5. Stochastic Dynamics and Brownian Motion

5.A. Introduction

In this chapter, we will derive differential equations of motion for the evolution in time of probability distributions and densities. The connection of these phenomenological time evolution to specific dynamical models will be dealt with in the next chapter. Here, we shall restrict our attention to Markov processes, which are stochastic processes that have memories only of their immediate past.

The equation governing the stochastic dynamics of Markov processes is called the **master equation**. Its importance lies in its almost universal applicability to far-ranging fields such as chemistry, biology, population dynamics, laser physics, Brownian motion, fluids, semiconductors, etc. We shall restrict ourselves to processes that tend to some equilibrium (steady) states after a long enough period of time.

Other topics discussed include the **Langevin equation** and the **Fokker- Planck equation** formulations of the Brownian motion.

5.B. General Theory

5.B.1. Probability Densities

The following notations will be used for the various probability densities for the stochastic variable *Y*:

$$P_1\left(y_1,t_1\right) \equiv P_1\left(1\right) \equiv \text{ probability density for } Y = \left\{y_1,t_1\right\} = \left\{1\right\}. \tag{5.1}$$

$$P_2\left(y_1,t_1;y_2,t_2\right) \equiv P_2\left(1,2\right) \equiv \text{ joint probability density for}$$

$$Y = \left\{y_1,t_1;y_2,t_2\right\} = \left\{1,2\right\}. \tag{5.2}$$

$$P_n\left(y_1,t_1;y_2,t_2;\cdots;y_n,t_n\right) \equiv P_n\left(1,2,\cdots,n\right) \equiv \text{ joint probability density for}$$

$$Y = \left\{y_1,t_1;y_2,t_2;\cdots;y_n,t_n\right\} = \left\{1,2,\cdots,n\right\} \tag{5.3}$$

where $Y = \left\{y_1,t_1;y_2,t_2;\cdots;y_n,t_n\right\} = \left\{1,2,\cdots,n\right\}$ is the short-hand for having $Y = y_1$ at time t_1, $Y = y_2$ at time t_2, …, and $Y = y_n$ at time t_n. The usual properties of probability densities apply, so that

$$P_n \ge 0 \tag{5.4}$$

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

$$\int dy_n\ P_n\left(1,2,\cdots,n\right) = P_{n-1}\left(1,2,\cdots,n-1\right) \tag{5.5'}$$

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

$$\int dy_1 P_1\left(1\right) = 1 \tag{5.6'}$$

Note that to facilitate comparisons with the textbook, both long- and short- handed versions are given for most equations. They are distinguished by labels that are unprimed and primed, respectively. For *Y* discrete, these formulae, as well as subsequent ones, are still valid if we interpret all probability densities as probabilities and replace all integrals with sums. For example, (5.6) becomes

$$\sum_{y_1} P_1\left(y_1,t_1\right) = 1$$

$$\sum_{y_1} P_1\left(1\right) = 1$$

5.B.2. Time-Dependent Moments

Time-dependent moments are defined by

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

which describe the correlation between values of Y at different times.

A process is called **stationary** if

$$P_n(y_1,t_1;y_2,t_2;\cdots;y_n,t_n) = P_n(y_1,t_1+\tau;y_2,t_2+\tau;\cdots;y_n,t_n+\tau) \tag{5.8}$$

for all n and τ. This means

$$P_1(y_1,t_1) = P_1(y_1,t_1-t_1) = P_1(y_1,0) \equiv P_1(y_1) \tag{5.9}$$

$$P_2(y_1,t_1;y_2,t_2) = P_2(y_1,0;y_2,t_2-t_1) = P_2(y_1,y_2;t_2-t_1)$$

$$= P_2(y_1,t_1-t_2;y_2,0) = P_2(y_1,y_2;t_1-t_2) = P_2\left(y_1,y_2;\left|t_1-t_2\right|\right) \tag{5.9a}$$

$$\vdots$$

Thus,

$$\left\langle y_1(t_1)\,y_2(t_2)\right\rangle = \int dy_1 \int dy_2 \; y_1 y_2 P_2(y_1,t_1;y_2,t_2)$$

$$= \int dy_1 \int dy_2 \; y_1 y_2 P_2\left(y_1,y_2;\left|t_1-t_2\right|\right)$$

$$= \left\langle y_1 y_2;\left|t_1-t_2\right|\right\rangle \tag{5.9b}$$

By definition, all equilibrium processes are stationary.

5.B.3. Conditional Probability Density

The quantity $P_{1/1}\left(y_1,t_1 \mid y_2,t_2\right) \equiv P_{1/1}(1|2)$ denotes the **conditional probability density** for $Y = \left(y_2,t_2\right)$ given that $Y = \left(y_1,t_1\right)$. By definition

$$P_2\left(y_1,t_1;y_2,t_2\right) = P_1\left(y_1,t_1\right)P_{1/1}\left(y_1,t_1 \mid y_2,t_2\right) \tag{5.11}$$

$$P_2(1,2) = P_1(1)P_{1/1}(1|2) \tag{5.11'}$$

which, with the help of (5.5), gives

$$P_1\left(y_2,t_2\right) = \int dy_1 P_2\left(y_1,t_1;y_2,t_2\right)$$

$$= \int dy_1 P_1\left(y_1,t_1\right)P_{1/1}\left(y_1,t_1 \mid y_2,t_2\right) \tag{5.12}$$

$$P_1(2) = \int dy_1 P_2(1,2) \quad = \int dy_1 P_1(1)P_{1/1}(1|2) \tag{5.12'}$$

and

$$P_1\left(y_1,t_1\right) = P_1\left(y_1,t_1\right)\int dy_2 P_{1/1}\left(y_1,t_1 \mid y_2,t_2\right)$$

$$P_1(1) = P_1(1)\int dy_2 P_{1/1}(1|2)$$

so that

$$\int dy_2 P_{1/1}\left(y_1,t_1 \mid y_2,t_2\right) = 1 \tag{5.13}$$

$$\int dy_2 P_{1/1}(1|2) = 1 \tag{5.13'}$$

For equilibrium processes,

$$P_2\left(y_1,t_1;y_2,t_2\right) = P_2\left(y_1,y_2;t_2-t_1\right)$$

$$= P_1\left(y_1,t_1\right)P_{1/1}\left(y_1,t_1 \mid y_2,t_2\right)$$

$$= P_1\left(y_1\right)P_{1/1}\left(y_1,t_1 \mid y_2,t_2\right)$$

so that

$$P_{1/1}\left(y_1,t_1 \mid y_2,t_2\right) = P_{1/1}\left(y_1,0 \mid y_2,t_2-t_1\right) \equiv P_{1/1}\left(y_1 \mid y_2;t_2-t_1\right)$$

5.B.4. Joint Conditional Probability Density

Let

$$P_{k/l}\left(y_1,t_1;\cdots;y_k,t_k \mid y_{k+1},t_{k+1};\cdots;y_{k+l},t_{k+l}\right) \equiv P_{k/l}\left(1,2,\cdots k \mid k+1,\cdots k+l\right)$$

be the joint conditional probability density for $Y=\left\{y_{k+1},t_{k+1};\cdots;y_{k+l},t_{k+l}\right\}$

$=\left\{k+1,\cdots,k+l\right\}$ given that $Y=\left\{y_1,t_1;\cdots;y_k,t_k\right\}$ $=\left\{1,\cdots k\right\}$. By definition, we have

$$P_{k+l}\left(y_1,t_1;\cdots;y_k,t_k;y_{k+1},t_{k+1};\cdots;y_{k+l},t_{k+l}\right)$$

$$=P_k\left(y_1,t_1;\cdots;y_k,t_k\right)P_{k/l}\left(y_1,t_1;\cdots;y_k,t_k \mid y_{k+1},t_{k+1};\cdots;y_{k+l},t_{k+l}\right) \qquad (5.15)$$

$$P_{k+l}\left(1,\cdots,k,k+1,\cdots,k+l\right)=P_k\left(1,\cdots k\right)P_{k/l}\left(1,\cdots,k \mid k+1,\cdots,k+l\right) \qquad (5.15')$$

Note that $P_{k/l}$ quantifies correlations between the values of *Y* at different times. This is important if *Y* possesses memory of its past.

5.B.5. Markov Processes

If Y has only memory of its immediate past, we write

$$P_{n-1/1}\left(y_1,t_1;\cdots;y_{n-1},t_{n-1}\,|\,y_n,t_n\right)=P_{1/1}\left(y_{n-1},t_{n-1}\,|\,y_n,t_n\right) \qquad (5.16)$$

$$P_{n-1/1}\left(1,\cdots,n-1\,|\,n\right)=P_{1/1}\left(n-1\,|\,n\right) \qquad (5.16')$$

where $t_1<t_2<\cdots<t_n$ and $P_{1/1}\left(y_1,t_1\,|\,y_2,t_2\right)=P_{1/1}\left(1|2\right)$ is called the **transition probability**.

A process that satisfies (5.16) is called a **Markov process**. It is fully determined by 2 functions $P_1\left(y_1,t_1\right)=P_1\left(1\right)$ and $P_{1/1}\left(y_1,t_1;y_2,t_2\right)=P_{1/1}\left(1|2\right)$. Consider,

$$P_3\left(y_1,t_1;y_2,t_2;y_3,t_3\right)=P_2\left(y_1,t_1;y_2,t_2\right)P_{2/1}\left(y_1,t_1;y_2,t_2\,|\,y_3,t_3\right)$$

$$=P_1\left(y_1,t_1\right)P_{1/1}\left(y_1,t_1\,|\,y_2,t_2\right)P_{2/1}\left(y_1,t_1;y_2,t_2\,|\,y_3,t_3\right) \qquad (5.17a)$$

$$P_3\left(1,2,3\right)=P_2\left(1,2\right)P_{2/1}\left(1,2\,|\,3\right) \quad =P_1\left(1\right)P_{1/1}\left(1|2\right)P_{2/1}\left(1,2\,|\,3\right) \qquad (5.17a')$$

so that for a Markov process,

$$P_3\left(y_1,t_1;y_2,t_2;y_3,t_3\right)=P_1\left(y_1,t_1\right)P_{1/1}\left(y_1,t_1\,|\,y_2,t_2\right)P_{1/1}\left(y_2,t_2\,|\,y_3,t_3\right) \qquad (5.17)$$

$$P_3\left(1,2,3\right)=P_1\left(1\right)P_{1/1}\left(1|2\right)P_{1/1}\left(2\,|\,3\right) \qquad (5.17')$$

Integrating over y_2 and assuming $t_1<t_2<t_3$, we have

$$P_2\left(y_1,t_1;y_3,t_3\right)=P_1\left(y_1,t_1\right)\int dy_2 P_{1/1}\left(y_1,t_1\,|\,y_2,t_2\right)P_{1/1}\left(y_2,t_2\,|\,y_3,t_3\right) \qquad (5.18)$$

$$P_2\left(1,3\right)=P_1\left(1\right)\int dy_2\; P_{1/1}\left(1|2\right)P_{1/1}\left(2\,|\,3\right) \qquad (5.18')$$

and

$$P_{1/1}\left(y_1,t_1\,|\,y_3,t_3\right)=\frac{P_2\left(y_1,t_1;y_3,t_3\right)}{P_1\left(y_1,t_1\right)}$$

$$=\int dy_2 P_{1/1}\left(y_1,t_1\,|\,y_2,t_2\right)P_{1/1}\left(y_2,t_2\,|\,y_3,t_3\right) \qquad (5.19)$$

$$P_{1/1}\left(1|3\right)=\int dy_2\; P_{1/1}\left(1|2\right)P_{1/1}\left(2\,|\,3\right) \qquad (5.19')$$

which is a closed set of equations for $P_{1/1}$. It is known as the **Chapman-Kolmogorov equation** and is the consequence of the statistical independence of successive steps in a Markov process.

Using (5.19), we can write (5.18) as

$$P_2(y_1,t_1;y_3,t_3) = P_1(y_1,t_1)P_{1/1}(y_1,t_1 \mid y_3,t_3)$$

$$P_2(1,3) = P_1(1)P_{1/1}(1|3)$$

which, when integrated over y_1, gives

$$P_1(y_3,t_3) = \int dy_1 P_1(y_1,t_1)P_{1/1}(y_1,t_1 \mid y_3,t_3)$$

$$P_1(3) = \int dy_1 P_1(1)P_{1/1}(1|3)$$

as expected.

5.C. Markov Chains

5.C.0. Definitions

A **Markov chain** is a Markov process involving a single discrete stochastic variable whose value changes only at discrete times.

Let the allowable values of the stochastic variable Y be

$$Y = \{ y(n) \mid n = 1, \cdots, M \}$$

and time be measured in discrete steps of interval τ, i.e.,

$$t = s\tau \qquad \text{with} \qquad s = 0, 1, 2, \cdots$$

Let $P(n,s)$ be the probability that $Y = y(n)$ at time $t = s\tau$. The only independent conditional probabilities are the **transition probabilities** $P_{1/1}(n,s \mid m,s+1)$. The constraint (5.12) implies

$$P(n,s+1) = \sum_{m=1}^{M} P(m,s) P_{1/1}(m,s \mid n,s+1) \qquad (5.20)$$

The Chapman-Kolmogorov equation (5.19) then becomes

$$P_{1/1}(n_0,s_0 \mid n,s+1) = \sum_{m=1}^{M} P_{1/1}(n_0,s_0 \mid m,s) P_{1/1}(m,s \mid n,s+1) \qquad (5.21)$$

where $0 \le s_0 \le s$. Next, we introduce the transition matrix $\mathbf{Q}(s) = \{ Q_{mn}(s) \}$ where

$$Q_{mn}(s) = P_{1/1}(m,s \mid n,s+1) \qquad (5.22)$$

In this section, we shalll consider the time-independent case $\mathbf{Q}(s) = \mathbf{Q}$. The oscillatory case $\mathbf{Q}(s) = \mathbf{Q}(s+N)$ will be considered in S5.A.

5.C.1. Spectral Properties

5.C.1.1. Iterative Solution

For a time-independent transition matrix $\mathbf{Q}(s)=\mathbf{Q}$, we have

$$Q_{mn} = P_{1/1}\left(m,0\,|\,n,1\right) \quad = P_{1/1}\left(m,s\,|\,n,s+1\right) \qquad \text{for all } s \qquad (5.23)$$

Eq(5.21) can be written as

$$P_{1/1}\left(n_0,s_0\,|\,n,s+1\right) = \sum_{m=1}^{M} P_{1/1}\left(n_0,s_0\,|\,m,s\right) Q_{m\,n}\left(s\right) \qquad [\ s \ge s_0\ ]$$

$$= \sum_{m_1=1}^{M}\sum_{m_2=1}^{M} P_{1/1}\left(n_0,s_0\,|\,m_2,s-1\right) Q_{m_2\,m_1}\left(s-1\right) Q_{m_1\,n}\left(s\right)$$

$$= \sum_{m_1=1}^{M}\sum_{m_2=1}^{M}\cdots\sum_{m_{k-1}=1}^{M}\sum_{m_k=1}^{M} Q_{n_0 m_k}\left(s_0\right) Q_{m_k m_{k-1}}\left(s_0+1\right)\cdots Q_{m_2\,m_1}\left(s-1\right) Q_{m_1\,n}\left(s\right)$$

where $k = s - s_0$, with the understanding that for $k=0$, $P_{1/1}\left(n_0,s_0\,|\,n,s_0+1\right) = Q_{n_0 n}$.

For $\mathbf{Q}(s)=\mathbf{Q}$, we have

$$P_{1/1}\left(n_0,s_0\,|\,n,s+1\right) = \sum_{m_1=1}^{M}\sum_{m_2=1}^{M}\cdots\sum_{m_{k-1}=1}^{M}\sum_{m_k=1}^{M} Q_{n_0 m_k} Q_{m_k m_{k-1}}\cdots Q_{m_2\,m_1} Q_{m_1\,n}$$

$$= \left(\mathbf{Q}^k\right)_{n_0 n} \quad = \left(\mathbf{Q}^{s-s_0}\right)_{n_0 n} \qquad (5.24)$$

Similarly, (5.20) can be written as

$$P\left(n,s\right) = \sum_{m=1}^{M} P\left(m,s-1\right) Q_{mn}\left(s-1\right) \qquad [\ s \ge 1\ ]$$

$$= \sum_{m_1=1}^{M}\sum_{m_2=1}^{M} P\left(m_2,s-2\right) Q_{m_2\,m_1}\left(s-2\right) Q_{m_1\,n}\left(s-1\right)$$

$$= \sum_{m_1=1}^{M}\sum_{m_2=1}^{M}\cdots\sum_{m_{s-1}=1}^{M}\sum_{m_s=1}^{M} P\left(m_s,0\right) Q_{m_s m_{s-1}}\left(1\right)\cdots Q_{m_2\,m_1}\left(s-1\right) Q_{m_1\,n}\left(s\right)$$

For $\mathbf{Q}(s)=\mathbf{Q}$, we have

$$P\left(n,s\right) = \sum_{m_1=1}^{M}\sum_{m_2=1}^{M}\cdots\sum_{m_{s-1}=1}^{M}\sum_{m_s=1}^{M} P\left(m_s,0\right) Q_{m_s m_{s-1}}\cdots Q_{m_2\,m_1} Q_{m_1\,n}$$

$$= \sum_{m_s=1}^{M} P\left(m_s, 0\right)\left(\mathbf{Q}^s\right)_{m_s n} \quad = \sum_{m=1}^{M} P\left(m, 0\right)\left(\mathbf{Q}^s\right)_{mn} \tag{5.25}$$

5.C.1.2. Dirac Notations

In the Dirac notation, we write

$$P(n,s) \equiv \langle \mathbf{p}(s) | n \rangle \qquad \text{and} \qquad P_{1/1}(m, s_0 \mid n, s) \equiv \langle m | \mathbf{P}(s_0 | s) | n \rangle$$

where $\langle \mathbf{p}(s) |$ is the **probability vector**, and $\mathbf{P}(s_0 | s)$ is the **conditional probability matrix**. The left $\langle n |$ and right $| n \rangle$ states denote possible realization of the stochastic variable *Y*. They are assumed to be complete, $\sum_{n=1}^{M} | n \rangle \langle n | = \mathbf{I}$, and orthonormal, $\langle n | m \rangle = \delta_{nm}$. The probability $P(n,s) \equiv \langle \mathbf{p}(s) | n \rangle$ can be taken as the *n*th component of the row vector $\langle \mathbf{p}(s) |$. Our task is to express everything in terms of the eigenstates of **Q**.

5.C.1.3. Eigenstates of Q

The transition matrix **Q** is in general not symmetric. Thus, its right and left eigenvectors are different. The eigenvalues of **Q** are given by the secular equation

$$\det\left|\ \mathbf{Q}-\lambda\mathbf{I}\ \right|=0 \qquad (5.26)$$

Let $\left|\chi_i\right\rangle$ and $\left|\psi_i\right\rangle$ be the left and right eigenvectors, respectively, that belong to the eigenvalue λ_i, i.e.,

$$\left\langle\chi_i\right|\mathbf{Q}=\left\langle\chi_i\right|\lambda_i \qquad \text{and} \qquad \mathbf{Q}\left|\psi_i\right\rangle=\lambda_i\left|\psi_i\right\rangle$$

$\Rightarrow$

$$\left\langle\chi_i\middle|n\right\rangle\lambda_i=\left\langle\chi_i\middle|\mathbf{Q}\middle|n\right\rangle \;=\sum_{m=1}^{M}\left\langle\chi_i\middle|m\right\rangle\left\langle m\middle|\mathbf{Q}\middle|n\right\rangle$$

i.e., $$\chi_i\left(n\right)\lambda_i=\sum_{m=1}^{M}\chi_i\left(n\right)Q_{mn} \qquad (5.27)$$

where $\chi_i\left(n\right)=\left\langle\chi_i\middle|n\right\rangle$ and $Q_{mn}=\left\langle m\middle|\mathbf{Q}\middle|n\right\rangle$. Similarly,

$$\lambda_i\left\langle n\middle|\psi_i\right\rangle=\left\langle n\middle|\mathbf{Q}\middle|\psi_i\right\rangle \;=\sum_{m=1}^{M}\left\langle n\middle|\mathbf{Q}\middle|m\right\rangle\left\langle m\middle|\psi_i\right\rangle$$

i.e., $$\lambda_i\psi_i\left(n\right)=\sum_{m=1}^{M}Q_{nm}\psi_i\left(m\right) \qquad (5.28)$$

where $\psi_i\left(n\right)=\left\langle n\middle|\psi_i\right\rangle$.

5.C.1.4. Orthonormality and Completeness

Consider

$$\langle \chi_i | \mathbf{Q} = \langle \chi_i | \lambda_i \qquad \text{and} \qquad \mathbf{Q} | \psi_j \rangle = \lambda_j | \psi_j \rangle$$

$\Rightarrow$

$$\langle \chi_i | \mathbf{Q} | \psi_j \rangle = \langle \chi_i | \psi_j \rangle \lambda_i \qquad \text{and} \qquad \langle \chi_i | \mathbf{Q} | \psi_j \rangle = \lambda_j \langle \chi_i | \psi_j \rangle$$

so that,

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

Thus, if $\lambda_i \neq \lambda_j$, then $\langle \chi_i | \psi_j \rangle = 0$. For the case $\lambda_i = \lambda_j$, we can always set

$\langle \chi_i | \psi_i \rangle = 1$ so that we have the orthonormality condition

$$\langle \chi_i | \psi_j \rangle = \delta_{ij} \tag{5.30}$$

Next, consider the expansion

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

$$\Rightarrow \qquad \langle \mathbf{p} | \psi_j \rangle = \sum_{i=1}^{M} \langle \chi_i | \psi_j \rangle c_i \quad = \sum_{i=1}^{M} \delta_{ij} c_i = c_j$$

Hence,

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

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

i.e., the eigenstates are complete.

5.C.2. Random Walk

5.C.2.1. Random Walk and the Diffusion Equation

Let a particle moves along the *x*-axis with step size *l* and time step τ.

The constraint (5.20) can be written as

$$P_1(n_2, s) = \sum_{n_1} P_1(n_1, s-1) P_{1/1}(n_1, s-1 \mid n_2, s) \qquad (5.41)$$

where $s\tau$ is the time and $n_j \tau$, with $n_j = 0, \pm 1, \cdots$, denotes the particle position.

If the probabilities for going right and left are equal, we have

$$P_{1/1}(n_1, s-1 \mid n_2, s) = \frac{1}{2}\delta_{n_2,\, n_1+1} + \frac{1}{2}\delta_{n_2,\, n_1-1} \qquad (5.42)$$

and (5.41) becomes

$$P_1(n, s) = \frac{1}{2} P_1(n-1, s-1) + \frac{1}{2} P_1(n+1, s-1) \qquad (5.43)$$

Going over to the continuum case, we set

$$x = nl, \qquad t = s\tau$$

so that

$$\begin{aligned} \frac{\partial P_1(x,t)}{\partial t} &= \lim_{\tau \to 0} \frac{1}{\tau}\left[P_1(n, s+1) - P_1(n, s) \right] \\ &= \lim_{\tau \to 0} \frac{1}{2\tau}\left[P_1(n-1, s) + P_1(n+1, s) - P_1(n, s) \right] \\ &= \lim_{l,\tau \to 0} \frac{l^2}{2\tau l^2}\left[P_1(n-1, s) + P_1(n+1, s) - P_1(n, s) \right] \\ &= D \frac{\partial^2 P_1(x,t)}{\partial x^2} \qquad (5.45) \end{aligned}$$

where

$$D = \lim_{l,\tau \to 0} \frac{l^2}{2\tau}$$

is called the **diffusion coefficient** and the Fokker-Planck eq(5.45) is called the **diffusion equation**.

5.C.2.2. Solution

We now seek a solution to (5.45) that satisfies the initial condition

$$P_1(x,0) = \delta(x) \qquad (5.46a)$$

which means the particle is at $x = 0$ at $t = 0$.

Using the Fourier transform

$$\tilde{P}_1(k,t) = \int_{-\infty}^{\infty} dx P_1(x,t) e^{i\,k\,x} \qquad (5.46b)$$

eq(5.46a) becomes

$$\frac{\partial \tilde{P}_1(x,t)}{\partial t} = -Dk^2 \tilde{P}_1(x,t) \qquad (5.47)$$

with solution

$$\tilde{P}_1(x,t) = Ae^{-D\,k^2\,t} \qquad (5.48)$$

where A is a constant that can be determined using (5.45, 46a) as

$$A = \tilde{P}_1(x,0) = \int_{-\infty}^{\infty} dx P_1(x,0) e^{i\,k\,x} = \int_{-\infty}^{\infty} dx \delta(x) e^{i\,k\,x} = 1$$

The inverse transform of (5.46b) is

$$P_1(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \tilde{P}_1(k,t) e^{-i\,k\,x}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{-i\,k\,x\,-\,D\,k^2\,t}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp\left[-Dt \left(k^2 + i \frac{x}{Dt} k \right) \right]$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp\left[-Dt \left(k + i \frac{x}{2Dt} \right)^2 - \frac{x^2}{4Dt} \right]$$

$$= \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \qquad (5.49)$$

where we've used the Gaussian integral formula

$$\int_{-\infty}^{\infty} dx \exp\left[-a(x+b)^2\right] = \sqrt{\frac{\pi}{a}}$$

Eq(5.49) gives the probability density of finding the particle at point *x* at time *t* if it starts at $x = 0$ at $t = 0$.

The 1st moment is

$$\langle x(t) \rangle = \int_{-\infty}^{\infty} dx x P_1(x,t)$$

$$= \frac{1}{\sqrt{4\pi D t}} \int_{-\infty}^{\infty} dx x e^{-x^2/4D\,t}$$

$$= 0$$

since the integrand is odd.

Alternatively, multiplying (5.47) with *x* and integrate gives

$$\frac{d\langle x(t) \rangle}{dt} = D \int_{-\infty}^{\infty} dx x \frac{\partial^2 P_1(x,t)}{\partial x^2}$$

$$= D\left[x \frac{\partial P_1(x,t)}{\partial x}\bigg|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dx \frac{\partial P_1(x,t)}{\partial x} \right]$$

$$= D\left[x \frac{\partial P_1(x,t)}{\partial x} - P_1(x,t) \right]_{-\infty}^{\infty}$$

$$= 0$$

where we've used

$$x \frac{\partial P_1(x,t)}{\partial x} = -\frac{x^2}{\sqrt{16\pi (Dt)^3}} e^{-x^2/4D\,t} \underset{x \to \pm\infty}{\longrightarrow} 0$$

The last limit is obtained by applying the L'Hospital rule repeatedly so that

$$\lim_{x\to\infty} x^n e^{-x} = \lim_{x\to\infty} \frac{x^n}{e^x} = \lim_{x\to\infty} \frac{n x^{n-1}}{e^x} = \lim_{x\to\infty} \frac{n!}{e^x} = 0$$

Hence, $\langle x(t) \rangle$ is a constant which must equal to 0 since $\langle x(0) \rangle = 0$.

The 2nd moment is

$$\langle x^2(t)\rangle = \int_{-\infty}^{\infty} dx x^2 P_1(x,t)$$

$$= \frac{1}{\sqrt{\pi D t}} \int_0^{\infty} dx x^2 e^{-x^2/4D\,t}$$

$$= \frac{4Dt}{\sqrt{\pi}} \int_0^{\infty} dy \sqrt{y} e^{-y} \qquad \text{where} \qquad y = \frac{x^2}{4Dt}$$

$$= \frac{4Dt}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}\right) = 2Dt \qquad (5.49a)$$

where the Gamma function is defined by

$$\Gamma(z) = \int_0^{\infty} dy y^{z-1} e^{-y}$$

with

$$\Gamma(z+1) = z\Gamma(z) \qquad \text{and} \qquad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

Alternatively, multiplying (5.45) with x^2 and integrate gives

$$\frac{d\langle x^2(t)\rangle}{dt} = D \int_{-\infty}^{\infty} dx x^2 \frac{\partial^2 P_1(x,t)}{\partial x^2}$$

$$= D\left[x^2 \frac{\partial P_1(x,t)}{\partial x}\bigg|_{-\infty}^{\infty} - 2\int_{-\infty}^{\infty} dx x \frac{\partial P_1(x,t)}{\partial x} \right]$$

$$= -2D\left[x P_1(x,t)\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dx P_1(x,t) \right]$$

$$= 2D \qquad (5.49b)$$

since

$$\int_{-\infty}^{\infty} dx P_1(x,t) = 1$$

Hence

$$\langle x^2(t) \rangle = 2Dt + C$$

where C is a constant that must be zero since $\langle x^2(0) \rangle = 0$.

5.D. The Master Equation

5.D.1. Derivation of the Master Equation

5.D.1.a. Master Equation for P_1

Eq(5.12) implies

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

so that

$$\frac{\partial P_1(n,t)}{\partial t}=\lim_{\Delta t\to 0}\frac{P_1(n,t+\Delta t)-P_1(n,t)}{\Delta t}$$

$$=\lim_{\Delta t\to 0}\frac{1}{\Delta t}\sum_{m=1}^{M}P_1(m,t)\left[P_{1/1}(m,t\,|\,n,t+\Delta t)-\delta_{mn}\right] \qquad (5.51)$$

For small Δt, $P_{1/1}(m,t\,|\,n,t+\Delta t)$ can be written in terms of the **transition probability rates** $w_{mn}(t)$. Thus,

$$P_{1/1}(m,t\,|\,n,t)=\delta_{mn}$$

$$P_{1/1}(m,t\,|\,n,t+\Delta t)=w_{mn}(t)\,\Delta t+O\left(\Delta t^2\right) \qquad \text{for } m\neq n$$

$$P_{1/1}(m,t\,|\,m,t+\Delta t)=1-\Delta t\sum_{k=1\,(\neq m)}^{M}w_{mk}(t)+O\left(\Delta t^2\right)$$

which can be combined into

$$P_{1/1}(m,t\,|\,n,t+\Delta t)\simeq\delta_{mn}\left[1-\Delta t\sum_{k=1}^{M}w_{mk}(t)\right]+w_{mn}(t)\,\Delta t+O\left(\Delta t^2\right) \qquad (5.52)$$

Note that $k=m$ is allowed in the summation so that the physically meaningless terms $w_{mm}(t)$ are always cancelled out. Putting (5.52) into (5.51) gives

$$\frac{\partial P_1(n,t)}{\partial t}=\sum_{m=1}^{M}P_1(m,t)\left[-\delta_{mn}\sum_{k=1}^{M}w_{mk}(t)+w_{mn}(t)\right]$$

$$=-\sum_{k=1}^{M}w_{nk}(t)\,P_1(n,t)+\sum_{m=1}^{M}P_1(m,t)\,w_{mn}(t)$$

$$=\sum_{m=1}^{M}\left[P_1(m,t)\,w_{mn}(t)-P_1(n,t)\,w_{nm}(t)\right] \qquad (5.53)$$

which is called the **master equation**. The 1st (2nd) sum on the right denotes increases (decreases) in $\dfrac{\partial P_1(n,t)}{\partial t}$ due to transitions into (out of) state *n*.

5.D.1.b. Master Equation for $P_{1/1}$

The Chapman-Kolmogorov equation (5.21) implies

$$P_{1/1}\left(n_0,0\,|\,n,t+\Delta t\right)=\sum_{m=1}^{M}P_{1/1}\left(n_0,0\,|\,m,t\right)P_{1/1}\left(m,t\,|\,n,t+\Delta t\right)$$

so that

$$\begin{aligned}\frac{\partial P_{1/1}\left(n_0,0\,|\,n,t\right)}{\partial t}&=\lim_{\Delta t\to 0}\frac{P_{1/1}\left(n_0,0\,|\,n,t+\Delta t\right)-P_{1/1}\left(n_0,0\,|\,n,t\right)}{\Delta t}\\&=\lim_{\Delta t\to 0}\frac{1}{\Delta t}\sum_{m=1}^{M}\left[P_{1/1}\left(m,t\,|\,n,t+\Delta t\right)-\delta_{mn}\right]P_{1/1}\left(n_0,0\,|\,m,t\right)\end{aligned}$$

With the help of (5.52), we have

$$\begin{aligned}\frac{\partial P_{1/1}\left(n_0,0\,|\,n,t\right)}{\partial t}&=\sum_{m=1}^{M}P_{1/1}\left(n_0,0\,|\,m,t\right)\left[-\delta_{mn}\sum_{k=1}^{M}w_{mk}\left(t\right)+w_{mn}\left(t\right)\right]\\&=-\sum_{k=1}^{M}w_{nk}\left(t\right)P_{1/1}\left(n_0,0\,|\,n,t\right)+\sum_{m=1}^{M}P_{1/1}\left(n_0,0\,|\,m,t\right)w_{mn}\left(t\right)\\&=\sum_{m=1}^{M}\left[P_{1/1}\left(n_0,0\,|\,m,t\right)w_{mn}\left(t\right)-P_{1/1}\left(n_0,0\,|\,n,t\right)w_{nm}\left(t\right)\right]\qquad(5.54)\end{aligned}$$

with

$$P_{1/1}\left(n_0,0\,|\,n,0\right)=\delta_{n_0 n}$$

5.D.1.c. Alternative Forms

Setting

$$W_{mn}(t) = w_{mn}(t) \qquad \text{for} \qquad m \neq n$$

$$W_{mm}(t) = -\sum_{k=1\,(\neq m)}^{M} w_{mk}(t)$$

or, more concisely,

$$W_{mn}(t) = w_{mn}(t) - \delta_{mn} \sum_{k=1}^{M} w_{nk}(t) \qquad (5.55)$$

we can write (5.52) as

$$P_{1/1}(m,t\,|\,n,t+\Delta t) = \delta_{mn} + W_{mn}(t)\,\Delta t + O\left(\Delta t^2\right)$$

so that (5.53) simplifies to

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

The matrix $\mathbf{W} = \{W_{mn}\}$ is called the **transition matrix**. From (5.55), we see that

$$W_{mn} = w_{mn} \geq 0 \qquad \text{for all} \quad m \neq n$$

and

$$\sum_{n=1}^{M} W_{mn} = W_{mm} + \sum_{n=1\,(\neq m)}^{M} w_{mn} \quad = 0 \qquad (5.57)$$

which means the sum of the elements in each row of **W** is zero.

Next, we introduce the Dirac notations

$$P_1(n,t) = \langle \mathbf{p}(t) | n \rangle$$

$$P_{1/1}(n_0,t_0\,|\,n,t) = \langle n_0 | \mathbf{P}(t_0\,|\,t) | n \rangle$$

$$W_{mn}(t) = \langle m | \mathbf{W}(t) | n \rangle$$

where $\langle \mathbf{p}(t) |$ is the **probability vector** and $\mathbf{P}(t_0\,|\,t)$ the **conditional probability operator**. The master equation (5.56) becomes

$$\frac{\partial}{\partial t} \langle \mathbf{p}(t) | n \rangle = \sum_{m=1}^{M} \langle \mathbf{p}(t) | m \rangle \langle m | \mathbf{W}(t) | n \rangle \quad = \langle \mathbf{p}(t) | \mathbf{W}(t) | n \rangle$$

Since this is true for all *n*, we have

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

Similarly, the master equation (5.54) for the conditional probability operator becomes

$$\frac{\partial P_{1/1}(n_0,0\,|\,n,t)}{\partial t} = \sum_{m=1}^{M} P_{1/1}(n_0,0\,|\,m,t)W_{mn}(t)$$

$\Rightarrow$

$$\frac{\partial}{\partial t}\langle n_0|\mathbf{P}(0\,|\,t)|n\rangle = \sum_{m=1}^{M}\langle n_0|\mathbf{P}(0\,|\,t)|m\rangle\langle m|\mathbf{W}(t)|n\rangle \quad = \langle n_0|\mathbf{P}(0\,|\,t)\mathbf{W}(t)|n\rangle$$

so that

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

Note that **W** is in general not symmetric so that its left and right eigenvectors may be different. Nevertheless, the techniques of §5.C.1 can often be used to obtain a spectral decomposition of **W**(t) and hence of $\langle \mathbf{p}(t)|$ and $\mathbf{P}(0\,|\,t)$. One exception is when the eigenvectors of **W**(t) fail to span the solution space. However, there is one type of system for which a spectral decomposition always exists, namely, the case where $w_{mn}(t)$ satisfy **detailed balance**.

5.D.2. Detailed Balance

5.D.3. Mean First Passage Time

5.E. Brownian Motion

5.E.1. Langevin Equation

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