. \quad (1.1.3)$$  

Equation (1.1.3) is one of the central results in non-equilibrium statistical physics, and we derived it using just dimensional analysis! To determine the numerical constant $C = 2$ in (1.1.3) one must work a bit harder (e.g., by solving (1.1.2), or by multiplying Eq. (1.1.2) by $x^2$ and integrating over the spatial coordinate to give $\frac{d}{dt} \langle x^2 \rangle = 2D$). We shall therefore use the power of dimensional analysis whenever possible.

Scaling

Let’s now apply dimensional analysis to the probability density $P(x, t|D)$; here $D$ is explicitly displayed to remind us that the density does depend on the diffusion coefficient. Since $[P] = L^{-1}$, the quantity $\sqrt{Dt} \, P(x, t|D)$ is dimensionless, so it must depend on dimensionless quantities only. From variables $x, t, D$ we can form a single dimensionless quantity $x/\sqrt{Dt}$. Therefore the most general dependence of the density on the basic variables that is allowed by dimensional analysis is

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} P(\xi), \quad \xi = \frac{x}{\sqrt{Dt}}. \quad (1.1.4)$$  

The density depends on a single scaling variable rather than on two basic variables $x$ and $t$. This remarkable feature greatly simplifies analysis of the typical partial differential equations that describe non-equilibrium systems. Equation (1.1.4) is often referred to as the scaling ansatz. Finding the right scaling ansatz for a physical problem often represents a large step toward a solution. For the diffusion equation (1.1.2), substituting in the ansatz (1.1.4) reduces this partial differential equation to the ordinary differential equation

$$2P'' + \xi P' + P = 0.$$  

Integrating twice and invoking both symmetry ($P'(0) = 0$) and normalization, we obtain $P = (4\pi)^{-1/2} e^{-\xi^2/4}$, and finally the Gaussian probability distribution

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp \left\{ -\frac{x^2}{4Dt} \right\}. \quad (1.1.5)$$  

In this example, the scaling form was rigorously derived from simple dimensional reasoning. In more complicated situations, arguments in favor of scaling are less rigorous, and scaling is usually achieved only in some asymptotic limit. The above example where scaling applies for all $t$ is an exception; for the diffusion equation with an initial condition on a finite rather than a point support, scaling holds only in the limit $x, t \to \infty$ with the scaling variable $\xi$ kept finite. Nevertheless, we shall see that where applicable, scaling provides a significant step toward the understanding of a problem.
1.2. SINGLE-SPECIES ANNIHILATION

Renormalization

The strategy of the renormalization group method is to understand the behavior on large ‘scale’—here large time—iteratively in terms of the behavior on smaller scales. For the diffusion equation, we start with identity

\[ P(x, 2t) = \int_{-\infty}^{\infty} dy P(y, t) P(x - y, t) \]  

(1.1.6)

that reflects the fact that the random walk is a Markov process. Namely, to reach \( x \) at time \( 2t \), the walk first reaches some intermediate point \( y \) at time \( t \) and then completes the journey to \( y \) in the remaining time \( t \). (Equation (1.1.6) is also the basis for the path integral treatment of diffusion processes but we will not delve into this subject here.)

The convolution form of Eq. (1.1.6) calls out for applying the Fourier transform,

\[ \hat{P}(k, t) = \int_{-\infty}^{\infty} dx e^{ikx} P(x, t), \]  

(1.1.7)

that recasts (1.1.6) into the algebraic relation \( \hat{P}(k, 2t) = [\hat{P}(k, t)]^2 \). The scaling form (1.1.4) shows that \( \hat{P}(k, t) = \tilde{\hat{P}}(\kappa) \) with \( \kappa = k\sqrt{Dt} \), so the renormalization group equation is

\[ \tilde{\hat{P}}(\sqrt{2}\kappa) = [\tilde{\hat{P}}(\kappa)]^2. \]

Taking logarithms and making the definitions \( z \equiv \kappa^2, Q(z) \equiv \ln \tilde{\hat{P}}(\kappa) \), we arrive at \( Q(2z) = 2Q(z) \), whose solution is \( Q(z) = -Cz \), or \( \hat{P}(k, t) = e^{-2k^2Dt} \). (The constant \( C = 2 \) may be found, e.g., by expanding (1.1.7) for small \( k \), \( \hat{P}(k, t) = 1 - k^2 2(x^2) \), and recalling that \( (x^2) = 2Dt \)). Performing the inverse Fourier transform we recover (1.1.5). Thus the Gaussian probability distribution represents an exact solution to a renormalization group equation. Our derivation shows that the renormalization group is ultimately related to scaling.

1.2 Single-Species Annihilation

In non-equilibrium statistical physics, we study systems that contain a macroscopic number of interacting particles. To understand collective behaviors it is useful to ignore complications resulting from finiteness, i.e., to focus on situations when the number of particles is infinite. Perhaps the simplest interacting infinite-particle system of this kind is single-species annihilation, where particles diffuse freely and annihilate instantaneously upon contact. This process has played an important role in development of non-equilibrium statistical physics and it provides a good illustration of techniques that can be applied to other infinite-particle systems.

The annihilation process is symbolically represented by the reaction scheme

\[ A + A \rightarrow \emptyset. \]  

(1.2.1)

The density \( n(t) \) of \( A \) particles obviously decays with time; the question is how.

Hydrodynamics

In the hydrodynamic approach, one assumes that the reactants are perfectly mixed at all times. This means that the density at every site is the same and that every particle has the same probability to react at the next instant. In this well-mixed limit, and also assuming the continuum limit, the global particle density \( n \) decays with time according to the rate equation

\[ \frac{dn}{dt} = -Kn^2. \]  

(1.2.2)

This equation reflects that fact that two particles are needed for a reaction to occur and the probability for two particle to be at the same location is proportional to the density squared. Here \( K \) is the reaction rate that describes the propensity for two diffusing particles to interact; the computation of this rate requires
a detailed microscopic treatment (see chapter 3). The rate equation (1.2.2) is a typical hydrodynamic-like equation whose solution is

\[ n(t) = \frac{n_0}{1 + Kn_0 t} \sim (Kt)^{-1}. \]  

(1.2.3)

However, simulations show more interesting long-time behaviors that depends on the spatial dimension \( d \):

\[ n(t) \sim \begin{cases} 
  t^{-1/2} & d = 1; \\
  t^{-1} \ln t & d = 2; \\
  t^{-1} & d > 2.
\end{cases} \]  

(1.2.4)

The sudden change at \( d_c = 2 \) illustrates the important notion of the critical dimension: above \( d_c \), the rate equation leads to asymptotically correct behavior; below \( d_c \), the rate equation is wrong; at \( d_c \), the rate equation approach is almost correct—it typically is in error by a logarithmic correction term.

To obtain a complete theory of the reaction, one might try to write formally exact equations for correlation functions. That is, if \( \rho(\mathbf{r}, t) \) is the microscopic density, the true dynamical equation for \( n(t) \equiv \langle \rho(\mathbf{r}, t) \rangle \) involves the second order correlators \( \langle \rho(\mathbf{r}, t)\rho(\mathbf{r}', t) \rangle \). Then an equation for the second-order correlation functions involves third-order correlators, etc. These equations are hierarchical and the only way to proceed is to impose some sort of closure scheme in which higher-order correlators are factorized in terms of lower-order correlators. In particular, the hydrodynamic equation (1.2.2) is recovered if we assume that second-order correlators factorize; that is, \( \langle \rho(\mathbf{r}, t)\rho(\mathbf{r}', t) \rangle = \langle \rho(\mathbf{r}, t) \rangle \langle \rho(\mathbf{r}', t) \rangle = n(t)^2 \). Thus Eq. (1.2.2) is the factorized version of the Boltzmann equation for the annihilation process (1.2.1). Attempts to describe this reaction scheme more faithfully by higher-order correlators have not been fruitful. Thus the revered kinetic theory approach is helpless for the innocent-looking process (1.2.1)! Let’s try some other approaches.

**Dimensional Analysis**

Let’s determine the dependence of the rate \( K \) on parameters, i.e., on the diffusion coefficient \( D \) and radius \( R \). From Eq. (1.2.2), \([K] = L^d/T\), and the only possible dependence is \(^{1} \)

\[ K = DR^{d-2} \]  

(1.2.5)

Using (1.2.5) in (1.2.2) and solving this equation yields

\[ n(t) \sim \frac{1}{R^{d-2}Dt}. \]  

(1.2.6)

We anticipate that the density ought to decay more quickly when the radius of the particles is increased. According to (1.2.6), this is true only when \( d > 2 \). Thus the rate equation could be correct in this regime. For \( d = 2 \), the decay is independent of the size of particles—already a bit of a surprising result. However, for \( d < 2 \), we obtain the obviously wrong result that the density decays more slowly if particles are larger.

The density is therefore actually independent of \( R \) for \( d < 2 \). This fact is easy to see for \( d = 1 \) because all that matters is the spacing between particles. If we now seek, on dimensional grounds, the density in the \( R \)-independent form \( n(D, t) \), we find that the only possibility is \( n \propto (Dt)^{-d/2} \) in agreement with prediction of (1.2.4) in one dimension.

**Heuristic Arguments**

Dimensional analysis often gives correct dependences but does not really explain why these behaviors are correct. For the annihilation process (1.2.1), we can understand the one-dimensional asymptotic, \( n \sim (Dt)^{-1/2} \), in a physical way by using a basic feature (1.1.3) of random walks: in a time interval \((0, t)\), each particle explores the region \( \ell \sim \sqrt{Dt} \), and therefore a typical separation between surviving particles is of order \( \ell \), from which \( n \sim \ell^{-1} \sim (Dt)^{-1/2} \) follows.

Guided by this understanding, let’s try to understand (1.2.4) for all dimensions. First, we slightly modify the process so that particles undergo diffusion on a lattice in \( d \) dimensions (lattice spacing plays the role of

---

\(^{1}\)Here we omit a numerical factor of order one; in the future, we shall often ignore such factors without explicit warning.
1.2. SINGLE-SPECIES ANNIHILATION

the radius). What is the average number of sites $N$ visited by a random walker after $N$ steps? This question has a well-known and beautiful answer:

$$N \sim \begin{cases} N^{1/2} & d = 1; \\ N/\ln N & d = 2; \\ N & d > 2. \end{cases} \quad (1.2.7)$$

With a little contemplation, one should be convinced the density in single-species annihilation scales as the inverse of the average number of sites visited by a random walker; if there is more that one particle in the visited region, it should have been annihilated previously. Thus (1.2.7) is essentially equivalent to (1.2.4).

Exact Solution in One Dimension

The diffusion-controlled annihilation process admits an exact solution in one dimension. This is an exceptional feature—most infinite-particle systems cannot be solved even in one dimension. Moreover, for these solvable cases, we can usually compute only a limited number of quantities. For one-dimensional annihilation, for example, while the density is known exactly, the distribution of distances $\ell$ between adjacent particles $P(\ell, t)$ is unknown even in the scaling limit $\ell \to \infty$ and $t \to \infty$, with $\xi = \ell/\sqrt{Dt}$ being finite. Although numerical simulations strongly indicate that the interval length distribution approaches the scaling form, $P(\ell, t) \to (Dt)^{-1/2}P(\xi)$, nobody yet knows how compute the scaled length distribution $P(\xi)$.

Exact results for the diffusion-controlled annihilation process will be presented later when we develop the necessary technical tools. However to illustrate a simple exact solution, let’s consider the diffusion-controlled coalescence process

$$A + A \longrightarrow A. \quad (1.2.8)$$

While this reaction is closely related to diffusion-controlled annihilation and exhibits the same time dependence of (1.2.4), diffusion-controlled coalescence is readily soluble in one dimension because it can be reduced to a two-particle problem. To compute the density it is convenient to define particle labels so that in each collision the left particle disappears and the right particle survives. Then to compute the survival probability of a test particle we may ignore all particles to the left. Such a reduction of the original two-sided problem to a one-sided one is extremely helpful. Furthermore, only the closest particle to the right of the test particles is relevant—the right neighbor can merge with other particles further to the right; however, these reactions never affect the fate of the test particle. Thus the system reduces to a soluble two-particle problem.

The interparticle distance between the test particle and its right neighbor undergoes diffusion with diffusivity $2D$ because the spacing diffuses at twice the rate of each particle. Consequently, the probability density $\rho(\ell, t)$ that the test particle is separated by distance $\ell$ from its right neighbor satisfies the diffusion equation subject to the absorbing boundary condition:

$$\frac{\partial \rho}{\partial t} = 2D \frac{\partial^2 \rho}{\partial \ell^2}, \quad \rho(0, t) = 0. \quad (1.2.9)$$

The solution (1.2.9) for an arbitrary initial condition $\rho_0(\ell)$ is

$$\rho(\ell, t) = \frac{1}{\sqrt{8\pi D t}} \int_0^\infty dy \rho_0(y) \left[ e^{-(\ell-y)^2/8Dt} - e^{-(\ell+y)^2/8Dt} \right]$$

$$= \frac{1}{\sqrt{2\pi Dt_0}} \exp \left( -\frac{\ell^2}{8Dt} \right) \int_0^\infty dy \rho_0(y) \exp \left( -\frac{y^2}{8Dt} \right) \sinh \left( \frac{\ell y}{4Dt} \right). \quad (1.2.10)$$

In the first line, the solution is expressed as the superposition of a Gaussian and an image anti-Gaussian that automatically satisfies the absorbing boundary condition. In the long time limit, the integral on the second line tends to $\frac{\ell}{4Dt} \int_0^{\infty} dy \rho_0(y) y = \frac{\ell}{4Dt_0}$. Therefore

$$\rho(\ell, t) \to \frac{\ell}{4Dt_0 \sqrt{2\pi D t}} \exp \left( -\frac{\ell^2}{8Dt} \right),$$

so that the survival probability is

$$S(t) = \int_0^{\infty} d\ell \rho(\ell, t) \to n_0^{-1}(2\pi D t)^{-1/2},$$
and the density \( n(t) = n_0 S(t) \) decays as
\[
n(t) \to (2\pi Dt)^{-1/2} \text{ when } t \to \infty.
\] (1.2.11)

To summarize, the interval length distribution \( P(\ell, t) \) is just the probability density \( \rho(\ell, t) \) conditioned on the survival of the test particle. Hence
\[
P(\ell, t) = \frac{\rho(\ell, t)}{S(t)} \to \frac{\ell}{4Dt} \exp\left(-\frac{\ell^2}{8Dt}\right).
\]
The average interparticle spacing grows as \( \sqrt{Dt} \) which equivalent to the particle density decaying as \( 1/\sqrt{Dt} \).

### 1.3 Two-Species Annihilation

Consider two diffusing species \( A \) and \( B \) which are initially distributed at random with equal concentrations: \( n_A(0) = n_B(0) = n_0 \). When two particles of opposite species approach within the reaction radius, they immediately annihilate:
\[
A + B \to \emptyset.
\] (1.3.1)

For this reaction, the density decreases as
\[
n(t) \sim \begin{cases} t^{-d/4} & d \leq 4; \\ t^{-1} & d > 4, \end{cases}
\] (1.3.2)
as \( t \to \infty \), so the critical dimension is \( d_c = 4 \). This result shows that hydrodynamic description is wrong even in the most relevant three-dimensional case.

In this striking example, neither a hydrodynamic description (that gives \( n \sim t^{-1} \)) nor dimensional analysis can explain the decay of the density. Here, a simple heuristic argument helps us determine the density decay of Eq. (1.3.2). To understand why the naive approaches fail, consider a snapshot of a two-dimensional system at some time \( t \gg 1 \) (Fig. fig-c1-snapshot). We see that the system spontaneously organizes into a mosaic of alternating domains. Because of this organization, annihilation can occur only along domain boundaries rather than throughout the system. This screening effect explains why the density is much larger than in the hydrodynamic picture where particles are assumed to be well-mixed.

Figure 1.1: Snapshot of the particle positions in two-species annihilation in two dimensions.

To turn this picture into a semi-quantitative estimate for the density, note that in a spatial region of linear size \( \ell \), the initial number of \( A \) particles is \( N_A = n_0 \ell^d \pm (n_0 \ell)^{d/2} \) and similarly for \( B \) particles. Here the \( \pm \) term signifies that the particle number in a finite region is a stochastic variable that typically fluctuates in a range of order \( (n_0 \ell)^{d/2} \) about the mean value \( n_0 \ell^d \). The typical value of the difference \( N_A - N_B \) for this \( d \)-dimensional region
\[
N_A - N_B = \pm (n_0 \ell)^{d/2},
\]
arises because of initial fluctuations and is not affected by annihilation events. Therefore after the minority species in a given region is eliminated, the local density becomes \( n \sim (n_0 \ell)^{d/2}/\ell^d \). Because of the diffusive
spreading (1.1.3), the average domain size scales as $\ell \sim \sqrt{D t}$, and thus $n \sim \sqrt{n_0 (D t)^{-d/4}}$. Finally, notice that the density decay cannot be obtained by dimensional analysis alone because now are there at least two independent length scales, the domain size $\sqrt{D t}$ and the interparticle spacing. Additional physical input, here in the form of the domain picture, is needed to obtain $n(t)$.

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 leads for the bacterium gives the Langevin equation

$$m \frac{dv}{dt} = -\gamma v + \eta(t).$$  \hspace{1cm} (2.1.1)

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 1\mu m, 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:

$$\frac{dx}{dt} = \frac{1}{\gamma} \eta(t) = \xi(t).$$  \hspace{1cm} (2.1.2)

In this limit of no inertia ($m = 0$) the instantaneous velocity equals the force. In spite of this strange feature, Eq. (2.1.2) 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. (2.1.1), we obtain

\[ x(t) = \int_0^t \xi(t') \, dt'. \tag{2.1.3} \]

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

\[ \langle x(t)^2 \rangle = \int_0^t \int_0^t \langle \xi(t') \xi(t'') \rangle \, dt' \, dt''. \tag{2.1.4} \]

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 \( \int_0^t \delta(t) \, dt = 1 \)), the statement \( \langle \xi(t) \xi(t') \rangle = 2D \delta(t-t') \) means that \( \xi \) has the units \( \sqrt{D/t} \). Thus from Eq. (2.1.3), \( x(t) \) 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

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 \( N \)th time step. Then evolution of this occupation probability is described by the master equation

\[ P(x, N + 1) = p P(x - 1, N) + q P(x + 1, N). \tag{2.2.1} \]

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 summation over all \( N \) and \( x \) gives

\[ \sum_{N=0}^\infty \sum_{x=-\infty}^\infty z^{N+1} e^{ikx} [P(x, N + 1) = p P(x - 1, N) + q P(x + 1, N)] . \tag{2.2.2} \]

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 (2.2.2) 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 \( \pm 1 \) in the spatial argument to the phase factors \( e^{\pm ik} \), respectively. Thus

\[ P(k, z) = \sum_{x=-\infty}^\infty P(x, N = 0) e^{ikx} = zu(k) P(k, z), \tag{2.2.3} \]
where \( u(k) = pe^{ik} + qe^{-ik} \) 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

\[
P(k, z) = \frac{1}{1 - zu(k)}.
\]

(2.2.4)

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

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

(2.2.5)

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

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

(2.2.6)

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

\[
P(x, N) = \frac{N!}{(N+x)!(N-x)!} p^{N+x} q^{N-x}.
\]

(2.2.7)

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

\[
P(x, N) \to \frac{1}{\sqrt{2\pi Npq}} e^{-(x-\langle x \rangle)^2/(2Npq)}.
\]

(2.2.8)

The general statement of the central-limit theorem is that a Gaussian distribution arises for any memoryless hopping process in which the mean displacement \( \langle x \rangle \) and the mean-square displacement \( \langle x^2 \rangle \) in a single step are both finite. Here \( u(k) \) has the small-\( k \) form

\[
u(k) = 1 + ik\langle x \rangle - \frac{k^2\langle x^2 \rangle}{2} + \ldots \sim e^{ik\langle x \rangle - \frac{k^2\langle x^2 \rangle}{2}} - k \rightarrow 0.
\]

The second asymptotic relation is obtained by matching its expansion to second order in \( k \) with the Taylor series. Substituting the asymptotic result for \( u(k) \) into Eq. (2.2.5), we perform the integral by completing the square in the exponent to again give the Gaussian form

\[
P(x, N) \to \frac{1}{\sqrt{2\pi N\langle x^2 \rangle - \langle x \rangle^2}} e^{-(x-\langle x \rangle)^2/(2N\langle x^2 \rangle - \langle x \rangle^2)},
\]

(2.2.9)

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 (2.2.1) to first order in \( \delta t \). These steps give

\[
\frac{\partial P(x,t)}{\partial t} = w_+ P(x-1,t) + w_- P(x+1,t) - w_0 P(x,t)
\]

(2.2.10)

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. (2.2.10) calls out for applying the Fourier transform. After doing so, the master equation becomes

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

(2.2.11)

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. (2.2.11) 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 the modified Bessel function of the first kind of order \( x \),

\[
P(k, t) = e^{-t} \sum_{x=-\infty}^{\infty} e^{ikx} I_x(t),
\]

from which we immediately obtain

\[
P(x, t) = e^{-t} I_x(t).
\]

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 (2.2.10) to give

\[
sP(x, s) - P(x, t = 0) = \frac{1}{2} P(x + 1, s) + \frac{1}{2} P(x - 1, s) - P(x, s).
\]

For \( x \neq 0 \), we solve the resulting difference equation, \( P(x, s) = a[P(x+1, s)+P(x-1, s)] \), with \( a = 1/(s+1) \), 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 \( \lambda \) whose solution is \( \lambda = (1 \pm \sqrt{1-4a^2})/2a \). For all \( s > 0 \), \( \lambda_+ \) and \( \lambda_- \) 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

\[
sP(0, s) - 1 = \frac{1}{2} P(1, s) + \frac{1}{2} P(-1, s) - P(0, s) = P(1, s) - P(0, s).
\]

The \(-1\) on the left-hand side arises from the initial condition, and the second equality follows by spatial symmetry. Substituting \( P(n, s) = A\lambda_+^n \) into Eq. (2.2.15) gives \( A \), from which we finally obtain

\[
P(x, s) = \frac{1}{s+1-\lambda_-} \lambda_+^x.
\]

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

\[
P(x, s) \approx (1 - \sqrt{2s})^x \frac{e^{-x\sqrt{2s}}}{\sqrt{2s}}.
\]

We now invert the Laplace transform \( P(x, t) = \int_{0-\infty}^{0+\infty} P(x, s) e^{st} ds \) by using the integration variable \( u = \sqrt{s} \). This immediately leads to the Gaussian probability distribution quoted in Eq. (2.2.9) for the case \( \langle x \rangle = 0 \) and \( \langle x^2 \rangle = 1 \).

When both space and time are continuous, we expand the master equation (2.2.1) 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,

\[
\frac{\partial P(x,t)}{\partial t} + v \frac{\partial P(x,t)}{\partial x} = D \frac{\partial^2 P(x,t)}{\partial x^2},
\]

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 \( \delta x \) 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 \( \delta x \) and \( \delta t \) approach zero. Much more about this relation between discrete hopping processes and the continuum can be found, for example, in [?], [?], or [?].

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 \( \hat{P}(k, t) = (ikv - Dk^2)\hat{P}(k, t) \), with solution

\[
P(k, t) = P(k, 0) e^{(ikv - Dk^2)t} = e^{(ikv - Dk^2)t},
\]
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,
\[
P(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-(x-ct)^2/4Dt}.
\] (2.2.20)

Alternatively, we may first Laplace transform in the time domain. For the convection-diffusion equation, this yields the ordinary differential equation
\[
sP(x, s) - \delta(x) + vP(x, s) = De''(x, s),
\] (2.2.21)

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. (2.2.21) 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 $\alpha_{\pm} = (v \pm \sqrt{v^2 + 4Ds}) / 2D$ 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 $\frac{dc}{dx}$ at $x = 0$ whose magnitude is determined by integrating Eq. (2.2.21) over an infinitesimal domain which includes the origin. The continuity condition trivially gives $A_+ = A_- = A$, and the condition for the discontinuity in $P(x, s)$ is $D \frac{dc}{dx} |_{x=0} = 1$. This gives $A = 1/\sqrt{v^2 + 4Ds}$. Thus the Laplace transform of the probability distribution is
\[
c_\pm(x, s) = \frac{1}{\sqrt{v^2 + 4Ds}} e^{-\alpha_\pm |x|}.
\] (2.2.22)

For zero bias, this coincides with Eq. (2.2.17) and thus recovers the Gaussian probability distribution.

### 2.3 Connection to First-Passage Properties

Because of its application to reaction kinetics, we now discuss how to extract first-passage characteristics of a random walk from the occupation probability. Let $P(\vec{r}, t)$ be probability that a random walk is at $\vec{r}$ at time $t$ when it starts at the origin. Similarly, let $F(\vec{r}, t)$ be the first-passage probability, namely, the probability that the random walk visits $\vec{r}$ for the first time at time $t$ with the same initial condition.

For a random walk to be at $\vec{r}$ at time $t$, the walk must first reach $\vec{r}$ at some earlier time step $t'$ and then return to $\vec{r}$ after $t - t'$ (Fig. 2.1). This connection between $F(\vec{r}, t)$ and $P(\vec{r}, t)$ may therefore be expressed as the convolution
\[
P(\vec{r}, t) = \delta_{\vec{r}, 0} \delta_{t, 0} + \int_0^t F(\vec{r}, t') P(0, t - t') dt'.
\] (3.3.1)

The delta function term accounts for the initial condition. The second term accounts for the ways that a walk can be at $\vec{r}$ at time $t$. To reach $r$ at time $t$, the walk must first reach $r$ at some time $t', \leq t$. 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 $\vec{r}$ 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 \( P(\vec{r}, s) = \delta_{F,0} + F(\vec{r}, s)P(0, s) \). Thus we obtain the fundamental connection

\[
F(\vec{r}, s) = \begin{cases} 
\frac{P(\vec{r}, s)}{P(0, s)}, & \vec{r} \neq 0 \\
1 - \frac{1}{P(0, s)}, & \vec{r} = 0,
\end{cases}
\]

(2.3.2)

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

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, \( P(\vec{r} = 0, t) = (4\pi Dt)^{-d/2} \) in \( d \) dimensions. Then Eq. (A.2.1) gives

\[
P(0, s) \approx \int_0^\infty P(0, t) z^t dt \sim \int_0^\infty (4\pi Dt)^{-d/2} z^t dt.
\]

(2.3.3)

As discussed in Section A.2, this integral has two fundamentally different behaviors, depending on whether \( \int_0^\infty P(0, t) dt \) diverges or converges. In the former case, we apply the last step in Eq. (A.2.1) to obtain

\[
P(0, s) \propto \int_0^{\infty} (4\pi Dt)^{-d/2} dt \sim \begin{cases} 
A_d(t^*)^{1-d/2} = A_d(1 - z)^{d/2-1}, & d < 2 \\
A_2 \ln t^* = -A_2 \ln(1 - z), & d = 2,
\end{cases}
\]

(2.3.4)

where the dimension-dependent prefactor \( A_d \) is of the order of 1 and does not play any role in the asymptotic behavior.

For \( d > 2 \), the integral \( \int_0^\infty P(0, t) dt \) 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

\[
P(0, s) \sim (1 - R)^{-1} + B_d(1 - z)^{d/2-1} + \ldots, \quad d > 2,
\]

(2.3.5)

where \( R \) 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. (2.3.2), we infer that the Laplace transform for the first-passage probability has the asymptotic behaviors

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

(2.3.6)

From this Laplace transform, we determine the time dependence of the survival probability by approximation (A.2.7); that is,

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

(2.3.7)

where \( T(t) \) is the probability that the particle gets trapped (reaches the origin) by time \( t \) and \( S(t) \) is the survival probability, namely, 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. (2.3.6) and (2.3.7) we thus find

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

(2.3.8)

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 \( 1 - S(t) \sim \int_0^t F(0, t) dt \) to give

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

(2.3.9)
A crucial feature is that the asymptotic time dependence is determined by only the spatial dimension. For $d \leq 2$, the survival probability $S(t)$ ultimately decays to zero. Thus a random walk is recurrent, that is, certain to eventually return to its starting point, and indeed visit any site of an infinite lattice. Because a random walk has no memory, recurrence implies that every site is visited infinitely often. There is a simple physical explanation for this efficient visitation. 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 proportional to $t$. The density of visited sites within this exploration sphere is $\rho \propto t/d^{1/2} \propto t^{1-d/2}$ in $d$ dimensions. Since this density diverges as $t \to \infty$ for $d < 2$, a random walk visits each site within the sphere infinitely often (\?). Paradoxically, although every site is surely visited, these visitations take forever because the mean time to return to the origin, $\langle t \rangle = \int t P(0,t) \, dt$, diverges for all $d \leq 2$. Conversely, Eq. (2.3.8) predicts that there is a non-zero chance for a diffusing particle to never return to its starting point when $d > 2$. This phenomenon is known as transience (\?; \?).

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 $E_+(x)$ be the probability that a particle, which starts at $x$, eventually hits $x = 1$ without hitting $x = 0$. This eventual hitting probability $E_+(x)$ is obtained by summing the probabilities for all paths that start at $x$ and reach 1 without touching 0. Thus

$$E_+(x) = \sum_p P_p(x),$$

where $P_p(x)$ 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

$$E_+(x) = \sum_p \left[ \frac{1}{2} P_p(x + \delta x) + \frac{1}{2} P_p(x - \delta x) \right] = \frac{1}{2} [E_+(x + \delta x) + E_+(x - \delta x)].$$

By a simple rearrangement, this equation is equivalent to

$$\Delta^{(2)} E_+(x) = 0,$$

where $\Delta^{(2)}$ is the second-difference operator. Notice the opposite sense of this recursion formula compared to the master equation Eq. (2.2.1) for the probability distribution. Here $E_+(x)$ 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. (2.3.11) 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 (2.3.12) is subject to the boundary conditions $E_+(0) = 0$ and $E_+(1) = 1$; 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. (2.3.12) 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: $E_+(x) = x$.

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 $\delta t$, 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. (2.3.10)

$$t(x) = \sum_p P_p(x) t_p(x),$$
where \( t_p(x) \) is the exit time of a specific path to the boundary that starts at \( x \).

In analogy with Eq. (2.3.11), this mean exit time obeys the recursion

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

(2.3.14)

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 \( \delta t \). 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 \( D t''(x) = -1 \). For diffusion in a \( d \)-dimensional domain with absorption on a boundary \( B \), the corresponding Poisson equation for the exit time is \( D \nabla^2 t(\vec{r}) = -1 \), subject to the boundary condition \( t(\vec{r}) = 0 \) for \( \vec{r} \in B \). 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

\[
 t(x) = \frac{1}{2D} x(1 - x).
\]

(2.3.15)

Problems

1. 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. \textbf{Hint:} Consider the behavior of moments beyond second order, \( \langle x^k \rangle \) with \( k > 2 \).

2. 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). \textbf{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.

3. 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?