A Modern Course in Statistical Physics

2nd Edition

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This book is dedicated to
Ilya Prigogine
for his encouragement and support
and because
he has changed our view of the world.

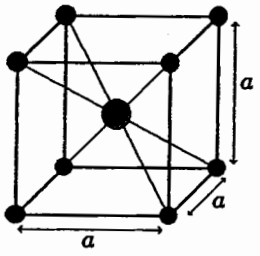


Fig. 4.20. Unit cell for a body-centered cubic lattice.

$(l_1 = 0, l_2 = 0, l_3 = 0)$. Compute the generating function. $U(\rho, 0)$, and the escape probability. [*Hint*: Make a change of variables, $x_i = \tan(\phi_i/2)$. Then change to spherical coordinates, $x_1 = r\sin(\theta)\cos(\phi), x_2 = r\sin(\theta)\sin(\phi)$, and $x_3 = r\cos(\theta)$. Replace the integration over r by an integration over t, where $t = r\sin(\theta)\sqrt{\frac{1}{2}\cos(\theta)\sin(\frac{\phi}{2})}$. The three integrations over t, θ, and ϕ then separate.]

Problem S4.4. Consider a Rayleigh–Pearson random walk in which the walker has a probability $P(r)dr = rdr/(1+r^2)^{3/2}$ to take a step of length $r \to r + dr$. If the walker starts at the origin, compute the probability $P_N(R)$ to find the walker within a circle of radius R after N steps. (d=2) Can approximately by projection as in Feller II, Ch. 1 but integrals hard to do.

Problem S4.5. A stochastic variable X has characteristic function $f_X(k) = 1/(1+k^2)$. (a) Compute the probability density, $P_X(x)$, the average, $\langle x \rangle$, and variance. (b) Write Kolmogorov's formula for this characteristic function. What is $K(u)$? Is the stochastic variable X infinitely divisible? exp dist.

Problem S4.6. Consider the gamma distribution function for stochastic variable X: 2-sided

$$F(x) = \left(\frac{1}{2}\right)^{n/2} \frac{1}{\Gamma(n/2)} \int_0^x dy y^{(n/2)-1} e^{-y/2} \qquad \text{for} \quad x > 0$$

and $F(x) = 0$ for $x < 0$ (n is an integer). (a) Find the characteristic function for this distribution. (b) Write the Levy–Khintchine formula for the characteristic function. That is, find α and $G(x)$. Is X infinitely divisible? [*Hint*: First find $F_N(x)$ and use it to find $G_N(x)$ and take the limit.] Yes. $n \to n/N$

Problem S4.4: Could also try $\vec{R}_N = \vec{R}_{N-1} + \vec{\xi}$ and compute
$\langle e^{i\lambda |\vec{R}_N|^2} \rangle$
$= \langle e^{i\lambda (|R_{N-1}|^2 + \vec{\xi}\cdot\vec{R}_{N-1} + |\vec{\xi}|^2)} \rangle$
and try to average over angle first, but then get Bessel functions.

S4.5b) Could attempt by expansion of both sides in powers of k but combinatorial headache on L.H.S. No ∞ divisible. Sums of exp dist variables are Γ-distributed.

S4.6a) Contour integral or invert S.Y.S. $f_\gamma(k) = (1-2ik)^{-n/2}$

b) $\alpha = \frac{n}{2}\int_0^\infty e^{-x/2}(1+x^2)^{-1}dx$ $\quad dG = \frac{n\gamma}{2(1+\gamma^2)} e^{-x/2}$

Maybe integrate by gram. series exp. of denom

5

STOCHASTIC DYNAMICS AND BROWNIAN MOTION

5.A. INTRODUCTION

Now that we have reviewed some of the basic ideas of probability theory (cf. Chapter 4), we will begin to study more complicated situations in which probability can evolve in time. In Chapter 4 we already considered some simple random walks which are elementary stochastic processes that can be built from repeated application of the same transition process at discrete time intervals. In this chapter we will derive differential equations of motion for the evolution of probability distributions and densities in time. The level at which we discuss this time evolution is phenomenological because we will not concern ourselves with the relation of these equations to Newtonian mechanics. That will be the subject of Chapter 6. Also, in this chapter we will limit ourselves to Markov processes, which are stochastic processes with a very limited memory of previous events.

The equation which governs the stochastic dynamics of Markov processes is the *master equation*. It is one of the most important equations in statistical physics because of its almost universal applicability. It has been applied to problems in chemistry, biology, population dynamics, laser physics, Brownian motion, fluids, and semiconductors, to name a few cases. As a system of stochastic variables evolves in time, transitions occur between various realizations of the stochastic variables. Because of these transitions, the probability of finding the system in a given state changes until the system reaches a final steady state in which transitions cannot cause further changes in the probability distribution (it can happen that the system never reaches a steady state, but we will be most concerned with cases for which it can). To derive the master equation, we must assume that the probability of each transition depends only on the preceding step and not on any previous history. This assumption applies to many different types of physical system found in nature.

One of the simplest types of Markov processes that we will consider is the Markov chain. Markov chains are processes in which transitions occur between realizations of discrete stochastic variables at discrete times, as in the case for

the random walks we treated in Chapter 4 using simple probability theory. In this chapter we will formulate such problems in a more elegant manner. We will get a very good picture of how stochastic systems can decay to a unique steady state for the case in which the transition matrix is "regular" and we can introduce the concept of *ergodicity*, which we shall come back to in Chapter 6. The dynamics of Markov chains is totally governed by a "transition matrix" which is real and generally is nonsymmetric. We shall show how the stochastic dynamics can be expressed in terms of a spectral decomposition of the probability in terms of the left and right eigenvectors of the transition matrix.

If the time interval between events can vary in a continuous manner, then we must introduce the *master equation* which is a differential difference equation governing the time evolution of the probability. For the very special case when the transition rate between realizations exhibits *detailed balance*, solutions of the master equation can also be expressed in terms of a spectral decomposition. Detailed balance holds for many types of systems which are near thermal equilibrium or do not have internal probability currents as they reach the long time state. Some examples for which detailed balance holds can include chemical reactions near equilibrium, electronic transitions, and some random walks. The master equation for birth–death processes, which include chemical reactions and population dynamics, is derived in the section on *special topics*.

One often encounters systems with many degrees of freedom but for which a few of the degrees of freedom evolve on a much slower time scale than the others. An example of this is Brownian motion, in which a relatively massive particle, such as a grain of pollen, is immersed in a fluid, such as water. The grain of pollen is observed to undergo rapid, apparently random, agitated motion. Brownian motion, which was first made popular by the work of biologist Robert Brown, was used by Einstein as evidence of the atomic nature of matter. Indeed, it only occurs because of the discrete particulate nature of matter. A phenomenological theory of this motion can be obtained by writing Newton's equation of motion for the massive particle and including in it a systematic friction force and a random force to mimic the effects of the many degrees of freedom of the fluid in which the massive particle is immersed. This gives rise to the Langevin equation of motion for the massive particle.

Given a Langevin equation for a Brownian motion process, we can obtain an equation for time evolution of the probability distribution in phase space of the Brownian particle, called the Fokker–Planck equation. In the sections devoted to *special topics* we will derive the Fokker–Planck equation and we will solve it for Brownian motion with one spatial degree of freedom in the presence of strong friction. We shall also mention the interesting connection of Fokker–Planck dynamics to chaos theory when one considers more than one spatial degree of freedom. For cases in which the master equation cannot be solved exactly, it can sometimes be approximated by a Fokker–Planck equation. We will discuss some of those cases in this chapter. In later chapters we will use the concepts developed here to describe other types of Brownian motion in many body systems.

5.B. GENERAL THEORY [1–4]

Let us consider a system whose properties can be described in terms of a single stochastic variable Y. Y could denote the velocity of a Brownian particle, the number of particles in a box, or the number of people in a queue, to name a few of many possibilities.

We will use the following notation for the probability density for the stochastic variable Y:

$$P_1(y_1, t_1) \equiv \text{(the probability density that the stochastic variable } Y \text{ has value } y_1 \text{ at time } t_1); \tag{5.1}$$

$$P_2(y_1, t_1; y_2, t_2) \equiv \text{(the joint probability density that the stochastic variable } Y \text{ has value } y_1 \text{ at time } t_1 \text{ and } y_2 \text{ at time } t_2); \tag{5.2}$$

$$P_n(y_1, t_1; y_2, t_2; \ldots; y_n, t_n) \equiv \text{(the joint probability density that the stochastic variable } Y \text{ has value } y_1 \text{ at time } t_1, y_2 \text{ at time } t_2, \ldots, y_n \text{ at time } t_n. \tag{5.3}$$

The joint probability densities are positive:

$$P_n \geq 0; \tag{5.4}$$

they can be reduced:

$$\int P_n(y_1, t_1; y_2, t_2, ; \ldots; y_n, t_n) dy_n = P_{n-1}(y_1, t_1; y_2, t_2; \ldots; y_{n-1}, t_{n-1}); \tag{5.5}$$

and they are normalized:

$$\int P_1(y_1, t_1) dy_1 = 1. \tag{5.6}$$

In Eqs. (5.5) and (5.6) we have assumed that Y is a continuous stochastic variable. However, if Y is discrete we simply replace the integrations by summations. We can introduce time-dependent moments of the stochastic variables, $\langle y_1(t_1) y_2(t_2) \times \cdots \times y_n(t_n) \rangle$. They are defined as

$$\langle y_1(t_1) y_2(t_2) \cdots y_n(t_n) \rangle = \int\int y_1 y_2 \cdots y_n P_n(y_1, t_1; \ldots; y_n, t_n) dy_1 \cdots y_n \tag{5.7}$$

and give the correlation between values of the stochastic variable at different

times. A process is called *stationary* if

$$P_n(y_1, t_1; y_2, t_2; \ldots; y_n, t_n) = P_n(y_1, t_1 + \tau; y_2, t_2 + \tau; \ldots; y_n, t_n + \tau) \quad (5.8)$$

for all n and τ. Thus, for a stationary process

$$P_1(y_1, t_1) = P_1(y_1), \quad (5.9)$$

and $\langle y_1(t_1) y_2(t_2) \rangle$ depends only on $|t_1 - t_2|$—the absolute value of the difference in times. All physical processes in equilibrium are stationary.

We shall also introduce a conditional probability:

$$P_{1|1}(y_1, t_1 | y_2, t_2) = \text{(the conditional probability density for the stochastic variable } Y \text{ to have value } y_2 \text{ at time } t_2 \text{ given that it had value } y_1 \text{ at time } t_1) \quad (5.10)$$

It is defined by the identity

$$P_1(y_1, t_1) P_{1|1}(y_1, t_1 | y_2, t_2) = P_2(y_1, t_1; y_2, t_2). \quad (5.11)$$

Combining Eqs. (5.5) and (5.11) we obtain the following relation between the probability densities at different times:

$$P_1(y_2, t_2) = \int P_1(y_1, t_1) P_{1|1}(y_1, t_1 | y_2, t_2) dy_1 \quad (5.12)$$

where the conditional probability $P_{1|1}(y_1, t_1 | y_2, t_2)$ has the property

$$\int P_{1|1}(y_1, t_1 | y_2, t_2) dy_2 = 1, \quad (5.13)$$

as can be demonstrated easily.

We can also introduce a joint conditional probability density as follows:

$$P_{k|l}(y_1, t_1; \ldots; y_k, t_k | y_{k+1}, t_{k+1}, ; \ldots; y_{k+l}, t_{k+l}) = \text{(the joint conditional probability density that the stochastic variable } Y \text{ has values } (y_{k+1}, t_{k+1}; \ldots; y_{k+l}, t_{k+l}) \text{ given that } (y_1, t_1; \ldots; y_k, t_k) \text{ are fixed).} \quad (5.14)$$

The joint conditional probability density is defined as

$$P_{k|l}(y_1, t_1; \ldots; y_k, t_k | y_{k+1}, t_{k+1}; \ldots; y_{k+l}, t_{k+l}) = \frac{P_{k+1}(y_1, t_1; \ldots; y_k, t_k; y_{k+1}, t_{k+1}; \ldots; y_{k+l}, t_{k+l})}{P_k(y_1, t_1; \ldots; y_k, t_k)}. \quad (5.15)$$

The joint probability densities are important when there are correlations between values of the stochastic variable at different times—that is, if the stochastic variable has some memory of its past. However, if the stochastic variable has memory only of its immediate past, then the expressions for the joint probability densities and the joint probability densities simplify considerably.

If the stochastic variable has memory only of its immediate past, the joint conditional probability density $P_{n-1|1}(y_1, t_1; \ldots; y_{n-1}, t_{n-1} | y_n, t_n)$, where $t_1 < t_2 < \cdots < t_n$; must have the form

$$P_{n-1|1}(y_1, t_1; \ldots; y_{n-1}, t_{n-1} | y_n, t_n) = P_{1|1}(y_{n-1}, t_{n-1} | y_n, t_n). \quad (5.16)$$

That is, the conditional probability density for y_n at t_n is fully determined by the value of y_{n-1} at t_{n-1} and is not affected by any knowledge of the stochastic variable Y at earlier times. The conditional probability density $P_{1|1}(y_1, t_1 | y_2, t_2)$ is called the *transition probability*. A process for which Eq (5.16) is satisfied is called a *Markov process*. A Markov process is fully determined by the two functions $P_1(y, t)$ and $P_{1|1}(y_1, t_1 | y_2, t_2)$. The whole hierarchy of probability densities can be constructed from them. For example,

$$\begin{aligned} P_3(y_1, t_1; y_2, t_2; y_3, t_3) &= P_2(y_1, t_1; y_2, t_2) P_{2|1}(y_1, t_1; y_2, t_2 | y_3, t_3) \\ &= P_1(y_1, t_1) P_{1|1}(y_1, t_1 | y_2, t_2) P_{1|1}(y_2, t_2 | y_3, t_3). \end{aligned} \quad (5.17)$$

If we integrate Eq. (5.17) over y_2 assuming $t_1 < t_2 < t_3$, we obtain

$$P_2(y_1, t_1; y_3, t_3) = P_1(y_1, t_1) \int P_{1|1}(y_1, t_1 | y_2, t_2) P_{1|1}(y_2, t_2 | y_3, t_3) dy_2. \quad (5.18)$$

If we now divide Eq. (5.18) by $P_1(y_1, t_1)$, we obtain

$$P_{1|1}(y_1, t_1 | y_3, t_3) = \int P_{1|1}(y_1, t_1 | y_2, t_2) P_{1|1}(y_2, t_2 | y_3, t_3) dy_2. \quad (5.19)$$

Equation (5.19) is called the *Chapman–Kolmogorov equation*. Notice that we have broken the probability of transition from y_1, t_1 to y_3, t_3 into a process involving two successive steps, first from y_1, t_1, to y_2, t_2 and then from y_2, t_2 to y_3, t_3. The Markov character is exhibited by the fact that the probability of the two successive steps is the product of the probability of the individual steps. The successive steps are statistically *independent*. The probability of the transition $y_2, t_2 \to y_3, t_3$ is not affected by the fact that it was preceded by a transition $y_1, t_1 \to y_2, t_2$.

In the next section we will use these equations to study some of the simplest Markov processes, namely those of Markov chains.

5.C. MARKOV CHAINS [2–6]

One of the simplest examples of a Markov process is that of a Markov chain. This involves transitions, at discrete times, between values of a discrete stochastic variable, Y. Let us assume that Y has realizations $\{y(n)\}$, where $n = 1, 2, \ldots, M$, and that transitions occur at times $t = s\tau$, where $s = 0, 1, \ldots, \infty$. We let $P(n, s)$ denote the probability that Y has realization, $y(n)$, at "time" $t = s$. We let $P_{1|1}(n_1, s_1|n_2, s_2)$ denote the conditional probability that Y has realization $y(n_2)$ at time s_2, given that it had realization $y(n_1)$ at time s_1. The two quantities $P(n, s)$ and $P_{1|1}(n_1, s_1|n_2, s_2)$ completely determine the evolution of a Markov chain.

We can write Eq. (5.12) for the probability $P(n, s)$ in the form

$$P(n, s+1) = \sum_{m=1}^{M} P(m, s) P_{1|1}(m, s|n, s+1) \tag{5.20}$$

and from the Chapman–Kolmogorov equation, (5.19), we can write the conditional probability in the form

$$P_{1|1}(n_0, s_0|n, s+1) = \sum_{m=1}^{M} P_{1|1}(n_0, s_0|m, s) P_{1|1}(m, s|n, s+1). \tag{5.21}$$

The quantity $P_{1|1}(m, s|n, s+1)$ is called the *transition probability*. It is the conditional probability that if the system is in state m at time s, it will jump to state n in the next step. It therefore contains all necessary information about the basic transition mechanism in the system.

Let us now introduce the transition matrix $\mathbf{Q}(s)$, whose (m, n)th element is the transition probability

$$Q_{m,n}(s) \equiv P_{1|1}(m, s|n, s+1). \tag{5.22}$$

In this section we will consider Markov chains for which the transition matrix is independent of time, $\mathbf{Q}(s) = \mathbf{Q}$. In Section S5.A, we consider the case when the transition matrix depends periodically on time $\mathbf{Q}(s) = \mathbf{Q}(s+N)$.

5.C.1. Spectral Properties

For the case of a time-independent transition matrix, we have

$$\mathbf{Q}_{m,n} = P_{1|1}(m, 0|n, 1) = P_{1|1}(m, s|n, s+1). \tag{5.23}$$

The formal solution of Eq. (5.21) for the conditional probability can be obtained by iteration and is given by

$$P_{1|1}(m, s_0|n, s) = (\mathbf{Q}^{s-s_0})_{m,n}, \tag{5.24}$$

where the right-hand side denotes the (m, n)th element of the matrix $\mathbf{Q}$ raised to the $s - s_0$ power. The probability $P(n, s)$ is given by

$$P(n, s) = \sum_{m=1}^{M} P(m, 0)(\mathbf{Q}^s)_{m,n}. \tag{5.25}$$

It is useful at this point to introduce Dirac vector notation. We will let $P(n, s) \equiv \langle \mathbf{p}(s)|n\rangle$, and $P_{1|1}(m, s_0|n, s) \equiv \langle m|\mathbf{P}(s_0|s)|n\rangle$. Here $\langle \mathbf{p}(s)|$ is the probability vector and $\mathbf{P}(s_0|s)$ is the conditional probability matrix. The left and right states, $\langle n|$ and $|n\rangle$ respectively, denote the possible realizations of the stochastic variable Y and are assumed to be complete, $\sum_{n=1}^{M} |n\rangle\langle n| = 1$, and orthonormal, $\langle m|n\rangle = \delta_{m,n}$. The probability $P(n, s) \equiv \langle \mathbf{p}(s)|n\rangle$ can be thought of as the nth component of a row vector. We shall now express $\mathbf{P}(s_0|s)$ and $\langle \mathbf{p}(s)|$ in terms of eigenstates of the transition matrix, $\mathbf{Q}$.

The transition matrix, $\mathbf{Q}$, in general is not a symmetric matrix. Therefore, the right and left eigenvectors of $\mathbf{Q}$ will be different. The eigenvalues, λ_i $(i = 1, \ldots, M)$, of $\mathbf{Q}$ are given by values of λ which satisfy the condition that the determinant of the matrix, $\mathbf{Q} - \lambda\mathbf{I}$, be zero. That is,

$$\det|\mathbf{Q} - \lambda\mathbf{I}| = 0 \tag{5.26}$$

($\mathbf{I}$ is the unit matrix). If $\mathbf{Q}$ is an $M \times M$ matrix, it will have M eigenvalues, which may or may not all be real. Corresponding to the ith eigenvalue, there will be a left eigenstate, $\langle \chi_i|$, and a right eigenstate, $|\psi_i\rangle$. The left eigenstate satisfies the eigenvalue equation, $\langle \chi_i|\lambda_i = \langle \chi_i|\mathbf{Q}$, or

$$\chi_i(n)\lambda_i = \sum_{m=1}^{M} \chi_i(m) Q_{m,n}, \tag{5.27}$$

where $\chi_i(n) \equiv \langle \chi_i|n\rangle$ and $Q_{m,n} \equiv \langle m|\mathbf{Q}|n\rangle$. The right eigenstate satisfies the eigenvalue equation, $\lambda_i|\psi_i\rangle = \mathbf{Q}|\psi_i\rangle$, or

$$\lambda_i\psi_i(n) = \sum_{m=1}^{M} Q_{n,m}\psi_i(m), \tag{5.28}$$

where $\psi_i(n) \equiv \langle n|\psi_i\rangle$.

We can prove that the left and right eigenvectors of $\mathbf{Q}$ are complete and orthogonal. Let us first prove *orthogonality*. Consider the eigenvalue equations $\lambda_j|\psi_j\rangle = \mathbf{Q}|\psi_j\rangle$ and $\langle \chi_i|\lambda_i = \langle \chi_i|\mathbf{Q}$. Multiply the first equation by $\langle \chi_i|$ and the second equation by $|\psi_j\rangle$, and subtract the first equation from the second. We get

$$(\lambda_i - \lambda_j)\langle \chi_i|\psi_j\rangle = \langle \chi_i|\mathbf{Q}|\psi_j\rangle - \langle \chi_i|\mathbf{Q}|\psi_j\rangle = 0. \tag{5.29}$$

Thus, if $\lambda_i \neq \lambda_j$, then $\langle \chi_i | \psi_j \rangle = 0$. If $\lambda_i = \lambda_j$, then $\langle \chi_i | \psi_i \rangle$ can be nonzero. We shall always normalize the left and right eigenvectors so that

$$\langle \chi_i | \psi_j \rangle = \delta_{i,j}. \tag{5.30}$$

Let us next consider *completeness*. Let us expand a probability vector $\langle \mathbf{p}|$, in terms of left eigenvectors so that $\langle \mathbf{p}| = \sum_{i=1}^{M} \alpha_i \langle \chi_i|$. We then multiply on the right by $|\psi_j\rangle$ and use the orthonormality condition, Eq. (5.30). We find $\alpha_j = \langle \mathbf{p}|\psi_j\rangle$ so that

$$\langle \mathbf{p}| = \sum_{i=1}^{M} \langle \mathbf{p}|\psi_i\rangle \langle \chi_i|$$

This expresses the completeness condition

$$\sum_{i=1}^{M} |\psi_i\rangle \langle \chi_i| = \mathbf{I} \tag{5.31}$$

for the left and right eigenstates.

We next obtain some general properties of the eigenvalues, λ_i. First, we will prove that $|\lambda_i| \leq 1$ for all i. To do this, first take the absolute value of Eq. (5.28), $|\lambda_i \psi_i(n)| = |\sum_{m=1}^{M} Q_{n,m} \psi_i(m)|$. Both λ_i and $\psi_i(n)$ are complex (or real) numbers while $Q_{m,n}$ is a real number. It is easy to show that $|\lambda_i \psi_i(n)| = |\lambda_i||\psi_i(n)|$. We next use the triangle inequality, $|\sum_{i=1}^{M} x_i| \leq \sum_{i=1}^{M} |x_i|$, where x_i is a complex number. Thus, we find

$$|\lambda_i||\psi_i(n)| \leq \sum_{m=1}^{M} Q_{n,m} |\psi_i(m)|. \tag{5.32}$$

Let us assume that $|\psi_i(n)| \leq C$ for all n, where C is a positive constant. Then

$$\sum_{m=1}^{M} Q_{n,m} |\psi_i(m)| \leq C \sum_{m=1}^{M} Q_{n,m} = C. \tag{5.33}$$

Assume that for $n = n_0$, $|\psi_i(n_0)| = C$. Then Eqs. (5.32) and (5.33) give $|\lambda_i| C \leq C$ and

$$|\lambda_i| \leq 1. \tag{5.34}$$

Thus, all eigenvalues of the transition matrix have a magnitude less than or equal to one.

Now that we have established that $|\lambda_i| \leq 1$, we can also prove that $\lambda_i = 1$ is always an eigenvalue. Let us first note that the particular choice, $\psi_i(n) = 1$ for

all n, is a right eigenvector with eigenvalue, $\lambda_i = 1$ [cf. Eq. (5.28) and note that $\sum_{m=1}^{M} Q_{nm} = 1$]. The corresponding left eigenvector, $\langle \chi_i|$, with eigenvalue, $\lambda_i = 1$, must satisfy the eigenvalue equation

$$\chi_i(n) = \sum_{m=1}^{M} \chi_i(m) Q_{m,n}. \tag{5.35}$$

Equation (5.35) is the equation for a stationary probability vector, $\chi_i(n) \equiv P_{ST}(n)$—that is, one that does not change with time.

We can expand the transition matrix, $\mathbf{Q}$, in terms of its left and right eigenvectors. Consider the left eigenvalue equation, $\langle \chi_i | \lambda_i = \langle \chi_i | \mathbf{Q}$. Multiply from the left by the right eigenstate, $|\psi_i\rangle$, and sum over i. If we use the completeness relation, Eq. (5.31), we obtain $\mathbf{Q} = \sum_{i=1}^{M} \lambda_i |\psi_i\rangle \langle \chi_i|$ or

$$Q_{m,n} = \sum_{i=1}^{M} \lambda_i \psi_i(m) \chi_i(n). \tag{5.36}$$

If we now combine Eqs. (5.24) and (5.36) and use the orthonormality of the left and right eigenvectors, we obtain

$$P_{1|1}(m, s_0|n, s) = \sum_{i=1}^{M} \lambda_i^{s-s_0} \psi_i(m) \chi_i(n). \tag{5.37}$$

Thus, we have obtained the general solution for the discrete Markov process in terms of the eigenvalues and left and right eigenvectors of the transition matrix $\mathbf{Q}$.

The detailed behavior of the conditional probability depends on the structure of the transition matrix. There is one case that we are particularly interested in, and that is the case when the transition matrix is regular. The transition matrix $\mathbf{Q}$ is called *regular* if all elements of some power $\mathbf{Q}^N$ (N an integer) are nonzero. If $\mathbf{Q}$ is regular, the probability $P(n, s)$ tends to a unique stationary state $P_{ST}(n)$ after a long time. This means that there will be only one eigenvalue of $\mathbf{Q}$ with eigenvalue $\lambda = 1$. Let us denote it $\lambda_1 = 1$. Then Eq. (5.37) can be written

$$P_{1|1}(m, s_0|n, s) = \psi_1(m) P_{ST}(n) + \sum_{i=2}^{M} \lambda_i^{s-s_0} \psi_i(m) \chi_i(n), \tag{5.38}$$

where $\psi_1(m) = 1$ for all m. Since $\lambda_i < 1$ for $i \neq 1$, we can take the limit $s \to \infty$ and obtain

$$\lim_{s \to \infty} P_{1|1}(m, s_0|n, s) = \psi_1(m) P_{ST}(n) \qquad \text{with } \psi_1(m) = 1 \text{ for all } m. \tag{5.39}$$

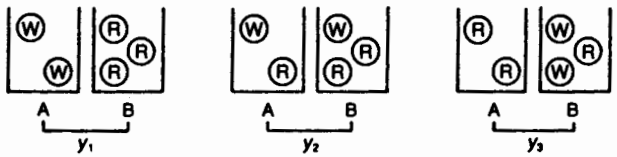
Thus, for regular transition matrices, the conditional probability tends to a unique value for long times. Similarly,

$$\lim_{s\to\infty} P(n, s) = P_{ST}(n). \tag{5.40}$$

In Exercise 5.1, we shall illustrate these ideas with an example.

Markov chains which are governed by regular transition matrices are *ergodic*. That is, it is possible, starting from any one realization of the stochastic variable, to reach every other realization through transitions during the evolution of the system. This is no longer true if, for example, the transition matrix is block-diagonal. Then some realizations will be decoupled from others. When the transition matrix is block-diagonal, the system can have multiple long-time states.

■ **EXERCISE 5.1.** Consider two pots, A and B, with three red balls and two white balls distributed between them so that A always has two balls and B always has three balls. There are three different configurations for the pots, as shown in the figure below. We obtain transitions between these three configurations by picking a ball out of A at random and one out of B at random and interchanging them. (a) Compute the transition matrix $\mathbf{Q}$ and the conditional probability $P_{1|1}(m, s_0|n, s)$. (b) If initially $P_i(1, 0) = 1$, $P_1(2,0) = 0$, and $P_1(3, 0) = 0$, compute the probability $P_1(n, s)$ ($n = 1, 2,$ and 3) at time s. (c) Assume that the realization, $y(n) = n$. Compute the first moment, $\langle y(s)\rangle$, and the autocorrelation function, $\langle y(0)y(s)\rangle$, for the same initial conditions as in part (b).



Answer:

(a) Inspection shows that we can make the following transitions from y_i to y_j with transition probability, Q_{ij}, such that $Q_{11} = 0$, $Q_{12} = 1$, $Q_{13} = 0$, $Q_{21} = \frac{1}{6}$, $Q_{22} = \frac{1}{2}$, $Q_{23} = \frac{1}{3}$, $Q_{31} = 0$, $Q_{32} = \frac{2}{3}$, and $Q_{33} = \frac{1}{3}$. The transition matrix and its square are given by

$$\mathbf{Q} = \begin{pmatrix} 0 & 1 & 0 \\ \frac{1}{6} & \frac{1}{2} & \frac{1}{3} \\ 0 & \frac{2}{3} & \frac{1}{3} \end{pmatrix} \quad \text{and} \quad \mathbf{Q}^2 = \begin{pmatrix} \frac{1}{6} & \frac{1}{2} & \frac{1}{3} \\ \frac{1}{12} & \frac{23}{36} & \frac{10}{36} \\ \frac{1}{9} & \frac{20}{36} & \frac{1}{3} \end{pmatrix},$$

respectively. The transition matrix is regular so this system has a

unique long-time stationary state. The eigenvalues of $\mathbf{Q}$ are $\lambda_1 = 1$, $\lambda_2 = \frac{1}{6}$, and $\lambda_3 = -\frac{1}{3}$. The right eigenstates can be written

$$|\psi_1\rangle = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \qquad |\psi_2\rangle = \begin{pmatrix} -\frac{3}{2} \\ -\frac{1}{4} \\ 1 \end{pmatrix}, \qquad |\psi_3\rangle = \begin{pmatrix} 3 \\ -1 \\ 1 \end{pmatrix}.$$

The left eigenstates can be written

$$\langle\chi_1| = \left(\tfrac{1}{10} \quad \tfrac{6}{10} \quad \tfrac{3}{10}\right), \qquad \langle\chi_2| = \left(-\tfrac{4}{15} \quad -\tfrac{4}{15} \quad \tfrac{8}{15}\right),$$
$$\langle\chi_3| = \left(\tfrac{1}{6} \quad -\tfrac{1}{3} \quad \tfrac{1}{6}\right).$$

We can now construct the conditional probability matrix

$$\mathbf{P}(s_0|s) = \sum_{i=1}^{3} \lambda_i^{s-s_0} |\psi_i\rangle\langle\chi_i| = \begin{pmatrix} \frac{1}{10} & \frac{6}{10} & \frac{3}{10} \\ \frac{1}{10} & \frac{6}{10} & \frac{3}{10} \\ \frac{1}{10} & \frac{6}{10} & \frac{3}{10} \end{pmatrix}$$
$$+ \left(\tfrac{1}{6}\right)^{s-s_0} \begin{pmatrix} \frac{2}{5} & \frac{2}{5} & -\frac{4}{5} \\ \frac{1}{15} & \frac{1}{15} & -\frac{2}{15} \\ -\frac{4}{15} & -\frac{4}{15} & \frac{8}{15} \end{pmatrix}$$
$$+ \left(-\tfrac{1}{3}\right)^{s-s_0} \begin{pmatrix} \frac{1}{2} & -1 & \frac{1}{2} \\ -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} \\ \frac{1}{6} & -\frac{1}{3} & \frac{1}{6} \end{pmatrix}.$$

Note that all the probabiliy is carried by the long-time state.

(b) Denote the probability vector as $\langle\mathbf{p}(s)| = (P(1, s), P(2, s), P(3, s))$. Then $\langle\mathbf{p}(s)| = \langle\mathbf{p}(0)|\mathbf{P}(0|s)$. If we assume an initial condition $\langle\mathbf{p}(0)| = (1,0,0)$, then the probability vector at time s is

$$\langle\mathbf{p}(s)| = \left\{\left[\frac{1}{10} + \frac{2}{5}\left(\frac{1}{6}\right)^s + \frac{1}{2}\left(-\frac{1}{3}\right)^s\right], \left[\frac{3}{5} + \frac{2}{5}\left(\frac{1}{6}\right)^s - \left(-\frac{1}{3}\right)^s\right],\right.$$
$$\left.\left[\frac{3}{10} - \frac{4}{5}\left(\frac{1}{6}\right)^s + \frac{1}{2}\left(-\frac{1}{3}\right)^s\right]\right\}.$$

(c) The first moment is given by $\langle y(s)\rangle = \sum_{n=1}^{3} nP_1(n, s)$. From the expression for $\langle\mathbf{p}(s)|$ we obtain

$$\langle y(s)\rangle = \frac{11}{5} - \frac{6}{5}\left(\frac{1}{6}\right)^s.$$

Finally, we compute the autocorrelation function,

$$\langle y(0)y(s)\rangle = \sum_{m=1}^{3}\sum_{n=1}^{3} mnP_1(m, 0)P_{1|1}(m, 0|n, s).$$

We obtain

$$\langle y(0)y(s)\rangle = \frac{66}{5} + \frac{4}{5}\left(\frac{1}{6}\right)^s.$$

Note that the eigenvalue $\lambda_3 = -\frac{1}{3}$ does not contribute to $\langle y(s)\rangle$ and $\langle y(0)y(s)\rangle$. However, if we choose the dependence of $y(n)$ on n differently, it will, in general, contribute to these.

5.C.2. Random Walk

The problem of random walk on a lattice which was considered in Sections 4.E and 4.F can be formulated as a Markov chain of transition probabilities. For simplicity, let us consider random walk on an infinite one dimensional lattice with lattice spacing, Δ, along the x axis, and let us assume that the time between steps is τ. Let $P_1(n\Delta, s\tau)$ be the probability to find the particle at point $x = n\Delta$ after s steps. Then

$$P_1(n\Delta, (s+1)\tau) = \sum_{m=-\infty}^{\infty} P_1(m\Delta, s\tau) P_{1|1}(m\Delta, s\tau \,|\, n\Delta, (s+1)\tau), \quad (5.41)$$

where $P_{1|1}(m\Delta, s\tau | n\Delta, (s+1)\tau)$ is the transition probability to go from site $x = m\Delta$ to site $x = n\Delta$ in one step.

As a specific example, let us consider the case in which the random walker has an equal probability to go one lattice site to the left or right during each step. Then the transition probability is

$$P_{1|1}(m\Delta, s\tau \,|\, n\Delta, (s+1)\tau) = \tfrac{1}{2}\delta_{n,m+1} + \tfrac{1}{2}\delta_{n,m-1} \quad (5.42)$$

and Eq. (5.41) takes the form

$$P_1(n\Delta, (s+1)\tau) = \tfrac{1}{2}P_1((n+1)\Delta, s\tau) + \tfrac{1}{2}P_1((n-1)\Delta, s\tau). \quad (5.43)$$

We can obtain a differential equation for the probability $P_1(n\Delta, s\tau)$ in the continuum limit. Let us subtract $P_1(n\Delta, s\tau)$ from both sides of Eq. (5.43) and divide by τ. We then can write

$$\frac{P_1(n\Delta, s\tau + \tau) - P_1(n\Delta, s\tau)}{\tau} = \frac{\Delta^2}{2\tau}\left[\frac{P_1(n\Delta + \Delta, s\tau) + P_1(n\Delta - \Delta, s\tau) - 2P_1(n\Delta, s\tau)}{\Delta^2}\right]. \quad (5.44)$$

If we now let $x = n\Delta$, $t = s\tau$, and take the limit $\Delta \to 0$ and $\tau \to 0$ so that $D \equiv \Delta^2/2\tau$ is finite and x and t are finite, we obtain the following differential equation for $P(x,t)$:

$$\frac{\partial P_1(x,t)}{\partial t} = D\frac{\partial^2 P_1(x,t)}{\partial x^2}. \quad (5.45)$$

(cf. Eqs. (4.62)–(4.64)). Equation (5.45) is a *diffusion equation* for the probability density $P_1(x,t)$.

Let us solve Eq. (5.45) for the case $P_1(x,0) = \delta(x)$. We first introduce the Fourier transform of $P_1(x,t)$:

$$\tilde{P}_1(k,t) = \int_{-\infty}^{\infty} dx\, P_1(x,t) e^{ikx}.$$

Then Eq. (5.45) takes the form

$$\frac{\partial \tilde{P}(k,t)}{\partial t} = -Dk^2 \tilde{P}_1(k,t). \quad (5.47)$$

We can solve Eq. (5.47) to obtain

$$\tilde{P}(k,t) = e^{-Dk^2 t}, \quad (5.48)$$

where we have used the fact that $\tilde{P}(k,0) = 1$ since $P_1(x,0) = \delta(x)$. We can now take the inverse transform to obtain

$$P_1(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-ikx} e^{-Dk^2 t} = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}. \quad (5.49)$$

It is easy to show that $\langle x(t)\rangle = 0$ and $\langle x^2(t)\rangle = 2Dt$.

5.D. THE MASTER EQUATION [3, 4]

We often need to consider processes for which the time interval between events can vary in a continuous and random manner, but as in Section 6.C the realizations of the stochastic variable Y are discrete. For such processes, we need to obtain a differential equation for the time dependence of the probability $P_1(n,t)$. In this section we consider processes for which the elementary events or transitions occur over a very short time interval compared to the time during which the stochastic process evolves. The time evolution of such processes is governed by the *master equation*.

5.D.1. Derivation of the Master Equation

To begin, let us rewrite Eq. (5.12) in the form

$$P_1(n, t+\Delta t) = \sum_{m=1}^{M} P_1(m, t) P_{1|1}(m, t|n, t+\Delta t). \tag{5.50}$$

The differential equation for $P_1(n, t)$ can be constructed from Eq. (5.50) if we note that

$$\begin{aligned} \frac{\partial P_1(n, t)}{\partial t} &\equiv \lim_{\Delta t \to 0} \left(\frac{P_1(n, t+\Delta t) - P_1(n, t)}{\Delta t} \right) \\ &= \lim_{\Delta t \to 0} \frac{1}{\Delta t} \sum_{m=1}^{M} P_1(m, t)(P_{1|1}(m, t|n, t+\Delta t) - \delta_{m,n}). \end{aligned} \tag{5.51}$$

Since we will take the limit $\Delta t \to 0$, we can expand the transition probability $P_{1|1}(m, t|n, t+\Delta t)$ in a power series in Δt and keep only the lowest-order term. In order to conserve probability at all times, its most general form is

$$P_{1|1}(m, t|n, t+\Delta t) = \delta_{m,n}\left[1 - \Delta t \sum_{l=1}^{M} w_{m,l}(t)\right] + w_{m,n}(t)\Delta t + \ldots, \tag{5.52}$$

where $w_{m,n}(t)$ is the *transition probability rate*. In Eq. (5.52), $w_{m,n}(t)\Delta t$ is the probability of a transition from state m to state n during the time interval $t \to t+\Delta t$. Similarly, $[1 - \sum_{l=1}^{M} w_{m,l}(t)\Delta t]$ is the probability that *no* transition occurs during the time interval $t \to t+\Delta t$. If we now substitute Eq. (5.52) into Eq. (5.51), we obtain

$$\frac{\partial P_1(n, t)}{\partial t} = \sum_{m=1}^{M} [P_1(m, t) w_{m,n}(t) - P_1(n, t) w_{n,m}(t))]. \tag{5.53}$$

Equation (5.53) is called the *master equation*. The master equation gives the rate of change of the probability $P_1(n, t)$ due to transitions into the state n from all others states (first term on the right) and due to transitions out of state n into all others states (second term on the right).

The conditional probability $P_{1|1}(n_0, 0|n, t)$ also satisfies a master equation

$$\frac{\partial P_{1|1}(n_0, 0|n, t)}{\partial t} = \sum_{m=1}^{M} [P_{1|1}(n_0, 0|m, t) w_{m,n}(t) - P_{1|1}(n_0, 0|n, t) w_{n,m}(t))], \tag{5.54}$$

where $P_{1|1}(n_0, 0|n, t)$ is the probability to find the system in the state n at time t, given that it was in the state n_0 at time $t = 0$. The conditional probability satisfies an initial condition $P_{1|1}(n_0, 0|n, 0) = \delta_{n,n_0}$.

The master equation can be written in a more concise form if we introduce the transition matrix

$$W_{m,n}(t) = w_{m,n}(t) - \delta_{m,n} \sum_{n'=1}^{M} w_{n,n'}(t). \tag{5.55}$$

The master equation then takes the form

$$\frac{\partial P_1(n, t)}{\partial t} = \sum_{m=1}^{M} P_1(m, t) W_{m,n}(t). \tag{5.56}$$

From Eq. (5.55), we see that the transition matrix must satisfy the conditions

$$W_{m,n} \geqslant 0 \text{ for } n \neq m \quad \text{and} \quad \sum_{n} W_{m,n} = 0 \qquad \text{for each } m. \tag{5.57}$$

Thus, the entries in the rows of $W_{m,n}$ must add to zero.

We can write Eq. (5.56) in still more concise form if we introduce Dirac notation. We let $P_1(n, t) = \langle \mathbf{p}(t)|n\rangle$, where $\langle \mathbf{p}(t)|$ is the probability vector, and $P_{1|1}(n_0, t_0|n, t) = \langle n_0|\mathbf{P}(t_0|t)|n\rangle$, where $\mathbf{P}(t_0|t)$ is the conditional probability operator. Similarly we let $W_{m,n}(t) = \langle m|\mathbf{W}(t)|n\rangle$. The master equation for the probability vector becomes

$$\frac{\partial \langle \mathbf{p}(t)|}{\partial t} = \langle \mathbf{p}(t)|\mathbf{W}(t), \tag{5.58}$$

and the master equation for the conditional probability operator becomes

$$\frac{\partial \mathbf{P}(0|t)}{\partial t} = \mathbf{P}(0|t)\mathbf{W}(t), \tag{5.59}$$

The transition matrix, $W_{m,n}(t)$, in general is not symmetric so its left and right eigenvectors will be different. However, one can often use the method of Section 5.C.1 to obtain a spectral decomposition of $\mathbf{W}(t)$ and therefore of $\langle \mathbf{p}(t)|$ and $\mathbf{P}(0|t)$. However, care must be used. There may be cases where the eigenvectors of $\mathbf{W}(t)$ do not span the solution space [7]. Then the spectral decomposition cannot be used. There is one type of system for which a spectral decomposition cannot be used. There is one type of system for which a spectral decomposition can always be done, and that is the case for which the transition rates $w_{m,n}(t)$ satisfy detailed balance.

5.D.2. Detailed Balance [3, 4, 8]

The transition rates satisfy *detailed balance* if

$$P^s(n)w_{n,m} = P^s(m)w_{m,n}, \tag{5.60}$$

where $P^s(n) \equiv \lim_{t\to\infty} P_1(n, t)$ is the long-time stationary probability of the system (we assume the transition rates, $w_{m,n}$, are independent of time) and is independent of time. $P^{s](n)}$ is the left eigenvector of the transition matrix, **W**, so that $\langle \mathbf{p}^s|\mathbf{W} = 0$ where $P^s(n) = \langle \mathbf{p}^s|n\rangle$. Equation (5.60) tells us that at equilibrium, the flow of probability into level n from level m is equal to the flow of probability from level m to level n. It is useful to note that the state, $P^s(n)$, can be obtained from Eq. (5.60) by iterating. For example, $P^s(2) = P^s(1)(w_{1,2}/w_{2,1})$, $P^s(3) = P^s(2)(w_{2,3}/w_{3,2}) = P^s(1)(w_{1,2}/w_{2,1})\,(w_{2,3}/w_{3,2})$ and so on. $P^s(1)$ can then be found by requiring that the probability be normalized to one, $\sum_{n=1}^{M} P^{s](n)=1}$.

Given Eq. (5.60), we can show that the dynamical evolution of the master equation is governed by a symmetric matrix. Let us define

$$\begin{aligned} V_{n,m} &= \sqrt{\frac{P^s(n)}{P^s(m)}}W_{n,m} = \sqrt{\frac{P^s(n)}{P^s(m)}}w_{n,m} - \delta_{n,m}\sum_{n'} w_{n,n'} \\ &= \sqrt{\frac{P^s(m)}{P^s(n)}}w_{m,n} - \delta_{n,m}\sum_{n'} w_{m,n'} = V_{m,n}, \end{aligned} \tag{5.61}$$

where we have used Eq. (5.60). If we now introduce a new function, $\tilde{P}(n, t) = P_1(n, t)/\sqrt{P^s(n)}$, the master equation takes the form

$$\frac{\partial \tilde{P}(n, t)}{\partial t} = \sum_{m=1}^{M} \tilde{P}(m, t)V_{m,n}. \tag{5.62}$$

Let us again use Dirac notation to write $\langle \tilde{\mathbf{p}}(t)|n\rangle = \tilde{P}(n, t)$ and $V_{n,m} = \langle n|\mathbf{V}|m\rangle$. Then the solution of the master equation becomes

$$\langle \tilde{\mathbf{p}}(t)| = \langle \tilde{\mathbf{p}}(0)|e^{\mathbf{V}t}. \tag{5.63}$$

Since $V_{n,m}$ is a symmetric matrix, it has a complete orthonormal set of eigenvectors. We shall denote the eigenvalues of **V** by λ_i and left and right eigenvectors by $\langle\psi_i|$ and $|\psi_i\rangle$, respectively, where $i = 0, \ldots, M-1$. The left and right eigenvectors are the same. Thus, $\langle\psi_i|\mathbf{V} = \langle\psi_i|\lambda_i$ and $\mathbf{V}|\psi_i\rangle = \lambda_i|\psi_i\rangle$. Since the eigenvectors form a complete orthonormal set, we can write orthonormality condition as $\langle\psi_i|\psi_j\rangle = \delta_{i,j}$ and the completeness condition as $\sum_{i=0}^{M-1} |\psi_i\rangle\langle\psi_i| = \mathbf{1}$.

The solution to the master equation can now be written in terms of a spectral decomposition

$$\langle \tilde{\mathbf{p}}(t)| = \sum_{i=0}^{M-1} \langle \tilde{\mathbf{p}}(0)|\psi_i\rangle e^{\lambda_i t}\langle\psi_i|. \tag{5.64}$$

In terms of the probability $P_1(n, t)$, it takes the form

$$P_1(n, t) = \sum_{i=0}^{M-1}\sum_{m=1}^{M} \sqrt{\frac{P^s(n)}{P^s(m)}}\, P_1(m, 0)\langle m|\psi_i\rangle e^{\lambda_i t}\langle\psi_i|n\rangle. \tag{5.65}$$

The eigenvalues λ_i must be negative or zero. Let $i = 0$ denote the zero eigenvalue, $\lambda_0 = 0$. Then

$$P^s(n) = \lim_{t\to\infty} P_1(n, t) = \sum_{m=1}^{M} \sqrt{\frac{P^s(n)}{P^s(m)}}\, P_1(m, 0)\langle m|\psi_0\rangle\langle\psi_0|n\rangle. \tag{5.66}$$

In order to be consistent we must have $\langle m|\psi_0\rangle = \langle\psi_0|m\rangle = \sqrt{P^s(m)}$, for all m, since $\sum_m P_1(m, 0) = 1$. Thus,

$$P_1(n, t) = P^s(n) + \sum_{i=1}^{M-1}\sum_{m=1}^{M} \sqrt{\frac{P^s(n)}{P^s(m)}}\, P_1(m, 0)\langle m|\psi_i\rangle e^{\lambda_i t}\langle\psi_i|n\rangle. \tag{5.67}$$

In Exercise 5.2 we give an example of a random walk which obeys detailed balance and in Exercise 5.3 we give an example of one that does not obey detailed balance.

■ **EXERCISE 5.2** Consider an asymmetric random walk on an open-ended lattice with four lattice sites. The transition rates are $w_{1,2} = w_{4,3} = 1, w_{2,3} = w_{3,4} = \frac{3}{4}, w_{2,1} = w_{3,2} = \frac{1}{4}$, and $w_{i,j} = 0$ for all other transitions. (a) Write the transition matrix, **W**, and show that this system obeys detailed balance. (b) Compute **V** and find its eigenvalues and eigenvectors. (c) Write $P_1(n, t)$ for the case $P_1(n, 0) = \delta_{n,1}$. What is $P_1(2, t)$?

Answer:

(a) The transition matrix, **W**, is given by

$$\mathbf{W} = \begin{pmatrix} -1 & 1 & 0 & 0 \\ \frac{1}{4} & -1 & \frac{3}{4} & 0 \\ 0 & \frac{1}{4} & -1 & \frac{3}{4} \\ 0 & 0 & 1 & -1 \end{pmatrix}.$$

It has eigenvalues $\lambda_0 = 0$, $\lambda_1 = -1 + \frac{\sqrt{3}}{4}$, $\lambda_2 = -2$, and $\lambda_3 = -1 - \frac{\sqrt{3}}{4}$. The left eigenvector of **W** with eigenvalue, $\lambda_0 = 0$, is the stationary probability distribution, $\langle \mathbf{p}^s | = (\frac{1}{26}, \frac{2}{13}, \frac{6}{13}, \frac{9}{26})$. This system satisfies detailed balance because $P^s(n)w_{n,n+1} = P^s(n+1)w_{n+1,n}$. For example, $P^s(1)w_{1,2} = (\frac{1}{26})(1) = \frac{1}{26}$ and $P^s(2)w_{2,1} = (\frac{2}{13})(\frac{1}{4}) = \frac{1}{26}$.

(b) The matrix **V** is given by

$$\mathbf{V} = \begin{pmatrix} -1 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & -1 & \frac{\sqrt{3}}{4} & 0 \\ 0 & \frac{\sqrt{3}}{4} & -1 & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -1 \end{pmatrix}.$$

It also has eigenvalues $\lambda_0 = 0$, $\lambda_1 = -1 + \frac{\sqrt{3}}{4}$, $y_2 = -2$, and $\lambda_3 = -1 - \frac{\sqrt{3}}{4}$. The orthonormalized eigenstates are

$$\langle \psi_0 | = \left(\sqrt{\frac{1}{26}}, \sqrt{\frac{2}{13}}, \sqrt{\frac{6}{13}}, \sqrt{\frac{9}{26}} \right) \approx (0.196, 0.392, 0.679, 0.588),$$

$$\langle \psi_1 | \approx (0.679, 0.588, -0.196, -0.392),$$

$$\langle \psi_2 | \approx (-0.196, 0.392, -0.679, 0.588),$$

and $\langle \psi_3 | \approx (-0.679, 0.588, 0.196, -0.392)$.

(c) For the initial condition, $P_1(n, 0) = \delta_{n,1}$, $P_1(n, t)$ can be written

$$P_1(n, t) = P(n)^s + \sum_{i=1}^{3} \sqrt{\frac{P^s(n)}{P^s(1)}} \langle 1 | \psi_i \rangle e^{\lambda_i t} \langle \psi_i | n \rangle.$$

Using the numbers from (b) we find

$$P_1(2, t) \approx 0.154 + (0.799)e^{-0.567t} - (0.154)e^{-2t} - (0.799)e^{-1.433t}.$$

Note that $P_1(2, 0) = 0$ as it should.

■ **EXERCISE 5.3** Consider an asymmetric random walk on a periodic lattice with four lattice sites. The transition rates are $w_{1,2} = w_{2,3} = w_{3,4} = w_{4,1} = \frac{3}{4}$, $w_{2,1} = w_{3,2} = w_{4,3} = w_{1,4} = \frac{1}{4}$, and $w_{i,j} = 0$ for all other transitions. Write the transition matrix, **W**, and show that this system does not obey detailed balance.

Answer:

The transition matrix, **W**, is given by

$$\mathbf{W} = \begin{pmatrix} -1 & \frac{3}{4} & 0 & \frac{1}{4} \\ \frac{1}{4} & -1 & \frac{3}{4} & 0 \\ 0 & \frac{1}{4} & -1 & \frac{3}{4} \\ \frac{3}{4} & 0 & \frac{1}{4} & -1 \end{pmatrix}.$$

The left eigenvector of **W** with eigenvalue, $\lambda_0 = 0$, is the stationary probability distribution, $\langle \mathbf{p}^s | = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. Therefore, detailed balance cannot be satisfied and we cannot find a symmetric matrix which governs the dynamics of this system. It is interesting that the long-time state is one for which it is equally likely to find the random walker at any lattice site. Yet because detailed balance is not satisfied, there is also a probability current around the lattice.

5.D.3. Mean First Passage Time [9]

One of the useful quantities we can compute is a *mean first passage time*. If we consider the random walk problem, the mean first passage time is the average time for the walker to reach some site, n_p, *for the first time* assuming that the walker started at site n_0 at time $t = 0$. Computing this quantity involves a trick. We will assume that $P_1(n_p, t) \equiv 0$ for all time. This way, if the walker steps on site n_p, it can never return to the random walk. This is called an *absorbing boundary condition* at site n_p.

To be clear about what we are doing, we will let $Q_n(t)$ denote the conditional probability to find the walker at site n, assuming that it starts at site n_0 at time $t = 0$ (we suppress its dependence on n_0 for simplicity). Then $Q_n(0) = \delta_{n,n_0}$ and $Q_{n_p}(t) = 0$ (the absorbing boundary condition). The equations of motion for $Q_n(t)$ are the same as for $P_1(n, t)$ [cf. Eqs. (5.55) and (5.56)], except that we set $Q_{n_p}(t) = 0$. Thus,

$$\frac{\partial Q_n(t)}{\partial t} = \sum_{m(\neq n_p)=1}^{M} Q_m(t)w_{m,n}(t) - Q_n(t) \sum_{m=1}^{M} w_{m,n}(t)) \qquad \text{for } n \neq n_p. \tag{5.68}$$

Note that we set $Q_{n_p}(t) = 0$ but $w_{n_p,n} \neq 0$ in Eq. (5.68). In Dirac notation we write Eq. (5.68) as

$$\frac{\partial \mathbf{Q}(t)}{\partial t} = \mathbf{QM}, \tag{5.69}$$

where $Q_n(t) \equiv \langle n_0 | \mathbf{Q}(t) | n \rangle$ and $\langle m | \mathbf{M} | n \rangle = w_{m,n} - \delta_{m,n} \sum_{n'=1}^{M} w_{n,n'}$ with $m \neq n_p$. The matrix **M** is not symmetric in general, and therefore its left and right eigenvectors will not be the same. We can use the methods of Section 5.C to expand the solution of Eq. (5.69) in terms of left and right eigenvectors of **M** and its eigenvalues (see Exericse 5.4). However, when using this approach one must check that the eigenvectors are complete. Since $Q_n(t)$ must decay, at least for a finite lattice (the walker eventually steps on site, n_p), all the eigenvalues of **M** must be negative.

this makes Q not a probability transition matrix, but more of a submatrix. Equivalently $\sum_{n \neq n_p} Q_n(t) = \text{Prob}(X(t)$ with n_p made absorbing.

The probability that the walker is still "alive" (i.e., has not stepped on the site, $n = n_p$) at time t is

$$P_{n_0}(t) \equiv \sum_{n(\neq n_p)=1}^{M} Q_n(t). \tag{5.70}$$

We now define

$$f_{n_0,n_P}(t) \equiv \{\text{the probability to reach the site, } n_P, \text{ during the time interval } t \to t+dt\} \tag{5.71}$$

We then note that to be "alive" at time t, the probability must equal the sum of the probabilities to either have "died" during the time $t \to t+dt$ or still be alive at time $t+dt$. Thus, we can write

$$P_{n_0}(t) = f_{n_0,n_P}(t)dt + P_{n_0}(t+dt). \tag{5.72}$$

If we now note that $P_{n_0}(t+dt) = P_{n_0}(t) + (dP_{n_0}(t)/dt)dt + \cdots$, then we can write

$$f_{n_0,n_P}(t) = -\frac{dP_{n_0}(t)}{dt}. \tag{5.73}$$

From Eqs. (5.68) and (5.70), the probability density, $f_{n_0,n_P}(t)$, can also be written

$$\begin{aligned} f_{n_0,n_P}(t) &= -\sum_{n(\neq n_P)=1}^{M} \frac{dQ_n(t)}{dt} \\ &= \sum_{n'(\neq n_P)=1}^{M} \sum_{m(\neq n_P)=1}^{M} Q_m(t) w_{m,n'}(t) - \sum_{n'(\neq n_P)=1}^{M} Q_{n'}(t) \sum_{m=1}^{M} w_{m,n'}(t) \\ &= -\sum_{n'(\neq n_P)=1}^{M} Q_{n'}(t) w_{n_P,n'}(t)). \end{aligned} \tag{5.74}$$

Thus $f_{n_0,n_P}(t)$ can be expressed in terms of the probability to find the walker on neighbors of the site n_P and the transition rate between n_P and its neighbors.

The average time it takes the walker to reach the site n_p, given that it starts at site n_0 at time $t = 0$, is

$$\langle t \rangle = \int_0^\infty dt\, t f_{n_0,n_P}(t) = \int_0^\infty dt P_{n_0}(t), \tag{5.75}$$

$Q = e^{ML} Q(0)$ so with 5.70, this can be expressed in terms of M^{-1} and no time integral,

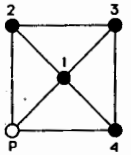
where we have used Eq. (5.72) and have integrated by parts. $\langle t \rangle$ is the *mean first passage time.*

■ **EXERCISE 5.4** Consider an asymmetric random walk on a lattice with five lattice sites. Assume that the fifth site, P, absorbs the walker. The transition rates $w_{1,2} = w_{1,3} = w_{1,4} = w_{1,P} = \frac{1}{4}$, $w_{2,1} = w_{2,3} = w_{2,P} = \frac{1}{3}$, $w_{3,1} = w_{3,2} = w_{3,4} = \frac{1}{3}$, $w_{4,1} = w_{4,3} = w_{4,P} = \frac{1}{3}$, $w_{P,1} = w_{P,2} = w_{P,4} = \frac{1}{3}$, and $w_{i,j} = 0$ for all other transitions. (a) Write the transition matrix, **M**, and compute its eigenvalues and left and right eigenvectors. (b) If the walker starts at site $n = 3$ at time $t = 0$, compute the mean first passage time.

Answer:

(a) The transition matrix, **M**, is given by

$$\mathbf{W} = \begin{pmatrix} -1 & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{3} & -1 & \frac{1}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & -1 & \frac{1}{3} \\ \frac{1}{3} & 0 & \frac{1}{3} & -1 \end{pmatrix}.$$



It has eigenvalues $\lambda_1 \approx -0.216$, $\lambda_2 = -1.0$, $\lambda_3 \approx -1.284$, and $\lambda_4 = -1.5$. The left eigenvectors are

$$\begin{aligned} \langle \chi_1^L | &\approx (0.286, 0.204, 0.265, 0.204), \\ \langle \chi_2^L | &= (0, -0.5, 0, 0.5), \\ \langle \chi_3^L | &\approx (0.614, -0.054, -0.415, -0.054), \\ \langle \chi_4^L | &= (-0.2, 0.3, -0.3, 0.3). \end{aligned}$$

The right eigenvectors are

$$|\chi_1^R\rangle \approx \begin{pmatrix} 1.0 \\ 0.950 \\ 1.234 \\ 0.950 \end{pmatrix}, \qquad |\chi_2^R\rangle = \begin{pmatrix} 0 \\ -1.0 \\ 0 \\ 1.0 \end{pmatrix},$$

$$|\chi_3^R\rangle \approx \begin{pmatrix} 1.0 \\ -0.117 \\ -0.901 \\ -0.117 \end{pmatrix}, \qquad |\chi_4^R\rangle = \begin{pmatrix} -0.5 \\ 1.0 \\ -1.0 \\ 1.0 \end{pmatrix}.$$

(b) The spectral decomposition of the matrix $\mathbf{Q}(t)$ can be written

$$\mathbf{Q}(t) = \mathbf{Q}(0) \sum_{i=1}^{4} e^{\lambda_i t} |\chi_i^R\rangle\langle\chi_i^L|. \tag{1}$$

If we take matrix elements and note that $\langle n_0|\mathbf{Q}(0)|n\rangle = \delta_{n,n_0}$, we find

$$\langle n_0|\mathbf{Q}(t)|n\rangle = \sum_{i=1}^{4} e^{\lambda_i t}\langle n_0|\chi_i^R\rangle\langle\chi_i^L|n\rangle. \tag{2}$$

The mean first passage time is

$$\begin{aligned}\langle t\rangle &= \int_0^\infty dt P_{n_0}(t) = \sum_{n=1}^{4}\int_0^\infty dt\langle n_0|\mathbf{Q}(t)|n\rangle \\ &= \sum_{n=1}^{4}\sum_{i=1}^{4}\langle n_0|\chi_i^R\rangle\left(\frac{-1}{\lambda_i}\right)\langle\chi_i^L|n\rangle.\end{aligned} \tag{3}$$

If we now let $n_0 = 3$ and use the numbers from part (a), we find $\langle t\rangle \approx 5.33$.

5.E. BROWNIAN MOTION

Brownian motion provides some of the most spectacular evidence, on the "macroscopic" scale, for the discrete or atomic nature of matter on the "microscopic" scale. The discreteness of matter causes fluctuations in the density of matter, which, in turn, causes observable effects on the motion of the Brownian particle. This can be seen if one immerses a large particle (usually about one micron in diameter) in a fluid with the same density as the particle. When viewed under a microscope, the large particle (the Brownian particle) appears to be in a state of agitation, undergoing rapid and random movements. Early in the nineteenth century, the biologist Robert Brown wrote a paper on this phenomenon [10] which received wide attention, and as a result it has been named for him.

The modern era in the theory of Brownian motion began with Albert Einstein, who, initially unaware of the widely observed phenomenon of Brownian motion, was looking for a way to confirm the atomic nature of matter. Einstein obtained a relation between the macroscopic diffusion coefficient, D, and the atomic properties of matter. This relation is $D = RT/N_A 6\pi\eta a$, where R is the gas constant, $N_A = 6.02 \times 10^{23}\,\text{mol}^{-1}$ is Avogadro's number, T is the temperature in kelvins, η is the viscosity, and a is the radius of the Brownian particle [11, 12]. It has since been confirmed by many experiments on Brownian motion [13].

In this section we derive the theory of Brownian motion starting from the Langevin equations for a Brownian particle. That is, we focus on a large particle (the Brownian particle) immersed in a fluid of much smaller atoms. The agitated motion of the large particle is much slower than that of the atoms and is the result of random and rapid kicks due to density fluctuations in the fluid. Since the time scales of the Brownian motion and the atomic motions are vastly different, we can separate them and focus on the behavior of the Brownian particle. The effect of the fluid on the Brownian particle can be reduced to that of a random force and a systematic friction acting on the Brownian particle.

The Langevin theory of Brownian motion provides a paradigm theory for treating many-body systems in which a separation of time scales can be identified between some of the degrees of freedom. For this reason we consider it in some detail here.

5.E.1. Langevin Equation [3, 4]

Consider a particle in a fluid undergoing Brownian motion. For simplicity we will consider motion in one dimension. The results can easily be generalized to three dimensions. We assume that the particle is free to move in the fluid but that the effect of the fluid is included by adding a friction, which is proportional to the velocity, and a random force, $\xi(t)$, due to random density fluctuations in the fluid. The equations of motion of the Brownian particle are

$$\frac{dv(t)}{dt} = -\frac{\gamma}{m}v(t) + \frac{1}{m}\xi(t), \tag{5.76}$$

$$\frac{dx(t)}{dt} = v(t), \tag{5.77}$$

where $v(t)$ and $x(t)$ are the velocity and position, respectively, of the particle at time t, m is the mass of the particle, and γ is the friction coefficient. Equations (5.76) and (5.77) are the *Langevin equations* of motion for the Brownian particle.

The random force, $\xi(t)$, is a stochastic variable giving the effect of background noise, due to the fluid, on the Brownian particle. We will assume that $\xi(t)$ is a Gaussian white noise process with zero mean so that $\langle\xi(t)\rangle_\xi = 0$. The noise is Markovian and stationary and the average, $\langle\,\rangle_\xi$, is an average with respect to the probability distribution of realizations of the stochastic variable $\xi(t)$. We will not write the probability distribution explicitly. The assumption that the noise is *white* means that the noise is delta-correlated,

$$\langle\xi(t_1)\xi(t_2)\rangle_\xi = g\delta(t_2 - t_1), \tag{5.78}$$

and therefore (as we shall show in Section 5.E.2 its power spectrum contains all frequency components. The weighting factor, g, is a measure of the strength of the noise. Such a correlation function indicates that the noise is not correlated

from one instant to the next, and therefore it is impossible to represent a single realization of $\xi(t)$ in terms of a continuously drawn line. The fact that the noise is *Gaussian* with zero mean (cf. Exercise 4.9 means that correlation functions containing an odd number of terms, $\xi(t)$, are zero and that correlation functions containing an even number of terms, $\xi(t)$, can be expressed in terms of sums of products of the pairwise correlation function, $\langle \xi(t_1)\xi(t_2)\rangle_\xi$. For example,

$$\langle \xi(t_1)\xi(t_2)\xi(t_3)\xi(t_4)\rangle_\xi = \langle \xi(t_1)\xi(t_2)\rangle_\xi \langle \xi(t_3)\xi(t_4)\rangle_\xi + \langle \xi(t_1)\xi(t_3)\rangle_\xi \langle \xi(t_2)\xi(t_4)\rangle_\xi + \langle \xi(t_1)\xi(t_4)\rangle_\xi \langle \xi(t_2)\xi(t_3)\rangle_\xi.$$

Equations (5.76) and (5.77) can be solved fairly easily. Let us assume that at time $t = 0$, the velocity and position of the Brownian particle are $v(0) = v_0$ and $x(0) = x_0$, respectively. Then the solution the Eqs (5.76) and (5.77) is

$$v(t) = v_0 e^{-(\gamma/m)t} + \frac{1}{m}\int_0^t ds e^{-(\gamma/m)(t-s)}\xi(s) \tag{5.79}$$

and

$$x(t) = x_0 + \frac{m}{\gamma}(1 - e^{-(\gamma/m)t})v_0 + \frac{1}{\gamma}\int_0^t ds(1 - e^{-(\gamma/m)(t-s)})\xi(s). \tag{5.80}$$

Equations (5.79) and (5.80) give $v(t)$ and $x(t)$ for a single realization of $\xi(t)$. Since $\xi(t)$ is a stochastic variable, $v(t)$ and $x(t)$ are also stochastic variables whose properties are determined by $\xi(t)$. The average velocity (subject to the condition that $v(0) = v_0$) is $\langle v(t)\rangle_\xi = v_0 e^{-(\gamma/m)t}$ and the average displacement is $\langle (x(t) - x_0)\rangle_\xi = \frac{m}{\gamma}(1 - e^{-(\gamma/m)t})v_0$.

We can also obtain correlation functions from Eqs. (5.78), (5.79), and (5.80). If we make use of the fact that $\langle v_0\xi(t)\rangle_\xi = 0$, then we can write

$$\langle v(t_2)v(t_1)\rangle_\xi = v_0^2 e^{-(\gamma/m)(t_2+t_1)} + \frac{g}{m^2}\int_0^{t_2} ds_2 \int_0^{t_1} ds_1 \delta(s_2 - s_1) e^{(\gamma/m)(s_1-t_1)} e^{(\gamma/m)(s_2-t_2)}. \tag{5.81}$$

The integral is easily done to yield

$$\langle v(t_2)v(t_1)\rangle_\xi = \left(v_0^2 - \frac{g}{2m\gamma}\right) e^{-(\gamma/m)(t_2+t_1)} + \frac{g}{2m\gamma} e^{-(\gamma/m)(t_2-t_1)}. \tag{5.82}$$

We can also obtain the variance in the displacement. If we use Eqs. (5.78) and (5.80) and the fact that $\langle x_0\xi(t)\rangle_\xi = 0$, we can write

$$\langle (x(t) - x_0)^2\rangle_\xi = \frac{m^2}{\gamma^2}\left(v_0^2 - \frac{g}{2m\gamma}\right)(1 - e^{-(\gamma/m)t})^2 + \frac{g}{\gamma^2}\left[t - \frac{m}{\gamma}(1 - e^{-(\gamma/m)t})\right]. \tag{5.83}$$

Thus, after a long time the variance goes as $\langle (x(t_2) - x_0)^2\rangle_\xi = (g/\gamma^2)t$ (neglecting some constant terms). This is the same behavior that we saw for random walks in Chapter 4, if we choose a *diffusion coefficient*, $D = g/2\gamma^2$.

We can use a simple trick to determine the value of g for a Brownian particle in equilibrium with a fluid. Let us assume that the Brownian particle is in equilibrium with the fluid and average over all possible initial velocities, v_0. We denote this "thermal" average by $\langle\rangle_T$. By the equipartition theorem, for a particle in equilibrium the average kinetic energy is $\frac{1}{2}k_BT$ for each degree of freedom, $\frac{1}{2}m\langle v_0^2\rangle_T = \frac{1}{2}k_BT$, where k_B is Boltzmann's constant and T is the temperature in kelvins. If the Brownian particle is in equilbrium, its velocity correlation function must be stationary. Therefore, we must have $v_0^2 = g/2m\gamma$ so the first term on the right in Eq. (5.82) is removed. If we now take the thermal average of Eq. (5.82), we see that we must have $g = 2\gamma k_BT$. The correlation function can be written

$$\langle\langle v(t_2)v(t_1)\rangle_\xi\rangle_T = \frac{k_BT}{m} e^{-(\gamma/m)|t_2-t_1|}. \tag{5.84}$$

The absolute value on the time difference ensures that correlations always decay as the time difference increases. Information about the initial velocity of the Brownian particle decays exponentially.

For the case when the Brownian particle is in equilibrium with the fluid, the variance of the displacement becomes

$$\langle\langle (x(t) - x_0)^2\rangle_\xi\rangle_T = \frac{2k_BT}{\gamma}\left[t - \frac{m}{\gamma}(1 - e^{-(\gamma/m)t})\right]. \tag{5.85}$$

where we have assumed that $\langle x_0\rangle_T = \langle v_0\rangle_T = 0$ and that x_0 and v_0 are statistically independent so that $\langle x_0v_0\rangle = 0$. Thus, after a long time, $\langle\langle (x(t) - x_0)^2\rangle_\xi\rangle_T = (2k_BT/\gamma)t$ and the *diffusion coefficient* becomes $D = k_BT/\gamma$. The friction coefficient, γ, can also be determined from properties of the fluid and and hydrodynamics. For large spherical Brownian particles, we can assume that the fluid sticks to the surface. The friction coefficient is then the Stokes friction, $\gamma = 6\pi\eta R$, where η is the shear viscosity of the fluid and R is the radius of the Brownian particle (see Sect. (S10.G)). For very small Brownian particles, stick boundary conditions might not apply and the friction coefficient, γ, might be different.

■ **EXERCISE 5.5.** Consider a Brownian particle of mass m which is attached to a harmonic spring with force constant k and is constrained to move in one dimension. The Langevin equations are

$$\frac{dv}{dt} = -\frac{\gamma}{m}v - \omega_0^2 x + \frac{1}{m}\xi(t) \quad \text{and} \quad \frac{dx}{dt} = v,$$

where $\omega_0 = \sqrt{k/m}$. Let x_0 and v_0 be the initial position and velocity, respectively, of the Brownian particle and assume that it is initially in equilibrium with the fluid. Then by the equipartition theorem, the average kinetic energy is $\frac{1}{2}m\langle v_0^2\rangle_T = \frac{1}{2}k_BT$ and average vibrational potential energy is $\frac{1}{2}\omega_0^2\langle x_0^2\rangle_T = \frac{1}{2}k_BT$. We also assume that x_0 and v_0 are statistically independent so $\langle x_0 v_0\rangle_T = 0$. (a) Show that a condition for the process to be stationary is that the noise strength is $g = 4\gamma k_BT$. (b) Compute the velocity correlation function, $\langle\langle v(t_2)v(t_1)\rangle_\xi\rangle_T$.

Answer: The Langevin equations can be solved and give the following expression for the velocity at time t:

$$v(t) = v_0 e^{-\Gamma t}C(t) - \frac{\omega_0^2}{\Delta}x_0 e^{-\Gamma t}\sinh(\Delta t) + \frac{1}{m}\int_0^t dt'\xi(t')e^{-\Gamma(t-t')}C(t-t'),$$

where $C(t) = \cosh(\Delta t) - (\Gamma/\Delta)\sinh(\Delta t)$, $\Gamma = \gamma/m$, and $\Delta = \sqrt{\Gamma^2 - \omega_0^2}$. If we use the fact that $\langle x_0 v_0\rangle_T = 0$ and assume that $t_2 > t_1$, the velocity correlation function can be written

$$\begin{aligned}\langle\langle v(t_2)v(t_1)\rangle_\xi\rangle_T =& e^{-\Gamma(t_2+t_1)}C(t_2)C(t_1)\langle v_0^2\rangle_T \\ &+ \frac{\omega_0^4}{\Delta^2}\langle x_0^2\rangle_T e^{-\Gamma(t_2+t_1)}\sinh(\Delta t_2)\sinh(\Delta t_1) \\ &+ \frac{g}{m^2}\int_0^{t_1} dt e^{-\Gamma(t_2+t_1-2t)}C(t_2-t)C(t_1-t).\end{aligned}$$

If we choose $g = 4\gamma k_BT$ to ensure stationarity then after some algebra we obtain

$$\langle\langle v(t_2)v(t_1)\rangle_\xi\rangle_T = \frac{k_BT}{m}e^{-\Gamma(t_2-t_1)}\left[\cosh(\Delta(t_2-t_1)) - \frac{\Gamma}{\Delta}\sinh(\Delta(t_2-t_1))\right].$$

A similar calculation for $t_1 > t_2$ yields the same answer but with $t_1 \leftrightarrow t_2$. Thus,

$$\langle\langle v(t_1+\tau)v(t_1)\rangle_\xi\rangle_T = \frac{k_BT}{m}e^{-\Gamma|\tau|}\left[\cosh(\Delta\tau) - \frac{\Gamma}{\Delta}\sinh(\Delta|\tau|)\right].$$

(expressed in overdamped form)

5.E.2. The Spectral Density (Power Spectrum)

A quantity of great interest in studying *stationary* stochastic processes is the spectral density (or power spectrum). If one has experimental data on a stochastic variable $\psi(t)$—that is, if one has a time series for $\psi(t)$—then it is useful to compute the power spectrum because this contains a great deal of information about the stochastic process, as we shall see below.

In practice, in dealing with data from experiments, one has a finite length of time series to work with. Let us assume that we have a time series of length T. We denote it $\psi(t;T)$, where $\psi(t;T) = \psi(t)$ for $-T/2 \leqslant t \leqslant T/2$ and $\psi(t;T) = 0$ otherwise. The $\lim_{T\to\infty}\psi(t;T) = \psi(t)$. The Fourier transform of $\psi(t;T)$ is

$$\tilde{\psi}(\omega;T) = \int_{-\infty}^{\infty} dt\psi(t;T)e^{i\omega t}. \tag{5.86}$$

Because $\psi(t;T)$ is real, we have $\tilde{\psi}(\omega;T) = \tilde{\psi}^*(-\omega;T)$, where $*$ denotes complex conjugation.

The spectral density is defined as

$$S_{\psi,\psi}(\omega) \equiv \lim_{T\to\infty}\frac{1}{T}\tilde{\psi}^*(\omega;T)\tilde{\psi}(\omega;T). \tag{5.87}$$

If we substitute Eq. (5.86) into (5.87), we find

$$\begin{aligned}S_{\psi,\psi}(\omega) &= \lim_{T\to\infty}\frac{1}{T}\int_{-\infty}^{\infty}dt_2\int_{-\infty}^{\infty}dt_1\psi(t_2;T)\psi(t_1;T)e^{-i\omega(t_2-t_1)} \\ &= \int_{-\infty}^{\infty}d\tau\, e^{-i\omega(\tau)}\lim_{T\to\infty}\frac{1}{T}\int_{-\infty}^{\infty}dt_1\psi(t_1+\tau;T)\psi(t_1;T) \\ &= \int_{-\infty}^{\infty}d\tau\, e^{-i\omega(\tau)}\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}},\end{aligned} \tag{5.88}$$

where $\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}}$ denotes the time average:

$$\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}} \equiv \lim_{T\to\infty}\frac{1}{T}\int_{-\infty}^{\infty}dt_1\psi(t_1+\tau;T)\psi(t_1;T). \tag{5.89}$$

Equation (5.89) denotes the average of the product of numbers, $\psi(t_1;T)\psi(t_1+\tau;T)$, over each point of the time series, $\psi(t)$. Since we assume that the stochastic process is stationary, the stochastic properties of the time series don't change as we shift along the time series. Therefore we expect that the time average, $\langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}}$, should be equal to the statistical average, $\langle\psi(t_1+\tau)\psi(t_1)\rangle_\psi$, in which we average the product, $\psi(t_1+\tau)\psi(t_1)$, at a given point, $t = t_1$, but over an infinite number of realizations of the time series, $\psi(t)$, at time t. Therefore, for a stationary process, we expect that

$$C_{\psi,\psi}(\tau) \equiv \langle\psi(t_1+\tau)\psi(t_1)\rangle_\psi = \langle\psi(t_1+\tau)\psi(t_1)\rangle_{\bar{t}} \tag{5.90}$$

If we now combine Eqs. (5.89) and (5.90), we obtain the following expression for the spectral density:

$$S_{\psi,\psi}(\omega) = \int_{-\infty}^{\infty}d\tau e^{-i\omega\tau}\langle\psi(t_1+\tau)\psi(t_1)\rangle_\psi = \int_{-\infty}^{\infty}d\tau e^{-i\omega\tau}C_{\psi,\psi}(\tau), \tag{5.91}$$

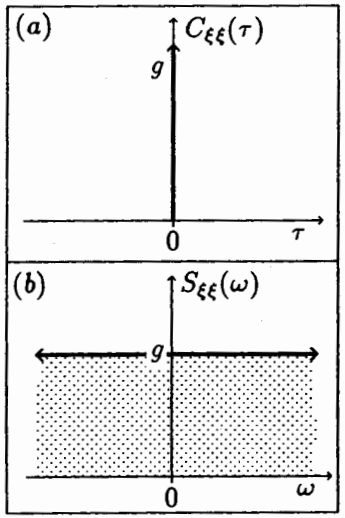


Fig. 5.1. (a) The correlation function, $C_{\xi\xi}(t)$. (b) The spectral density, $S_{\xi\xi}(\omega)$.

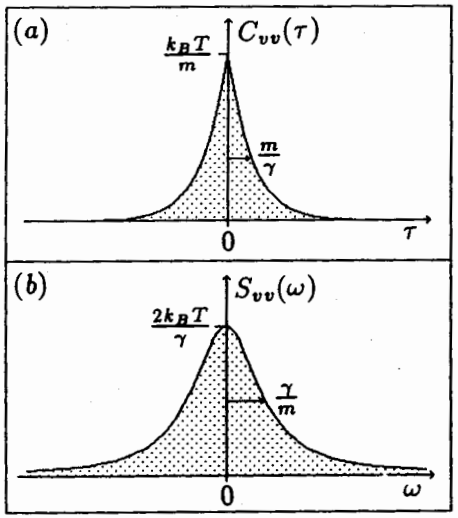


Fig. 5.2. (a) The correlation function, $C_{vv}(t)$. (b) The spectral density, $S_{vv}(\omega)$.

It is interesting to compute the spectral densities for the Brownian motion described in Section 5.E.1. Let us consider the case when the Brownian particle is in thermal equilibrium with the fluid and the process is stationary. From Eq. (5.78), the spectral density for the white noise is

$$S_{\xi,\xi}(\omega) = \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} \langle \xi(t_1+\tau)\xi(t_1)\rangle_\xi = g = 2\gamma k_B T. \tag{5.92}$$

Thus, a white noise process contains all frequencies with equal weight. The correlation function, $C_{\xi\xi}(t)$, and spectral density, $S_{\xi\xi}(\omega)$, are shown in Fig. 5.1.

The spectral density for the velocity time series is

$$S_{v,v}(\omega) = \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} \langle v(t_1+\tau)v(t_1)\rangle_\xi = \frac{2k_BT\gamma}{m^2\omega^2+\gamma^2}. \tag{5.93}$$

Plots of the velocity correlation function and spectral density for the Brownian particle are given in Fig. 5.2.

■ **EXERCISE 5.6.** Compute the spectral density, $S_{v,v}(\omega)$, for the harmonically bound Brownian particle considered in Exercise 5.5. Plot the velocity correlation function, $C_{v,v}(\tau)$, and spectral density $S_{v,v}(\omega)$ for the case $\omega_0 > \Gamma$ (this corresponds to an *underdamped* Brownian particle).

Answer: The velocity correlation function can be written

$$C_{v,v}(\tau) = \langle\langle v(t_1+\tau)v(t_1)\rangle_\xi\rangle_T = \frac{\Gamma k_BT}{m} e^{-\Gamma|\tau|}\left[\frac{1}{\Gamma}\cos(\delta|\tau|) - \frac{1}{\delta}\sin(\delta|\tau|)\right],$$

where $\Gamma = \frac{\gamma}{m}$ and $\delta = \sqrt{\omega_0^2 - \Gamma^2} = -i\Delta$. The spectral density can be written

$$S_{v,v}(\omega) = \int_0^{\infty} d\tau \cos(\omega\tau) e^{-\Gamma|\tau|}\left[\frac{1}{\Gamma}\cos(\delta|\tau|) - \frac{1}{\delta}\sin\delta|\tau|)\right]$$
$$= \frac{4\gamma k_BT\omega^2}{m(\omega_0^2 - 2\delta\omega + \omega^2)(\omega_0^2 + 2\delta\omega + \omega^2)}$$

Both $C_{v,v}(\tau)$ and $S_{v,v}(\omega)$ are plotted in the accompanying graphs.

Because the Brownian particle is underdamped, the velocity correlation function, $C_{v,v}(\tau)$, oscillates as it is damped out exponentially. The spectral density, $S_{v,v}(\omega)$, has peaks near $\omega = \pm\omega_0$ and the peaks have an approximate width, $\frac{2\gamma}{m}$.

When the noise is not "white", the spectral density still affords a means of making contact with experiment [14].

▶ SPECIAL TOPICS

▶ S5.A. Time Periodic Markov Chain

Let us now consider the case in which the transition probability is time-dependent but periodic in time with period N. That is, $Q_{n,m}(s) \equiv P_{1|1}(n, s|m, s+1) = P_{1|1}(n, s+N|m, s+N+1)$. The probability vector after one period of the transition probability can be written

$$\langle \mathbf{P}(N)| = \langle \mathbf{P}(0)|\mathbf{Q}(0)\mathbf{Q}(1) \times \cdots \times \mathbf{Q}(N-1) \equiv \langle \mathbf{P}(0)|\mathbf{U}, \tag{5.94}$$

where $\mathbf{U} = \mathbf{Q}(0)\mathbf{Q}(1) \times \cdots \times \mathbf{Q}(N-1)$ is the transition probability that takes the system from the initial state, $\langle \mathbf{P}(0)|$, to the state after one period, $\langle \mathbf{P}(N)|$. More generally, the probability vector after l periods of the transition matrix is

$$\langle \mathbf{P}(lN)| = \langle \mathbf{P}(0)|\mathbf{U}^l. \tag{5.95}$$

We can expand the probability vector, $\langle \mathbf{P}(lN)|$, in terms of left and right eigenvectors of the transition matrix, $\mathbf{U}$. Let Λ_α be the αth eigenvalue of $\mathbf{U}$, and let $\langle \chi_\alpha|$ and $|\psi_\alpha\rangle$ denote the left and right normalized eigenvectors of $\mathbf{U}$, respectively, where $\alpha = 1, \ldots, M$. Thus, $\mathbf{U}|\psi_\alpha) = \Lambda_\alpha|\psi_\alpha)$ and $\langle \chi_\alpha|\mathbf{U} = \langle \chi_\alpha|\Lambda_\alpha$. We then proceed as we did in Section 5.C.1. If $\mathbf{U}$ is an $M \times M$ matrix, then its spectral decomposition is given by

$$\mathbf{U} = \sum_{\alpha=1}^{M} \Lambda_\alpha |\psi_\alpha\rangle\langle\chi_\alpha|. \tag{5.96}$$

The probability vector after l periods of the transition matrix is given by

$$\langle \mathbf{P}(lN)| = \sum_{\alpha=1}^{M} \Lambda_\alpha^l \langle \mathbf{P}(0)|\psi_\alpha\rangle\langle\chi_\alpha|. \tag{5.97}$$

The probability for the nth realization of the stochastic variable Y at time $s = lN$ is given by

$$P(n, lN) = \sum_{m=1}^{M}\sum_{\alpha=1}^{M} \Lambda_\alpha^l P(m, 0)\psi_\alpha(m)\chi_\alpha(n). \tag{5.98}$$

We will demonstrate the use of these equations in Exercise 5.7.

■ **EXERCISE 5.7.** Let us consider a stochastic variable Y with three realizations, $y(1)$, $y(2)$, and $y(3)$. Let us assume that the transition probabilities between these states are $Q_{1,1}(s) = Q_{2,2}(s) = Q_{3,3}(s) = 0$, $Q_{1,2}(s) = Q_{2,3}(s) = Q_{3,1}(s) = \cos^2(2\pi s/3)$, and $Q_{1,3}(s) = Q_{2,1}(s) = Q_{3,2}(s) = \sin^2(2\pi s/3)$. If initially the system is in the state $y(1)$, what is the probability to find it in the state $y(2)$ after l periods of the transition matrix?

Answer: The transition matrix has a period $N = 3$. In general it is given by

$$\mathbf{Q}(s) = \begin{pmatrix} 0 & \cos^2(\frac{2\pi s}{3}) & \sin^2(\frac{2\pi s}{3}) \\ \sin^2(\frac{2\pi s}{3}) & 0 & \cos^2(\frac{2\pi s}{3}) \\ \cos^2(\frac{2\pi s}{3}) & \sin^2(\frac{2\pi s}{3}) & 0 \end{pmatrix}.$$

Therefore,

$$\mathbf{Q}(0) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \mathbf{Q}(1) = \mathbf{Q}(2) = \begin{pmatrix} 0 & \frac{1}{4} & \frac{3}{4} \\ \frac{3}{4} & 0 & \frac{1}{4} \\ \frac{1}{4} & \frac{3}{4} & 0 \end{pmatrix},$$

and the transition matrix $\mathbf{U}$ becomes

$$\mathbf{U} = \mathbf{Q}(0)\mathbf{Q}(1)\mathbf{Q}(2) = \begin{pmatrix} \frac{1}{16} & \frac{3}{8} & \frac{9}{16} \\ \frac{9}{16} & \frac{1}{16} & \frac{3}{8} \\ \frac{3}{8} & \frac{9}{16} & \frac{1}{16} \end{pmatrix}.$$

The eigenvalues of $\mathbf{U}$ are $\Lambda_1 = 1$, $\Lambda_2 = -\frac{7}{16}e^{-i\theta}$, and $\Lambda_3 = -\frac{7}{16}e^{+i\theta}$, where $\theta = \tan^{-1}(3\sqrt{3}/13)$.

The right eigenstates can be written

$$|\psi_1) = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \qquad |\psi_2\rangle = \begin{pmatrix} -e^{+i\pi/3} \\ -e^{-i\pi/3} \\ 1 \end{pmatrix}, \qquad |\psi_3\rangle = \begin{pmatrix} -e^{-i\pi/3} \\ -e^{+i\pi/3} \\ 1 \end{pmatrix}.$$

The left eigenstates can be written

$$\langle \chi_1| = (\tfrac{1}{3}, \tfrac{1}{3}, \tfrac{1}{3}), \qquad \langle \chi_2| = (-\tfrac{1}{3}\, e^{-i\pi/3}, -\tfrac{1}{3}e^{+i\pi/3}, \tfrac{1}{3})$$

and

$$\langle \chi_3| = (-\tfrac{1}{3}e^{+i\pi/3}, -\tfrac{1}{3}e^{-i\pi/3}, \tfrac{1}{3}).$$

We can now compute the probability $P(2, 3l)$. The initial probability density is $P(n, 0) = \delta_{n,1}$. From Eq. (5.98), the probability $P(2, 3l)$ is

$$\begin{aligned} P(2, 3l) &= \Lambda_1^l \psi_1(1)\chi_1(2) + \Lambda_2^l \psi_2(1)\chi_2(2) + \Lambda_3^l \psi_3(1)\chi_3(2) \\ &= \frac{1}{3} + (-1)^l \frac{2}{3}\left(\frac{7}{16}\right)^l \cos\left(l\theta - \frac{2\pi}{3}\right). \end{aligned}$$

▶ S5.B. Master Equation for Birth–Death Processes [3, 4]

One of the most common applications of the master equation is the description of *birth–death processes* such as one finds in chemistry and population dynamics. Birth–death processes are processes in which transitions can only take place between nearest-neighbor states. For example, if one considers a population in which only one individual is produced at each birth and one individual dies at each death, then we have a typical birth–death process.

▶ S5.B.1. The Master Equation

For concreteness let us consider a population of bacteria. We assume that at time t, there are n bacteria and we make the following assumptions:

(1) The probability of a bacterium dying during the time $t \to t + \Delta t$ is given by $w_{n,n-1}(t)\Delta t = d_n(t)\Delta t$.
(2) The probability of a bacterium being created in time $t \to t + \Delta t$ is given by $w_{n,n+1}(t)\Delta t = b_n(t)\Delta t$.
(3) The probability that no change occurs in the bacteria population in time $t \to t + \Delta t$ is given by $[1 - \sum_{l=1}^{M} w_{m,l}(t)\Delta t] = [1 - (b_m(t) + d_m(t))\Delta t]$.
(4) The probability of more than one birth or death in time $t \to t + \Delta t$ is zero.

The transition probability can be written

$$P_{1|1}(m, t|n, t + \Delta t) = [1 - (b_m(t) + d_m(t))\Delta t]\delta_{m,n} + (b_m(t)\delta_{n,m+1} + d_m(t)\delta_{n,m-1}\Delta t + \cdots \tag{5.99}$$

and the master equation takes the form

$$\frac{\partial P_1(n, t)}{\partial t} = b_{n-1}(t)P_1(n-1, t) + d_{n+1}(t)P_1(n+1, t) - (b_n(t) + d_n(t))P(n, t). \tag{5.100}$$

Note that we have allowed the birth and death rates, $b_n(t)$ and $d_n(t)$ respectively, to depend on time. In most applications of Eq. (5.100) that we will consider here, they will be independent of time.

Let us consider the case in which b_n and d_n are independent of time. Then the master equation will have at least one stationary state, $P_n^s \equiv P(n, \infty)$, which is independent of time and satisfies the condition $\partial P_n^s/\partial t = 0$. (If the transition matrix, **W**, is made up of uncoupled blocks, then there may be more than one stationary state.) The master equation for the stationary state can be written in

the form

$$0 = d_{n+1}P_{n+1}^s - b_nP_n^s - (d_nP_n^s - b_{n-1}P_{n-1}^s). \tag{5.101}$$

Note that since $d_{n+1}P_{n+1}^s - b_nP_n^s = d_nP_n^s - b_{n-1}P_{n-1}^s$, the quantity $J \equiv b_{n-1}P_{n-1}^s - d_nP_n^s$ must be independent of n. The quantity J is just the net probability current between pairs of sites.

The case where no probability flows, $J = 0$, is equivalent to detailed balance since

$$b_{n-1}P_{n-1}^s = d_nP_n^s. \tag{5.102}$$

Systems obeying detailed balance are very similar to systems in thermodynamic equilibrium, since no net probability current flows between microscopic states of those systems. For systems obeying detailed balance, we can iterate Eq. (5.102) to obtain an expression for P_n^s in terms of P_0^s:

$$P_n^s = \frac{b_{n-1}b_{n-2}\cdots b_0}{d_nd_{n-1}\cdots d_1}P_0^s. \tag{5.103}$$

The value of P_0^s is obtained by the condition that the total probability be normalized to one, $\sum_{n=0}^{M} P_n^s = 1$.

The full master equation can only be solved exactly for some special cases. In the following two sections, we give some techniques for solving it exactly for some of the few cases where that is possible. In Section S5.B.2 we consider the case when the birth and death rates depend linearly on the population number. In Section S5.B.3 we consider the case when the birth and death rates depend nonlinearly on the population number. We will discuss some approximation schemes for solving the master equation in Section S5.D.

▶ S5.B.2. Linear Birth–Death Processes

Let us assume that the probability of a birth or death is proportional to the number of bacteria present and is independent of time. Then $b_n = \beta n$ and $d_n = \gamma n$, where β and γ are constants, and the master equation takes the form

$$\frac{\partial P_1(n, t)}{\partial t} = \beta(n-1)P_1(n-1, t) + \gamma(n+1)P_1(n+1, t) - (\beta n + \gamma n)P(n, t). \tag{5.104}$$

Equation (5.104) describes a linear birth-death process because the coefficients of P_1 on the right-hand side of the equation depend linearly on n. Note that n is the number of bacteria and therefore $n \geq 0$. Thus, Eq. (5.104) must never allow probability to flow into regions where $n < 0$. We see that

Eq. (5.104) satisfies that condition. If $n = -1$, the coefficient of $P_1(n+1, t)$ is zero so flow can never occur from positive to negative values of n. Equation (5.104) is said to have a *natural boundary* at $n = 0$. This may not always be the case and one must be careful when using such master equations.

Linear master equations depending on discrete stochastic variables are often most easily solved by means of a generating function, $F(z, t)$. We will use this method to solve Eq. (5.104). The generating function is defined as

$$F(z, t) = \sum_{n=-\infty}^{\infty} z^n P_1(n, t). \tag{5.105}$$

Since we have a natural boundary at $n = 0$, it does not matter that the summation in Eq. (5.105) extends to $n = -\infty$. Various moments of the population number, n, are obtained by taking derivatives of $F(z, t)$ with respect of z and then allowing $z \to 1$. For example,

$$\langle n(t) \rangle = \lim_{z \to 1} \frac{\partial F(z, t)}{\partial z} = \sum_{n=-\infty}^{\infty} n P_1(n, t) \tag{5.106}$$

and

$$\langle n^2(t) \rangle - \langle n(t) \rangle = \lim_{z \to 1} \frac{\partial^2 F(z, t)}{\partial z^2} = \sum_{n=-\infty}^{\infty} (n^2 - n) P_1(n, t). \tag{5.107}$$

Higher moments may be obtained in an analogous manner.

We can now obtain a differential equation for the generating function, $F(z, t)$. Let us multiply Eq. (5.104) by z^n and sum over n. Note, for example, that

$$\sum_{n=-\infty}^{\infty} z^n (n-1) P_1(n-1, t) = z^2 \frac{d}{dz} \sum_{n=-\infty}^{\infty} z^{n-1} P_1(n-1, t) = z^2 \frac{dF(z, t)}{dz}$$

and

$$\sum_{n=-\infty}^{\infty} z^n (n+1) P_1(n+1, t) = \frac{d}{dz} \sum_{n=-\infty}^{\infty} z^{n+1} P_1(n+1, t) = \frac{dF(z, t)}{dz}.$$

We obtain the following differential equation for $F(z, t)$:

$$\frac{\partial F}{\partial t} = (z - t)(\beta z - \gamma) \frac{\partial F}{\partial z}. \tag{5.108}$$

If we substitute Eq. (5.105) into Eq. (5.108) and equate like powers of z, we

retrieve Eq. (5.104). Equation (5.108) is a first-order linear partial differential equation and may be solved using the method of characteristics.

■ **Method of Characteristics [15].** Let us consider a first order linear differential equation of the form

$$\frac{\partial F(z, t)}{\partial t} + g(z) \frac{\partial F(z, t)}{\partial z} + h(z) F(z, t) = 0, \tag{1}$$

where $g(z)$ and $h(z)$ are arbitrary functions of z. Write $F(z, t)$ in the form

$$F(z, t) = \left[e^{-\int^z \frac{h(z)}{g(z)}} \right] \Phi(z, t), \tag{2}$$

where $\Phi(z, t)$ is an unknown function of z and t. If we substitute Eq. (2) into Eq. (1), we find a partial differential equation for $\Phi(z, t)$:

$$\frac{\partial \Phi(z, t)}{\partial t} + g(z) \frac{\partial \Phi(z, t)}{\partial z} = 0. \tag{3}$$

We now find the characteristics for Eq. (3). These are lines in the z–t plane along which $\Phi(z, t)$ is constant. These lines satisfy the equation $dt = dz/g(z)$ or $\int^z dz/g(z) - t = C_1$, where C_1 is a constant. It is easy to show that any function of $\int^z dz/g(z) - t$ is a solution of Eq. (3). Generally we write the solution as $\Phi(z, t) = \Phi(e^{\int^z dz/g(z) - t})$, and the solution to Eq. (1) takes the form

$$F(z, t) = e^{\int^z [h(z)/g(z)] dz} \Phi(e^{\int^t dz/g(z) - t}). \tag{4}$$

If we use the method of characteristics to solve Eq. (5.108), we find

$$F(z, t) = F\left(\left(\frac{\beta(z-1)}{\beta z - \gamma} \right) e^{(\beta - \gamma)t} \right) \tag{5.109}$$

Although we know that $F(z, t)$ is a rather complicated function of β, γ, and t, we still do not know the exact form of $F(z, t)$. This we obtain from the initial conditions. Let us assume that at time $t = 0$ there are exactly m bacteria in the population. Thus, $P(n, 0) = \delta_{n,m}$ and $F(z, 0) = z^m$. From Eq. (5.109) we find

$$F\left(\frac{\beta(z-1)}{\beta z - \gamma} \right) = z^m. \tag{5.110}$$

If we now let $u = \beta(z-1)/(\beta z - \gamma)$, then we can write $z = (\gamma u - \beta)/\beta(u-1)$, so

$$F(u) = \left(\frac{\gamma u - \beta}{\beta(u-1)} \right)^m \tag{5.111}$$

and

$$F(z,t)=\left(\frac{\gamma(z-1)e^{(\beta-\gamma)t}-\beta z+\gamma}{\beta(z-1)e^{(\beta-\gamma)t}-\beta z+\gamma}\right)^m. \tag{5.112}$$

Equation (5.112) is exact and contains all possible information about the linear birth–death process. We can now obtain $P_1(n,t)$ and all the moments of n from Eq. (5.112). In order to obtain $P_1(n,t)$ we must expand Eq. (5.112) in a Taylor series in z. $P_1(n,t)$ is the coefficient of z^n. The first moment is

$$\langle n(t)\rangle=\left(\frac{\partial F}{\partial z}\right)_{z=1}=me^{(\beta-\gamma)t}. \tag{5.113}$$

The variance is

$$\langle n^2(t)\rangle-\langle n(t)\rangle^2=m\left(\frac{\beta+\gamma}{\gamma-\beta}\right)e^{(\beta-\gamma)t}(1-e^{(\beta-\gamma)t}) \tag{5.114}$$

If the birth rate is greater than the death rate, the population will grow exponentially with time. If the death rate is greater than the birth rate, the population will die out. Of course, Eq. (5.104) gives a vastly oversimplified description of the dynamics of a bacteria population. We have left out factors involving food supply, temperature, and so on, but it does give a good starting point. For an excellent discussion of the application of master equations to population dynamics, see Ref. 16.

Birth–death equations can also be applied to chemical reaction kinetics. For example, in Problem S5.2 we consider the reaction

$$\mathrm{A}+\mathrm{X}\underset{k_2}{\overset{k_1}{\rightleftharpoons}}\mathrm{A}+\mathrm{Y},$$

where the number of A molecules is kept constant but the number of X molecules and Y molecules can vary. $k_1(k_2)$ is the probability per unit time that a reaction takes place if an X molecule (Y molecule) collides with an A molecule. The reaction in the forward direction requires n_A A molecules, n_X+1 X molecules, and n_y-1 Y molecules to produce a system containing n_A A molecules, n_X X molecules, and n_Y Y molecules. Similarly, the backward reaction requires n_A A molecules, n_X-1 X molecules, and n_Y+1 Y molecules to produce a system containing n_A A molecules, n_X X molecules, and n_Y Y molecules. The transition rate for the forward reaction depends on the number of binary collisions, $n_A(n_X+1)$, between A molecules and X molecules. Similarly, the transition rate for the backward reaction depends on the product, $n_A(n_Y+1)$. Thus, the transition rate for the forward reaction is $w_1=k_1n_A(n_X+1)$, and for the backward reaction it is $w_2=k_2n_A(n_Y+1)$.

If we assume that the total number of X molecules and Y molecules is constant and equal to N, then the master equation can be written

$$\frac{\partial P_1(n,t)}{\partial t}=k_2(N-n+1)P_1(n-1,t)+k_1(n+1)P_1(n+1,t)-(k_1n+k_2(N-n))P(n,t). \tag{5.115}$$

where n is the number of X molecules and $N-n$ is the number of Y molecules. For simplicity we have absorbed n_A into k_1 and k_2. We leave it as a homework problem to solve this master equation.

▶ S5.B.3. Nonlinear Birth–Death Processes [3, 4, 17]

Some of the simplest examples of nonlinear birth-death processes come from population dynamics and chemical reaction kinetics. A nonlinear birth–death process is one for which one or both of the transition rates, $b_n(t)$ and $d_n(t)$, depend nonlinearly on n. The master equation for nonlinear birth–death processes usually cannot be solved exactly, except for the long-time state. However, for binary nonlinear processes they sometimes can be solved exactly because the partial differential equation for the generating function might be solvable in terms of orthogonal polynomials.

An example of an exactly soluble nonlinear system is the binary chemical reaction [18]

$$2\mathrm{X}\xrightarrow{k}\mathrm{B}.$$

The transition rate for this reaction is proportional both to the reaction rate, k, and to the number of different ways, $\frac{1}{2}n_X(n_X-1)$, to form pairs of X molecules if there are n_X X molecules in the system. If the system has n_X+2 X molecules and n_B-1 B molecules before the reaction, then it will have n_X X molecules and n_B B molecules after the reaction. The transition rate is $w=\frac{k}{2}(n_X+2)(n_X+1)$. The master equation can be written

$$\frac{\partial P(n,t)}{\partial t}=\frac{k}{2}(n+2)(n+1)P(n+2,t)-\frac{k}{2}n(n-1)P(n,t). \tag{5.116}$$

This equation has a natural boundary at $n=0$ since probability cannot flow into $P(-1,t)$ from above. The equation for the generating function takes the form

$$\frac{\partial F}{\partial t}=\frac{k}{2}(1-z^2)\frac{\partial^2F}{\partial z^2}. \tag{5.117}$$

The generating function, $F(z, t)$, in terms of Gegenbauer polynomials can be written

$$F(z, t) = \sum_{n=0}^{\infty} A_n e^{-(k/2)n(n-1)t} C_n^{-1/2}(z). \tag{5.118}$$

The coefficient A_n depends on initial conditions. The first few Gegenbauer polynomials are $C_0^{-1/2}(z) = 1$, $C_1^{-1/2}(z) = -z$, $C_2^{-1/2}(z) = \frac{1}{2}(1 - z^2)$, and $C_3^{-1/2}(z) = \frac{1}{2}z(1 - z^2)$. We shall not attempt to compute A_n here. Solutions can be found in Ref. 17.

It is important to note that most nonlinear master equations cannot be solved exactly. It is then often necessary to resort to approximation schemes or numerical methods for solutions.

▶ S5.C. The Fokker–Planck Equation [3, 4, 19]

The Fokker–Planck equation is the equation governing the time evolution of the probability density for the Brownian particle. It is a second-order differential equation and is exact for the case when the noise acting on the Brownian particle is Gaussian white noise. The derivation of the Fokker–Planck equation is a two-step process. We first derive the equation of motion for the probability density $\rho(x, v, t)$ to find the Brownian particle in the interval $x \to x + dx$ and $v \to v + dv$ at time t for one realization of the random force $\xi(t)$. We then obtain an equation for $P(x, v, t) = \langle \rho(x, v, t) \rangle_\xi$, the average of $\rho(x, v, t)$ over many realizations of the random force $\xi(t)$. The probability density $P(x, v, t)$ is the macroscopically observed probability density for the Brownian particle. Its dynamical evolution is governed by the Fokker–Planck equation.

▶ S5.C.1. Probability Flow in Phase Space

Let us obtain the probability to find the Brownian particle in the interval $x \to x + dx$ and $v \to v + dv$ at time t. We will consider the space of coordinates, $\mathbf{X} = (x, v)$ (x and v the displacement and velocity, respectively, of the Brownian particle), where $-\infty < x < \infty$ and $-\infty < v < \infty$. The Brownian particle is located in the infinitesimal area, $dxdv$, with probability $\rho(x, v, t)dxdv$. We may view the probability as a fluid whose density at point (x, v) is given by $\rho(x, v, t)$. The speed of the fluid at point (x, v) is given by $\dot{\mathbf{X}} = (\dot{x}, \dot{v})$. Since the Brownian particle must lie somewhere in this space, we have the condition

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv \rho(x, v, t) = 1. \tag{5.119}$$

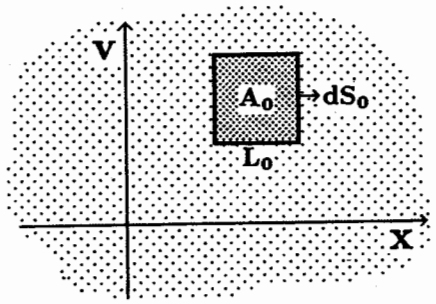


Fig. 5.3. A finite area in Brownian particle phase space.

Let us now consider a fixed finite area, A_0, in this space (cf. Fig. 5.3). The probability to find the Brownian particle in this area at time t is $P(A_0) = \int_{A_0} dxdv\rho(x, v, t)$. Since the Brownian particle cannot be destroyed, and change in the probability contained in A_0 must be due to a flow of probability through the sides of A_0. Thus

$$\frac{\partial}{\partial t} P(A_0) = \frac{\partial}{\partial t} \int\int_{A_0} dxdv\rho(x, v, t) = -\oint_{L_0} \rho(x, v, t)\dot{\mathbf{X}} \cdot d\mathbf{S}_0, \tag{5.120}$$

where $d\mathbf{S}_0$ denotes a differential surface element along the edge of area A_0, $\rho\dot{\mathbf{X}}$ is the probability current through the edge, and L_0 is the line around the edge of area element A_0. We can now use Gauss's theorem to change the surface integral into an area integral, $\oint_{L_0} \rho(x, v, t)\dot{\mathbf{X}} \cdot d\mathbf{S}_0 = \int_{A_0} dxdv\nabla_{\mathbf{X}} \cdot (\dot{\mathbf{X}}\rho(x, v, t))$, where $\nabla_{\mathbf{X}}$ denotes the gradient, $\nabla_{\mathbf{X}} = (\partial/\partial x, \partial/\partial v)$. We find

$$\frac{\partial}{\partial t} \int\int_{A_0} dxdv\rho(x, v, t) = -\int_{A_0} dxdv\nabla_{\mathbf{X}} \cdot (\dot{\mathbf{X}}\rho(x, v, t)). \tag{5.121}$$

Since the area A_0, is fixed, we can take the time derivative inside the integral. Since the area A_0, is arbitrary, we can equate integrands of the two integrals in Eq. (5.121). Then we find that $(\partial\rho(t)/\partial t) = -\nabla_{\mathbf{X}} \cdot (\dot{\mathbf{X}}\rho(t))$, or

$$\frac{\partial\rho(t)}{\partial t} = -\nabla_{\mathbf{X}} \cdot (\dot{\mathbf{X}}\rho(t)) = -\frac{\partial(\dot{x}\rho(t))}{\partial x} - \frac{\partial(\dot{v}\rho(t))}{\partial v} \tag{5.122}$$

where we have let $\rho(t) = \rho(x, v, t)$.

▶ S5.C.2. Probability Flow for Brownian Particle

In order to write Eq. (5.122) explicitly for a Brownian particle, we first must know the Langevin equation governing the evolution of the Brownian particle.

Let us assume that Brownian particle moves in the presence of a potential, $V(x)$. The Langevin equations are then

$$\frac{dv(t)}{dt} = -\frac{\gamma}{m}v(t) + \frac{1}{m}F(x) + \frac{1}{m}\xi(t) \quad \text{and} \quad \frac{dx(t)}{dt} = v(t), \tag{5.123}$$

where the force, $F(x)$ equals $-(dV(x)/dx)$. If we substitute these equations into Eq. (5.122), we find

$$\begin{aligned}\frac{\partial\rho(t)}{\partial t} &= -\frac{\partial(v\rho(t))}{\partial x} + \frac{\gamma}{m}\frac{\partial(v\rho(t))}{\partial v} - \frac{1}{m}F(x)\frac{\partial\rho(t)}{\partial v} - \frac{1}{m}\xi(t)\frac{\partial\rho(t)}{\partial v} \\ &= -\hat{L}_0\rho(t) - \hat{L}_1(t)\rho(t),\end{aligned} \tag{5.124}$$

where the differential operators $\hat{L}_0$ and $\hat{L}_1$ are defined as

$$\hat{L}_0 = v\frac{\partial}{\partial x} - \frac{\gamma}{m} - \frac{\gamma}{m}v\frac{\partial}{\partial v} + \frac{1}{m}F(x)\frac{\partial}{\partial v} \quad \text{and} \quad \hat{L}_1 = \frac{1}{m}\xi(t)\frac{\partial}{\partial v}. \tag{5.125}$$

Since $\xi(t)$ is a stochastic variable, the time evolution of $\rho(x,v,t)$ will be different for each realization of $\xi(t)$. However, when we observe an actual Brownian particle we are observing the average effect of the random force on it. Therefore, we introduce an *observable* probability, $P(x,v,t)dxdv$, to find the Brownian particle in the interval $x \to x+dx$ and $v \to v+dv$. We define this observable probability to be

$$P(x,v,t) = \langle\rho(x,v,t)\rangle_\xi. \tag{5.126}$$

We now must find the equation of motion of $P(x,v,t)$.

Since the random force, $\xi(t)$, has zero mean and is a Gaussian white noise, the derivation of $P(x,v,t)$ is straightforward and very instructive. It only takes a bit of algebra. We first introduce a new probability density, $\sigma(t)$, such that

$$\rho(t) = e^{-\hat{L}_0 t}\sigma(t). \tag{5.127}$$

Using Eqs. (5.124), (5.126), and (5.127), it is easy to show that $\sigma(t)$ obeys the equation of motion:

$$\frac{\partial\sigma(t)}{\partial t} = -\hat{V}(t)\sigma(t), \tag{5.128}$$

where $\hat{V}(t) = e^{+\hat{L}_0 t}\hat{L}_1(t)e^{-\hat{L}_0 t}$. Equation (5.128) has the formal solution

$$\sigma(t) = \exp\left[-\int_0^t dt'\hat{V}(t')\right]\sigma(0). \tag{5.129}$$

Let us now expand the exponential in Eq. (5.129) in a power series. Using the identity $e^x = \sum_{n=0}^{\infty}(x^n/n!)$, we obtain

$$\sigma(t) = \left[\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\left(\int_0^t dt'\hat{V}(t')\right)^n\right]\sigma(0). \tag{5.130}$$

We now can take the average, $\langle\rangle_\xi$, of Eq. (5.130). Because the noise, $\xi(t)$, has zero mean and is Gaussian, only even values of n will remain (cf. Exercise 4.9). Thus, we find

$$\langle\sigma(t)\rangle_\xi = \left[\sum_{n=0}^{\infty}\frac{1}{(2n)!}\left\langle\left(\int_0^t dt'\hat{V}(t')\right)^{2n}\right\rangle_\xi\right]\sigma(0). \tag{5.131}$$

We can use some results from Exercise 4.9 to simplify Eq. (5.131). The average, $\langle(\int_0^t dt'\hat{V}(t'))^{2n}\rangle_\xi$, will decompose into $(2n!/n!2^n)$ identical terms, each containing a product of n pairwise averages, $\langle\int_0^t dt_i\hat{V}(t_i)\int_0^t dt_j\hat{V}(t_j)\rangle_\xi$. Thus, Eq. (5.131) takes the form

$$\langle\sigma(t)\rangle_\xi = \left[\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{2}\int_0^t dt_2\int_0^t dt_1\langle\hat{V}(t_2)\hat{V}(t_1)\rangle_\xi\right)^n\right]\sigma(0). \tag{5.132}$$

We can now sum this series to obtain

$$\langle\sigma(t)\rangle_\xi = \exp\left[\frac{1}{2}\int_0^t dt_2\int_0^t dt_1\langle\hat{V}(t_2)\hat{V}(t_1)\rangle_\xi\right]\sigma(0). \tag{5.133}$$

like Pupanicolaou second order averaging

Let us compute the integral in Eq. (5.133),

$$\begin{aligned}&\frac{1}{2}\int_0^t dt_2\int_0^t dt_1\langle\hat{V}(t_2)\hat{V}(t_1)\rangle_\xi \\ &= \frac{g}{2m^2}\int_0^t dt_2\int_0^t dt_1\delta(t_2-t_1)e^{+\hat{L}_0 t_2}\frac{\partial}{\partial v}e^{-\hat{L}_0(t_2-t_1)}\frac{\partial}{\partial v}e^{-\hat{L}_0 t_1} \\ &= \frac{g}{2m^2}\int_0^t dt_1 e^{+\hat{L}_0 t_1}\frac{\partial^2}{\partial v^2}e^{-\hat{L}_0 t_1}.\end{aligned} \tag{5.134}$$

If we substitute Eq. (5.134) into Eq. (5.133) and take the derivative of Eq. (5.133) with respect to time t, we find the following equation of motion for $\langle\sigma(t)\rangle_\xi$,

$$\frac{\partial\langle\sigma(t)\rangle_\xi}{\partial t} = \frac{g}{2m^2}e^{+\hat{L}_0 t}\frac{\partial^2}{\partial v^2}e^{-\hat{L}_0 t}\langle\sigma(t)\rangle_\xi. \tag{5.135}$$

With this result, we can obtain the equation of motion of $P(x,v,t) = \langle\rho(x,v,t)\rangle_\xi$.

Let us note that $\langle \rho(t) \rangle_\xi = \hat{U}(t) \langle \sigma(t) \rangle_\xi$, where $\hat{U}(t) = e^{-\hat{L}_0 t}$, and take the derivative of $\langle \rho(t) \rangle_\xi$ with respect to time t. We then obtain

$$\frac{\partial \langle \rho(t) \rangle_\xi}{\partial t} = -\hat{L}_0 \langle \rho(t) \rangle_\xi + \hat{U}(t) \frac{\partial \langle \sigma(t) \rangle_\xi}{\partial t} = -\hat{L}_0 \langle \rho(t) \rangle_\xi + \frac{g}{2m^2} \frac{\partial \langle \rho(t) \rangle_\xi}{\partial v^2}. \tag{5.136}$$

If we combine Eqs. (5.125), (5.126), and (5.136), the equation for the observable probability density, $P(x, v, t)$, becomes

$$\frac{\partial P}{\partial t} = -v \frac{\partial P}{\partial x} + \frac{\partial}{\partial v} \left[\left(\frac{\gamma}{m} v - \frac{1}{m} F(x) \right) P \right] + \frac{g}{2m^2} \frac{\partial^2 P}{\partial v^2}, \tag{5.137}$$

where $P = P(x, v, t)$. Equation (5.134) is the *Fokker–Planck equation* for the probability $P(x, v, t)dxdv$ to find the Brownian particle in the interval $x \to x + dx$ and $v \to v + dv$ at time t.

It is important to note that the Fokker–Planck equation conserves probability. We can write it in the form of a *continuity equation*

$$\frac{\partial P}{\partial t} = -\nabla \cdot \mathbf{J}, \tag{5.138}$$

where $\nabla = \hat{\mathbf{x}}(\partial/\partial x) + \hat{\mathbf{v}}(\partial/\partial v)$ is a gradient operator in the (x, v) phase space and $\mathbf{J}$ is the probability current or flux,

$$\mathbf{J} = \hat{\mathbf{x}} v P - \hat{\mathbf{v}} \left(\frac{\gamma}{m} v P - \frac{1}{m} F(x) P + \frac{g}{2m^2} \frac{\partial P}{\partial v} \right), \tag{5.139}$$

in the (x, v) phase space. By the same arguments used in Eqs. (5.120) and (5.121), we see that any change in the probability contained in a given area of the (x, v) phase space must be due to flow of probability through the sides of the area, and therefore the probability is a conserved quantity. It cannot be created or destroyed locally.

In this section we have derived the Fokker–Planck equation for a Brownian particle which is free to move in one spatial dimension. The Fokker–Planck can be generalized easily to three spatial dimensions. However, when the force $\mathbf{F}(\mathbf{x})$ couples the degrees of freedom, little is known about the details of its dynamical evolution. Below we consider Brownian motion in the limit of very large friction. For this case, detailed balance holds, the force can be expressed in terms of a potential, and we can begin to understand some of the complex phenomena governing the dynamics of the Fokker–Planck equation.

hypothesis is not consequence

▶ S5.C.3. The Strong Friction Limit

Let us now consider a Brownian particle moving in one dimension in a potential well, $V(x)$, and assume that the friction coefficient, γ, is very large so that the

velocity of the Brownian particle relaxes to its stationary state very rapidly. Then we can neglect time variations in the velocity and in the Langevin equations [Eq. (5.123)], we assume that $(dv/dt) \approx 0$. The Langevin equations then reduce to

$$\frac{dx(t)}{dt} = \frac{1}{\gamma} F(x) + \frac{1}{\gamma} \xi(t), \tag{5.140}$$

where $F(x) = -(dV(x)/dx)$. We now can use the method of Section S5.C.2 to find the probability $P(x, t)dx$ to find the Brownian particle in the interval $x \to x + dx$ at time t. The probability density, $P(x, t)$, is defined as the average, $P(x, t) = \langle \rho(x, t) \rangle_\xi$, where the equation of motion for the density, $\rho(x, t)$, is given by

$$\begin{aligned} \frac{\partial \rho(t)}{\partial t} &= -\frac{\partial (\dot{x} \rho)}{\partial x} = -\frac{1}{\gamma} \frac{\partial (F(x) \rho)}{\partial x} - \frac{1}{\gamma} \xi(t) \frac{\partial \rho}{\partial x} \\ &= -L_0 \rho(t) - L_1(t) \rho(t). \end{aligned} \tag{5.141}$$

The differential operators L_0 and L_1 are defined as

$$L_0 = \frac{1}{\gamma} \frac{\partial F(x)}{\partial x} + \frac{1}{\gamma} F(x) \frac{\partial}{\partial x} \quad \text{and} \quad L_1 = \frac{1}{\gamma} \xi(t) \frac{\partial}{\partial x}. \tag{5.142}$$

If we now substitute into Eqs. (5.136) and (5.137), we obtain

$$\frac{\partial P(x, t)}{\partial t} = \frac{1}{\gamma} \frac{\partial}{\partial x} \left(\frac{dV}{dx} P(x, t) + \frac{g}{2\gamma} \frac{\partial P(x, t)}{\partial x} \right) = -\frac{\partial J}{\partial x}, \tag{5.143}$$

where $J = -(1/\gamma)(dV/dx)P + (g/2\gamma^2)(dP/dx)$ is the probability current. Equation (5.143) is now a Fokker–Planck equation for the probability density $P(x, t)$ to find the Brownian particle in the interval $x \to x + dx$ at time t. Because Eq. (5.143) has the form of a continuity equation, the probability is conserved.

▶ S5.C.4. Solution of Fokker–Planck Equations with One Variable

For the case of a "free" Brownian particle, one for which $V(x) = 0$, the Fokker–Planck equation (5.143) reduces to the *diffusion equation*

$$\frac{\partial P(x, t)}{\partial t} = \frac{g}{2\gamma^2} \frac{\partial^2 P(x, t)}{\partial x^2} = D \frac{\partial^2 P(x, t)}{\partial x^2}. \tag{5.144}$$

As we showed in Section 4.E, this has a solution

$$P(x,t) = \sqrt{\frac{1}{4\pi Dt}}\exp\left(\frac{-x^2}{4Dt}\right). \tag{5.145}$$

Note that $(1/D) = (2\gamma^2/g) = (\gamma/k_BT)$. Thus for large friction coefficient, γ, the spatial relaxation is very slow.

For the case when $V(x) \neq 0$, we can obtain a spectral decomposition of the probability density $P(x,t)$. Let us first introduce a rescaled time $\tau = t/\gamma$ and write the Fokker-Planck equation (5.143) as

$$\frac{\partial P(x,\tau)}{\partial \tau} = \frac{d^2V}{dx^2}P + \frac{dV}{dx}\frac{\partial P}{\partial x} + \frac{g}{2\gamma}\frac{\partial^2 P}{\partial x^2} = -\hat{L}_{FP}P(x,\tau). \tag{5.146}$$

The operator, $\hat{L}_{LP} = (d^2V/dx^2) + (dV/dx)(\partial/\partial x) + (g/2\gamma)(\partial^2/\partial x^2)$, is a non-self-adjoint operator because of its dependence on the first-order partial derivative. However, it is possible to rewrite the Fokker–Planck equation in terms of a self-adjoint operator via a simple transformation. Then the solutions become more intuitive.

Let us write the probability in the form

$$P(x,\tau) = e^{-\gamma V(x)/g}\Psi(x,\tau), \tag{5.147}$$

where $\Psi(x,\tau)$ is a function to be determined. If we now substitute into Eq. (5.146) we obtain the following equation for $\Psi(x,\tau)$:

$$\frac{\partial \Psi(x,\tau)}{\partial \tau} = \left(\frac{1}{2}\frac{d^2V}{dx^2} - \frac{\gamma}{2g}\left(\frac{dV}{dx}\right)^2\right)\Psi(x,\tau) + \frac{g}{2\gamma}\frac{\partial^2\Psi}{\partial x^2} = -\hat{H}_{FP}\Psi(x,\tau). \tag{5.148}$$

The operator, $\hat{H}_{FP} = -(\frac{1}{2}(d^2V/dx^2) - (\gamma/2g)(dV/dx)^2) - (g/2\gamma)(\partial^2/\partial x^2)$, is a self-adjoint operator and we can use the many well established techniques for dealing with such operators. We will let $\phi_n(x)$ and λ_n denote the nth eigenvector and eigenvalue, respectively, of H_{FP} so that $H_{FP}\phi_n(x) = \lambda_n\phi_n(x)$. The eigenvectors are complete and can be made orthonormal so that

$$\int_{-\infty}^{\infty} dx\phi_{n'}(x)\phi_n(x) = \delta_{n',n}. \tag{5.149}$$

Furthermore, the eigenvalues are real and must have zero or positive values in order that the probability remains finite. We can expand $\Psi(x,t)$ in terms of the eigenvectors and eigenvalues of $\hat{H}_{FP}$:

$$\Psi(x,\tau) = \sum_{n=0}^{\infty} a_n e^{-\lambda_n\tau}\phi_n(x). \tag{5.150}$$

It is interesting to note that $\hat{H}_{FP}$ has at least one zero eigenvalue, which we denote $\lambda_0 = 0$, and a corresponding eigenvector, $\phi_0(x)$, which satisfies the equation

$$\left(\frac{1}{2}\frac{d^2V}{dx^2} - \frac{\gamma}{2g}\left(\frac{dV}{dx}\right)^2\right)\phi_0(x) + \frac{g}{2\gamma}\frac{\partial^2\phi_0(x)}{\partial x^2} = 0. \tag{5.151}$$

Equation (5.150) has the solution

$$\phi_0(x) = Ce^{-\gamma V(x)/g}, \tag{5.152}$$

where C is a normalization constant. This is just the transformation used in Eq. (5.146). Therefore we can now combine Eqs. (5.147), (5.150), and (5.152) and write the probability as

$$P(x,\tau) = \phi_0^2(x) + \sum_{n=1}^{\infty} a_n e^{-\lambda_n\tau}\phi_0(x)\phi_n(x). \tag{5.153}$$

In this form, it is clear that the probability is conserved due to the orthonormality of the eigenstates. If we integrate over Eq. (5.153), we obtain

$$\int_{-\infty}^{\infty} dxP(x,\tau) = \int_{-\infty}^{\infty} dx\phi_0(x)^2 = 1. \tag{5.154}$$

The coefficients, a_n, can be determined from the initial conditions. Let us assume that we are given $P(x,0)$. Then we write

$$P(x,0) = \phi_0^2(x) + \sum_{n=1}^{\infty} a_n\phi_0(x)\phi_n(x). \tag{5.155}$$

If we now divide through by $\phi_0(x)$, multiply by $\phi_{n_0}(x)$, and integrate over x, we obtain

$$a_{n_0} = \int_{-\infty}^{\infty} dx\,\frac{\phi_{n_0}(x)}{\phi_0(x)}P(x,0). \tag{5.156}$$

After a long time, the probability approaches the stationary state:

$$P(x,\infty) = \phi_0^2(x). \tag{5.157}$$

There are several examples of Fokker–Planck equations with one variable which can be solved analytically. We will consider one of them in Exercise (5.8) and leave the others as homework problems.

This method can also be extended to Fokker–Planck equations with two or more spatial degrees of freedom when a transformation analogous to Eq. (5.146) can be found which allows us to write the Fokker–Planck equation in terms of a self-adjoint operator. For such cases, it is possible that the dynamics governed by the self-adjoint operator can undergo a transition to chaos. Examples of such cases have been studied in Refs. 22–24.

■ **EXERCISE 5.8.** Consider the "short-time" relaxation of a free Brownian particle. The Langevin equation for the velocity is $m(dv/dt) = -\gamma v + \xi(t)$. (a) Find the Fokker–Planck equation for the probability $P(v,t)dv$ to find the Brownian particle with velocity $v \to v + dv$ at time t. (b) Solve the Fokker–Planck equation, assuming that at time $t = 0$ the velocity is $v = v_0$.

Answer:

(a) To obtain the Fokker–Planck equation, we will follow the method of Section S5.C. The equation for the probability $\rho(v,t)$ for a specific realization of the random force $\xi(t)$ is

$$\frac{\partial \rho}{\partial t} = -\frac{\partial \dot{v}\rho}{\partial v} = \frac{\gamma}{m}\frac{\partial v\rho}{\partial v} - \frac{1}{m}\xi(t)\frac{\partial \rho}{\partial v}. \tag{1}$$

From Eq. (1) we see that $\hat{L}_0 = -(\gamma/m)(1 + v(\partial/\partial v))$. We can now plug into Eq. (5.136) to obtain a Fokker–Planck equation for the probability density $P(v,t)$. We find

$$\frac{\partial P}{\partial t} = \frac{\gamma}{m}\frac{\partial (vP)}{\partial v} + \frac{g}{2m^2}\frac{\partial^2 P}{\partial v^2}. \tag{2}$$

(b) To solve the Fokker–Planck equation, we follow the method of Section S5.C.3. Make a transformation, $P(v,t) = e^{-m\gamma v^2/2g}\Psi(v,t)$. If we plug this into Eq. (2), we obtain the following equation for $\Psi(v,t)$,

$$\frac{m}{\gamma}\frac{\partial \Psi}{\partial t} = \left(\frac{1}{2} - \frac{1}{4A}v^2 + A\frac{\partial^2}{\partial v^2}\right)\Psi \equiv \hat{H}\Psi. \tag{3}$$

where $A = (g/2m\gamma)$. The operator $\hat{H} = \frac{1}{2} - (1/4A)v^2 + A(\partial^2/\partial v^2)$ is self-adjoint and has eigenfunctions $\phi_n(v)$ $(n = 0, 1, 2, \ldots, \infty)$ which can be expressed in terms of Hermite polynomials [20]. The nth normalized eigenfunction of $\hat{H}$ is

$$\phi_n(v) = \frac{1}{\sqrt{2^n n!}\sqrt{2\pi A}} H_n\left(\frac{v}{\sqrt{2A}}\right)e^{-v^2/4A}, \tag{4}$$

where $H_n(y)$ is the nth-order Hermite polynomial and can be written $H_n(y) = (-1)^n e^{y^2}(d^n/dy^n)e^{-y^2}$. The operator $\hat{H}$ satisfies the eigenvalue equation $\hat{H}\phi_n(v) = -n\phi_n(v)$, so the nth eigenvalue is $\lambda_n = -n$. The eigenfunctions satisfy the orthonormality condition

$$\int_{-\infty}^{\infty} dv \phi_{n'}(v)\phi_n(v) = \delta_{n',n}. \tag{5}$$

If we redefine the time to be $\tau = (\gamma/m)t$, then we obtain the following spectral decomposition of $\Psi(v,t)$,

$$\Psi(v,t) = \sum_{n=0}^{\infty} a_n e^{-n\tau}\phi_n(v). \tag{6}$$

The probability $P(v,\tau)$ is

$$P(v,\tau) = \sum_{n=0}^{\infty} a_n e^{-n\tau}\phi_0(v)\phi_n(v). \tag{7}$$

The initial probability distribution is $P(v,0) = \delta(v - v_0)$. This gives $a_n = \phi_n(v_0)/\phi_0(v_0)$ and we obtain

$$\begin{aligned} P(v,\tau) &= \sum_{n=0}^{\infty} e^{-n\tau}\phi_n(v_0)\phi_n(v)\phi_0(v)/\phi_0(v_0) \\ &= \frac{1}{\sqrt{2\pi A}}e^{-v^2/2A}\sum_{n=0}^{\infty}\frac{1}{2^n n!}e^{-n\tau}H_n\left(\frac{v_0}{\sqrt{2A}}\right)H_n\left(\frac{v}{\sqrt{2A}}\right). \end{aligned} \tag{9}$$

We now can make use of an identity

$$\frac{1}{\sqrt{1-z^2}}\exp\left(\frac{-(x^2+y^2-2xyz)}{1-z^2}\right) = e^{-x^2-y^2}\sum_{n=0}^{\infty}\left(\frac{z^n}{2^n n!}\right)H_n(x)H_n(y) \tag{10}$$

(see Ref. 21, page 786). Using this identity, the probability can be written

$$P(v,\tau) = \frac{1}{\sqrt{2\pi A(1-e^{-2\tau})}}\exp\left(\frac{-(v - v_0 e^{-\tau})^2}{2A(1-e^{-2\tau})}\right). \tag{11}$$

Thus, the probability density has the form of a Gaussian. The average velocity decays as $\langle v(t)\rangle = v_0 e^{-\tau}$, and the velocity distribution has a standard deviation, $\sigma_v = \sqrt{A(1-e^{-2\tau})}$. In the limit of "long time" the probability density takes the form

$$P(v,t) \approx \frac{1}{\sqrt{2\pi\gamma k_B T/m^2}}\exp\left(\frac{-m^2v^2}{2\gamma k_B T}\right). \tag{12}$$

Thus, for large friction coefficient, γ, the relaxation time for the

Solving SDE is more direct.

velocity distribution goes as γ^{-1} while the relaxation time for the spatial distribution goes as γ.

▶ S5.D. Approximations to the Master Equation [3, 4]

The master equation, under some conditions, may be reduced to a Fokker–Planck equation. For example, if the step size shrinks and the transition rate grows as a small parameter decreases to zero, then we can use the Kramers–Moyal expansion to obtain a Fokker–Planck equation from the master equation. We have already used this fact in Chapter 4 when we obtained the continuum limit for discrete random walks.

Let us consider a random walk in which the step size is given by Δ. The master equation can be written

$$\frac{\partial P_1(n\Delta,t)}{\partial t} = \sum_{m=-\infty}^{\infty} [P_1(m\Delta,t)w_{m,n}(\Delta) - P_1(n\Delta,t)w_{n,m}(\Delta)], \tag{5.158}$$

where $P_1(n\Delta,t)$ is the probability to find the walker at point $x = n\Delta$ at time t. Let us choose the transition rate to be

$$w_{n',n}(\Delta) = \frac{1}{\Delta^2}(\delta_{n',n+1} + \delta_{n',n-1}). \tag{5.159}$$

Then the master equation becomes

$$\frac{\partial P_1(n\Delta,t)}{\partial t} = \frac{1}{\Delta^2}[P_1((n+1)\Delta,t) + P_1((n-1)\Delta,t) - 2P_1(n\Delta,t)]. \tag{5.160}$$

We now let $x = n\Delta$ in Eq. (5.159) and let $\Delta \to 0$. To determine what becomes of the left-hand side in this limit, we expand it in a Taylor series in the small parameter, Δ keeping $x = n\Delta$. Then

$$\begin{aligned}\frac{\partial P_1(x,t)}{\partial t} &= \lim_{\Delta\to 0}\frac{1}{\Delta^2}[P_1(x+\Delta,t) + P_1(x-\Delta,t) - 2P_1(x,t)] \\ &= \lim_{\Delta\to 0}\frac{1}{\Delta^2}\left[P_1(x,t) + \left(\frac{\partial P_1}{\partial x}\right)_{\Delta=0}\Delta + \frac{1}{2}\left(\frac{\partial^2 P_1}{\partial x^2}\right)_{\Delta=0}\Delta^2 + \cdots\right. \\ &\quad \left. + P_1(x,t) - \left(\frac{\partial P_1}{\partial x}\right)_{\Delta=0}\Delta + \frac{1}{2}\left(\frac{\partial^2 P_1}{\partial x^2}\right)_{\Delta=0}\Delta^2 + \cdots - 2P_1(x,t)\right] \\ &= \frac{\partial^2 P_1}{\partial x^2}.\end{aligned} \tag{5.161}$$

Thus, in the limit $\Delta \to 0$ the random walk is described by a simple Fokker–

Planck equation. Higher-order derivatives in the Taylor series do not contribute because their coefficients go to zero. Lower-order terms in the Taylor series cancel. We see that the condition to obtain a Fokker–Planck equation is that the step size, Δ, decreases and the transition rate, $w_{m,n}(\Delta)$, increases as $1/\Delta^2$. This is a simple example of a Kramers–Moyal-type expansion [25, 26].

It is useful to consider a more general example. Let us write the master equation for the continuous stochastic variable x:

$$\frac{\partial P_1(x,t)}{\partial t} = \int_{-\infty}^{\infty} dx'[P_1(x',t)w(x'|x) - P_1(x,t)w(x|x')], \tag{5.162}$$

where $w(x'|x)$ is the transition rate. Let $y = x' - x$ denote the change in stochastic variable x at a transition, and introduce the notation $\tau(x,y) = w(x|x+y)$ so that $\tau(x-y,y) = w(x-y|y)$. In Eq. (5.162), make the change of variables $x' = x + y$, and in the first term under the integral let $y \to -y$. Then the master equation can be rewritten

$$\frac{\partial P_1(x,t)}{\partial t} = \int_{-\infty}^{\infty} dy[P_1(x-y,t)\tau(x-y,y) - P_1(x)\tau(x,y)]. \tag{5.163}$$

We can now expand $P_1(x-y,t)\tau(x-y,y)$ in a Taylor series in y. This, of course, only makes sense if the function $\tau(x,y)$ is sharply peaked about $y = 0$. Equation (5.163) takes the form

$$\begin{aligned}\frac{\partial P_1(x,t)}{\partial t} &= \int_{-\infty}^{\infty} dy\left[\left(\sum_{n=0}^{\infty}\frac{(-y)^n}{n!}\frac{\partial^n}{\partial x^n}(P_1(x,t)\tau(x,y))\right) - P_1(x,t)\tau(x,y)\right] \\ &= \int_{-\infty}^{\infty} dy\sum_{n=1}^{\infty}\frac{(-y)^n}{n!}\frac{\partial^n}{\partial x^n}(P_1(x,t)\tau(x,y)).\end{aligned} \tag{5.164}$$

Thus,

$$\frac{\partial P_1(x,t)}{\partial t} = \sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\frac{\partial^n}{\partial x^n}(\alpha_n(x)P_1(x,t)), \tag{5.165}$$

where $\alpha_n(x)$ is the nth moment,

$$\alpha_n(x) = \int_{-\infty}^{\infty} dy\, y^n\tau(x,y) = \int_{-\infty}^{\infty} dy\, y^n\, w(x|x+y). \tag{5.166}$$

Equation (5.165) is the *Kramers–Moyal* expansion of the master equation. It only has meaning for those special forms of $w(x|x+y) = \tau(x,y)$ for which the infinite series of higher-order derivatives truncates. We shall now give an example of such a case.

Let us choose $w(x|x+y) = \tau(x,y)$ to be of the form

$$w(x|x+y) = \tau(x,y) = \frac{1}{\sqrt{\pi}\Delta^3}\exp\left(-\frac{(y-A(x)\Delta^2)^2}{\Delta^2}\right). \tag{5.167}$$

Then

$$\alpha_1 = \int_{-\infty}^{\infty} dy\, y\, w(x|x+y) = A(x), \tag{5.168}$$

and

$$\alpha_2 = \int_{-\infty}^{\infty} dy\, y^2\, w(x|x+y) = \tfrac{1}{2} + \Delta^2 A^2(x). \tag{5.169}$$

Higher-order odd moments are identically zero, and higher-order even moments are proportional to powers of Δ. Thus, for the choice of $w(x|x+y)$ given in Eq. (5.167), as $\Delta \to 0$, the master equation reduces to

$$\frac{\partial P_1(x,t)}{\partial t} = -A(x)\frac{\partial P_1(x,t)}{\partial x} + \frac{1}{4}\frac{\partial^2 P_1(x,t)}{\partial x^2}. \tag{5.170}$$

For this process the step size decreases because the width of the Gaussian shrinks, and the transition rate increases as $\Delta \to 0$. If this occurs in the particular manner shown in Eq. (5.167), then the Kramers–Moyal expansion has meaning.

For the case when the step size in a master equation cannot be made arbitrarily small, as is the case for chemical reactions or population dynamics, the Kramers–Moyal expansion of the master equation may not give a good approximation. Then one must use some other approximation scheme or solve the equation numerically. An alternative approximation scheme has been introduced by van Kampen. He has shown that it is still possible to approximate the master equation by a Fokker–Planck equation if the system has a large parameter, such as a volume or total particle number, and if the transition rates depend on that large parameter in a certain way. A full discussion of this method may be found in van Kampen's book [3].

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PROBLEMS

Problem 5.1. Urn A initially has one white and one red marble, and urn B initially has one white and three red marbles. The marbles are repeatedly interchanged. In each step of the process one marble is selected from each urn at random and the two marbles selected are interchanged. Let the stochastic variable Y denote "configuration of the urns." Three configurations are possible: (1) Urn A—2 white balls, Urn B—4 red balls;