Introduction to nonequilibrium physics

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Preface

This is a note for the lecture given in the **2017 KIAS-SNU Physics Winter Camp** which is held at KIAS in December 16–22, 2017. This is a slight revision of the note for the 2016 KIAS-SNU Physics Winter Camp.

Most systems in nature are in a nonequilibrium state. In contrast to the thermal equilibrium systems, dynamics is important for nonequilibrium systems. The lecture covers the Langevin equation and the Fokker-Planck equation formalism for the study of dynamics of both equilibrium and nonequilibrium systems. It also covers the basic concepts of stochastic thermodynamics and the fluctuation theorems. This lecture is mainly based on the books [Gar10, Ris89, VK11].

Contents

1
Brownian motion

Brown in 1827 observed small pollen grains suspended in water at finite temperature T through a microscope. He observed an irregular motion of the small particles, which is later called the Brownian motion.

1.1 Einstein's theory

Einstein in 1905 explain the nature of the Brownian motion by assuming the stochastic nature of interactions between Brownian particles and fluid molecules. Let $f(x,t)dx$ be the fraction of Brownian particles between x and $x + dx$ at time t. If a Brownian particle is kicked by fluid molecules during the time interval τ, it is displaced by the amount of Δ. It is reasonable to assume that Δ is a random variable with a distribution function

$\phi(\Delta) = \phi(-\Delta)$. Then, one obtains that

$$f(x, t + \tau) = \int_{-\infty}^{-\infty} f(x - \Delta, t)\phi(\Delta)d\Delta \tag{1.1}$$

Expansion upto $O(\Delta^2)$ leads to the diffusion equation

$$\frac{\partial f}{\partial t} = D_d \frac{\partial^2 f}{\partial x^2} \tag{1.2}$$

with the diffusion constant $D_d = \frac{1}{2\tau} \int \Delta^2 \phi(\Delta) d\Delta$. Its solution is given by

$$f(x, t) = \frac{1}{\sqrt{4\pi D_d t}} e^{-(x-x_0)^2/(4D_d t)} . \tag{1.3}$$

The root mean square displacement is then scales as

$$\sqrt{\langle (x - x_0)^2 \rangle} = \sqrt{2D_d t} \propto t^{1/2}. \tag{1.4}$$

The $t^{1/2}$ dependence is the hallmark of the diffusive motion.

1.2 Langevin's theory

Langevin in 1906 suggested another explanation for the Brownian motion. He incorporated the effects of the random interaction into the Newton's equation of motion, and proposed the following equation:

$$m\frac{d^2x}{dt^2} = -\gamma\frac{dx}{dt} + X(t). \tag{1.5}$$

This is the first appearance of the stochastic differential equation. In a rather crude way, Langevin derived the same relation in (1.4). He also derived the relation

$$D_d = \frac{k_B T}{\gamma} \tag{1.6}$$

known as the Einstein relation.

1.3 Perrin's experiment

Perrin in 1908 recorded the trajectory of a colloidal particle of radius $0.53\mu m$ every 30 seconds, and confirmed the diffusive motion of the Brownian particle experimentally. He was awarded the Nobel Prize in Physics in 1926.

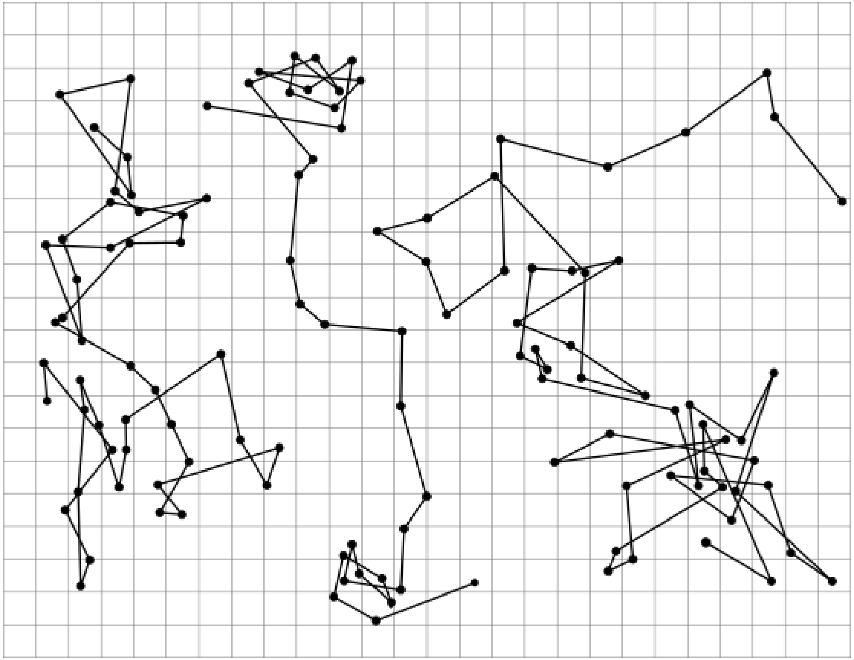

Figure 1.1: Perrin's experiment

2 Langevin equation

We are interested in a particle (or system of particles) in a thermal heat bath at temperature T. The thermal heat bath itself is a collection of many molecules and interact with the system in a complex way. At the phenomenological level, it is reasonable to assume that the heat bath provides a *damping force on average* and a *fluctuating random force*. This idea leads to the phenomenological Langevin equation for the system variables (x, v):

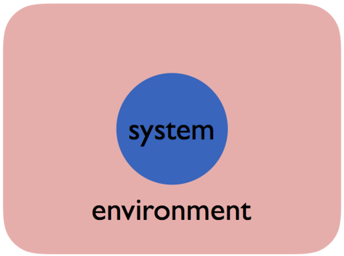

Figure 2.1: Thermal system

$$v = \frac{dx}{dt} \quad , \quad m\frac{dv}{dt} = f(x,t) - \gamma v + \xi(t), \tag{2.1}$$

where $\xi(t)$ is the Gaussian distributed white noise satisfying

$$\langle \xi(t) \rangle = 0 \quad , \quad \langle \xi(t)\xi(t') \rangle = 2B\delta(t - t') \tag{2.2}$$

with the noise strength B. More rigorous derivation of the Langevin equation is found in the lecture of Prof. Yeo given in **PSI 2014** (http://psi.kias.re.kr/2014/).

2.1 Brownian motion

The Langevin equation for a free Brownian particle is given by

$$m\dot{v} = -\gamma v + \xi(t) \tag{2.3}$$

with the initial condition $v(0) = v_0$. The formal solution is given by

$$v(t) = v_0 e^{-(\gamma/m)t} + \frac{1}{m}\int_0^t e^{-(\gamma/m)(t-t')}\xi(t')dt'. \tag{2.4}$$

From the formal solution, we can calculate the average value of various quantities.

- Average velocity

$$\langle v(t) \rangle = v_0 e^{-(\gamma/m)t} \tag{2.5}$$

- Two-time correlation function $C(t_1, t_2) \equiv \langle v(t_1)v(t_2)\rangle$

$$C(t_1, t_2) = \left(v_0^2 - \frac{B}{\gamma m}\right) e^{-\gamma(t_1+t_2)/m} + \frac{B}{\gamma m} e^{-\gamma|t_1-t_2|/m} \tag{2.6}$$

We now consider the equilibrium limit where $t_1, t_2 \to \infty$ with finite $|t_1 - t_2|$. In this limit the correlation function depends only on the time difference.

$$C_{eq}(t_1, t_2) = \langle v(t_1)v(t_2)\rangle_{eq} = \frac{B}{\gamma m} e^{-\gamma|t_1-t_2|/m} = C_{eq}(t_1 - t_2). \tag{2.7}$$

The equal-time correlation function $\langle v(t)^2\rangle_{eq}$ is given by $C_{eq}(t, t) = \frac{B}{\gamma m}$. The kinetic energy of a free particle in termal equilibrium is given by $E = \frac{m}{2}\langle v^2\rangle_{eq} = \frac{1}{2}k_B T$. It fixes the noise strength

$$B = \gamma k_B T. \tag{2.8}$$

Consider the displacement $\Delta x(t) \equiv x(t) - x(t)$ of the Brownian particle. The squared displacement is given by

$$\langle(\Delta x(t))^2\rangle = \int_0^t dt' \int_0^t dt'' \langle v(t')v(t'')\rangle. \tag{2.9}$$

In the long time limit, it behaves as

$$\langle(\Delta x(t))^2\rangle \simeq 2Dt, \tag{2.10}$$

where the diffusion constant D is given by

$$D = \int_0^{\infty} ds \langle v(s)v(0)\rangle_{eq} \quad \text{: Green-Kubo formula} \tag{2.11}$$

The explicit calcuation shows that

$$D = \frac{B}{\gamma^2} = \frac{k_B T}{\gamma} \quad \text{: Einstein relation} \tag{2.12}$$

2.2 Ornstein-Uhlenbeck process

Consider a harmonic oscillator in a heat bath at temperature T, whose Langevin equation is given by

$$\dot{x} = v \quad , \quad m\dot{v} = -kx - \gamma v + \xi(t) \ . \tag{2.13}$$

When the damping coefficient is very large or the mass is very small, the system is in the overdamped regime. The Langevin equation then becomes

$$\gamma \dot{x} = -kx + \xi(t) \ . \tag{2.14}$$

A stochastic process governed by the linear Langevin equation is called the OU process. In fact, the Brownian motion in the previous section is an example of the OU process for the velocity v. Using the connection, one can easily evaluate $\langle x^2\rangle_{eq}$.

The general form of the OU process is given by

$$\dot{q}_i = \sum_j a_{ij} q_j + \xi_i(t) \tag{2.15}$$

where $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t)\xi_j(t') \rangle = 2B_{ij}\delta(t-t')$ with the noise matrix $B_{ij} = B_{ji}$.

2.3 Wiener process

The Wiener process, the simplest stochastic process, has the Langevin equation

$$\dot{W} = \eta(t) \quad \text{with } \langle \eta(t) \rangle = 0 \text{ and } \langle \eta(t)\eta(t') \rangle = \delta(t-t') \tag{2.16}$$

The solution is given by

$$W(t) = W_0 + \int_0^t \eta(t')dt'. \tag{2.17}$$

One can show that

$$\langle W(t) \rangle = W_0 \quad \text{and} \quad \langle (W(t) - W_0)^2 \rangle = t\ . \tag{2.18}$$

The Wiener process describes the trajectory of a random walker.

Consider the displacement $dW(t) \equiv W(t+dt) - W(t) = \int_t^{t+dt} \xi(t')dt'$ during the infinitesimal time interval dt. It is Gaussian distributed random variable with

$$\langle dW(t) \rangle = 0 \quad \text{and} \quad \langle dW(t)^2 \rangle = dt\ . \tag{2.19}$$

It indicates that $dW = O(\sqrt{dt})$.

2.4 Integral form of the Langevin equation

The Langevin equation of the form $\dot{q} = f(q,t) + \xi(t)$ can be written as

$$dq = f(q,t)dt + \sqrt{2\gamma T}dW(t) \tag{2.20}$$

where $dq \equiv q(t+dt) - q(t)$.

2.5 Numerical integration of the Langevin equation

The Langevin equation in (2.20) can be integrated numerically. The simplest way is to apply the Euler method. First, discretize the time as $t_n = n(\Delta t)$ with a sufficiently small (Δt). Then, $q_n = q(t_n)$ are found from the recursion relation

$$q_{n+1} = q_n + f(q_n, t_n)(\Delta t) + \sqrt{2\gamma T(\Delta t)}\; r_n + o(\Delta t)\ , \tag{2.21}$$

where r_n is an Gaussian-distributed random variable of zero mean ($\langle r_n \rangle = 0$) and unit variance ($\langle r_n^2 \rangle = 1$). Advanced numerical methods are found in Ref. [GSH88].

[Exercise] Integrate numerically the Langevin equation (2.13) with $k = \gamma = k_B = T = m = 1$ starting from the initial condition $x(0) = v(0) = 0$. Confirm the equipartition theorem $\langle x(\infty)^2 \rangle = \langle v(\infty)^2 \rangle = 1$.

3 Fokker-Planck Equation

Figure 3.1 displays 6 different realizations of the Wiener process trajectory. Due to the stochastic nature of the Langevin equation, $W(t)$ is a random variable fluctuating from sample to sample. Thus, it is meaningful to consider the probability distribution $P(W(t) = X|W(0) = 0)$. In this chapter, we study the Fokker-Planck equation that governs the time evolution of the probability distribution function.

3.1 Markov process and Chapman-Kolmogorov equation

Consider a time-dependent random variable $X(t)$ generated from a stochastic process. It is fully characterized by the joint probability densities $p(x_1, t_1; x_2, t_2; x_3, t_3; \cdots)$. It describes how much probable it is to measure the values $x_1, x_2, x_3, \cdots$ at time $t_1 > t_2 > t_3 > \cdots$. In terms of the joint probability densities, one can also define conditional probability

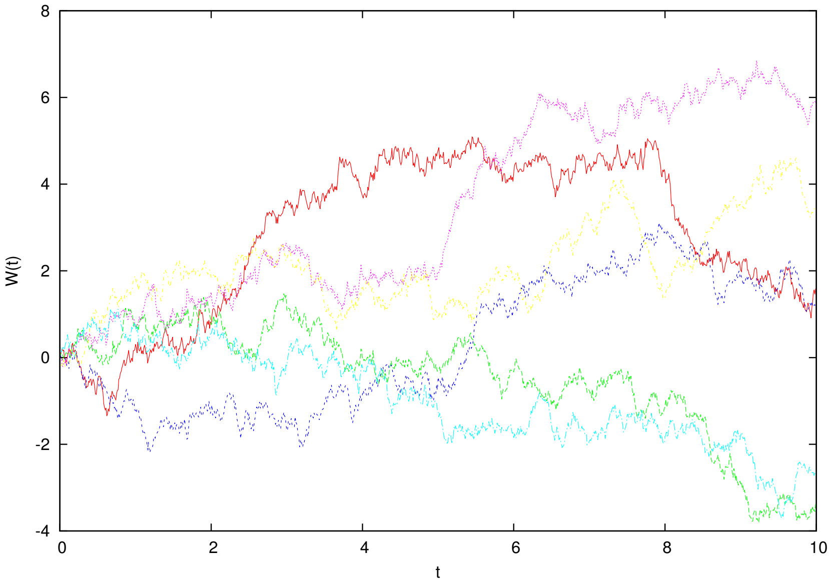

Figure 3.1: Trajectories of the Wiener process.

densities

$$p(x_1,t_1;x_2,t_2;\cdots|y_1,\tau_1;y_2,\tau_2;\cdots) = \frac{p(x_1,t_1;x_2,t_2;\cdots;y_1,\tau_1;y_2,\tau_2;\cdots)}{p(y_1,\tau_1;y_2,\tau_2;\cdots)}\,, \tag{3.1}$$

where the times are ordered as $t_1 > t_2 > \cdots > \tau_1 > \tau_2 > \cdots$.

A stochastic process is called the **Markov process**, named after a Russian mathematician Andrey Markov (1956–1922), if the conditional probability is determined entirely by the knowledge of the most recent condition, i.e.,

$$p(x_1,t_1;x_2,t_2;\cdots|y_1,\tau_1;y_2,\tau_2;\cdots) = p(x_1,t_1;x_2,t_2;\cdots|y_1,\tau_1). \tag{3.2}$$

In the Markov process, the future is determined by the present not by the past. A memory effect destroys the Markov property.

In the Markov process, any joint probability can be factorized as

$$p(1;2;\cdots;n) = p(1|2)p(2|3)\cdots p(n-1|n)p(n). \tag{3.3}$$

Therefore, the transition probability density $p(x,t|y,t')$ fully characterizes a Markov process. Once you know the transition probability densities and the initial probability density, any joint probability density is determined.

The Markov property is a very strong condition. The transition probability for a Markov process should satisfy the Chapmann-Kolmogorov equation

$$p(x_1,t_1|x_3,t_3) = \int dx_2\; p(x_1,t_1|x_2,t_2)p(x_2,t_2|x_3,t_3)\,. \tag{3.4}$$

It is named after a British mathematician Sydney Chapman (1888–1970) and a Russian mathematician Andrey Kolmogorov (1903–1987).

3.2 Fokker-Planck equation

A stochastic process governed by the Langevin equation

$$dx = A(x,t)dt + B\, dW(t) \tag{3.5}$$

belongs to the class of Markov processes. For convenience, we assume that B does not depend on x. The Langevin equation generates a stochastic time trajectory $x(t)$. Let $f(x)$ be an arbitrary well-behaved function. Then, the infinitesimal difference $df[x(t)] \equiv f[x(t+dt)] - f[x(t)]$ is given by

$$\begin{aligned} df[x(t)] &= f'[x(t)]dx(t) + \frac{1}{2}f''[x(t)]dx(t)^2 + \cdots \\ &= f'[x(t)]\left\{A[x(t),t]dt + B\, dW(t)\right\} + \frac{1}{2}f''[x(t)]B^2\, dW(t)^2 + \cdots \ . \end{aligned} \tag{3.6}$$

Taking the average, one obtains that

$$\frac{d}{dt}\langle f[x(t)]\rangle = \left\langle A[x(t),t]f'[x(t)] + \frac{1}{2}B^2 f''[x(t)]\right\rangle \ . \tag{3.7}$$

The averages are expressed in terms of the transition probability density $p(x,t|x_0,t_0)$ as

$$\begin{aligned}\int dx f(x)\partial_t p(x,t|x_0,t_0) &= \int dx \left[A(x,t)f'(x) + \frac{1}{2}bf''(x)\right] p(x,t|x_0,t_0) \\ &= \int dx f(x) \left[-\partial_x(Ap) + \frac{1}{2}\partial_x^2(Bp)\right] .\end{aligned} \tag{3.8}$$

Since this relation is valid for any function $f(x)$, the transition probability should satisfy

$$\frac{\partial}{\partial t}p(x,t|x_0,t_0) = -\frac{\partial}{\partial x}[A(x,t)p(x,t|x_0,t_0)] + \frac{1}{2}\frac{\partial^2}{\partial x^2}[B^2 p(x,t|x_0,t_0)] . \tag{3.9}$$

This is called the Fokker-Planck equation, named after a Dutch physicist Adriaan Fokker (1887–1972) and a German physicist Max Planck (1985–1947). The first and second terms are called the *drift* and the *diffusion* terms, respectively. One can also derive the Fokker-Planck equation from the Kramers-Moyal expansion, which is not covered in this lecture.

When the are many variables $\boldsymbol{x} = (x_1, x_2, \cdots)$ coupled through the Langevin equation

$$dx_i = A_i(\boldsymbol{x},t)dt + \sum_j B_{ij}dW_j(t), \tag{3.10}$$

the Fokker-Planck equation for $p(\boldsymbol{x},t|\boldsymbol{x}_0,t_0) = p(\boldsymbol{x},t)$ is given by

$$\partial_t p = -\sum_i \partial_i[A_i p] + \sum_{i,j}\partial_i\partial_j[D_{ij}p] = \mathsf{L}_{FP}\,p \tag{3.11}$$

with the noise matrix $D_{ij} = \frac{1}{2}\sum_k B_{ik}B_{jk}$ or $\mathsf{D} = \frac{1}{2}\mathsf{B}\mathsf{B}^t$.

The Fokker-Planck equation can be written in the form of the continuity equation

$$\partial_t p + \sum_i \partial_i J_i = 0 \tag{3.12}$$

with the probability current

$$J_i = A_i p - \sum_j \partial_j (D_{ij} p) \ . \tag{3.13}$$

The probability current consists of the drift current and the diffusion current.

3.2.1 Random walks

The motion of a random walker is described by $dx = \sqrt{2D}\, dW$ with $A = 0$ and $B = \sqrt{2D}$. The corresponding Fokker-Planck equation is then given by

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2} \ . \tag{3.14}$$

This is the diffusion equation Einstein obtained.

3.2.2 Brownian motion

The Langevin equation for the Brownian motion is given by $m dv = -\gamma v dt + \sqrt{2\gamma T} dW$. Comparing it with (3.5), one finds that $A = -(\gamma/m)v$ and $B = \sqrt{2\gamma T/m^2}$. So, the

Fokker-Planck equation for $P(v,t)$ becomes

$$\frac{\partial}{\partial t}p(v,t) = \frac{\gamma}{m}\frac{\partial}{\partial v}\left[vp(v,t)\right] + \frac{\gamma T}{m^2}\frac{\partial^2}{\partial v^2}p(v,t) \ . \tag{3.15}$$

The time-dependent solution can be obtained by solving the partial differential equation using the Fourier transformation technique. Here, I only calculate the steady-state distribution function $p_{ss}(v) = \lim_{t\to\infty} p(v,t)$. The steady-state distribution should satisfy

$$J_{ss}(v) = -\frac{\gamma}{m}vp_{ss}(v) - \frac{\gamma T}{m^2}p'_{ss}(v) = J_0(\text{ = constant}) \ . \tag{3.16}$$

The steady-state current J_0 should be 0. Otherwise, the probability would build up at $v = \infty$ for positive J_0 or $v = -\infty$ for negative J_0. The current-free condition yields that

$$p_{ss}(v) = \frac{1}{\sqrt{2\pi T/m}}e^{-\frac{mv^2}{2T}} \ . \tag{3.17}$$

This is the equilibrium Maxwell-Boltzmann distribution.

3.2.3 Three-Dimensional Brownian Motion in an External Force (Kramers problem)

The Langevin equations are

$$\begin{pmatrix} d\boldsymbol{x} \\ d\boldsymbol{v} \end{pmatrix} = \begin{pmatrix} \boldsymbol{v} \\ -\frac{\gamma \boldsymbol{v}}{m} + \frac{\boldsymbol{F}}{m} \end{pmatrix} dt + \begin{pmatrix} 0 \\ \frac{2\gamma T}{m} d\boldsymbol{W} \end{pmatrix} \tag{3.18}$$

The corresponding Fokker-Planck equation for $p(\boldsymbol{x}, \boldsymbol{v}, t)$ is

$$\partial_t p = \left[-\boldsymbol{\nabla}_{\boldsymbol{x}} \cdot \boldsymbol{v} + \boldsymbol{\nabla}_{\boldsymbol{v}} \cdot \left(\frac{\gamma}{m} \boldsymbol{v} - \frac{\boldsymbol{F}}{m} \right) + \frac{\gamma T}{m^2} \boldsymbol{\nabla}_{\boldsymbol{v}}^2 \right] p. \tag{3.19}$$

In general, even the steady state distribution is hard to find.

The steay state can be found in the special case with the conservative force

$$\boldsymbol{F}(\boldsymbol{x}) = -\boldsymbol{\nabla}_{\boldsymbol{x}} V(\boldsymbol{x}) \tag{3.20}$$

with a scalor potential $V(\boldsymbol{x})$. The steady state distribution is given by the equilibrium Boltzmann distribution

$$p_{ss}(\boldsymbol{x}, \boldsymbol{v}) = \frac{1}{Z} \exp \left[-\frac{1}{T} \left(\frac{1}{2} m \boldsymbol{v}^2 + V(\boldsymbol{x}) \right) \right] . \tag{3.21}$$

3.2.4 Biased diffusion in a ring

Consider a Langevin equation $d\theta = f_0 + \sqrt{2T}\, dW$ for an angle variable $0 \le \theta < 2\pi$. The Fokker-Planck equation for $p(\theta, t)$ is given by

$$\partial_t p = -\partial_\theta J_\theta \tag{3.22}$$

with the probability current $J_\theta = (f_0 - T\partial_\theta) p(\theta, t)$. In the steady state, the current should be a constant J_0 independent of θ. Therefore, $T p'_{ss}(\theta) = f_0 p_{ss}(\theta) - J_0$, which has a general solution $p_{ss}(\theta) = c\ e^{(f_0/T)\theta} + J_0/f_0$ with a constant c. The conitinuity $p_{ss}(0) = p_{ss}(2\pi)$ requires that $c = 0$ and the normalization $\int d\theta p_{ss}(\theta) = 1$ yields that $J_0 = \frac{f_0}{2\pi}$.

3.3 Path integral or Onsager-Machlup formalism

Consider the Langevin equation $dx = A(x)dt + B\ dW$ for a single variable x. Generalization to multivariate problems is straightforward. We want to calculate the transition probability for an infinitesimal time interval, $p(x', t+dt|x, t)$. A particle can move from x to $x' = x + (x' - x)$ only when the Langevin noise takes the right value $dW = (x' - x - A(x)dt)/B$. Recalling that dW is Gaussian distributed with mean zero and variance dt, we obtain that

$$p(x', t+dt|x, t) = \frac{1}{\sqrt{2\pi B^2 dt}} \exp\left(-\frac{[x' - x - A(x)dt]^2}{2B^2 dt}\right) . \tag{3.23}$$

The transition probability over a finite time interval $p(x, t|x_0, t_0)$ is obtained by using the Markov property. We divide the time interval $[0 : t]$ into N sub-intervals of duration $\tau = t/N$. Then, the transition probability is written as

$$p(x, t|x_0, 0) = \left[\prod_{i=1}^{N-1} \int dx_i\right] \left[\prod_{i=0}^{N-1} p(x_{i+1}, t_{i+1}|x_i, t_i)\right] . \tag{3.24}$$

In the $N \to \infty$ limit, it becomes

$$\begin{aligned} p(x, t|x_0, 0) &= \lim_{N\to\infty} \left[\prod_{i=0}^{N-1} \int \frac{dx_i}{\sqrt{2\pi B^2 \tau}}\right] \exp\left(-\sum_{i=0}^{N-1} \frac{[x_{i+1} - x_i - A(x_i)\tau]^2}{2B^2\tau}\right) \\ &= \int [\mathcal{D}x(s)]\, e^{-\int ds[\dot{x}(s) - A(x(s))]^2/(2B^2)} \end{aligned} \tag{3.25}$$

The multivariate system with $dx_i = A_i dt + B_{ij} dW_j$ has the transition probability

$$
\begin{aligned}
p(\boldsymbol{x}, t|\boldsymbol{x}_0, 0) &= \int [\mathcal{D}\boldsymbol{x}(s)]\, e^{-\frac{1}{4}\int_0^t ds [\dot{\boldsymbol{x}}(s) - \boldsymbol{A}(\boldsymbol{x}(s))]_i D_{ij}^{-1} [\dot{\boldsymbol{x}}(s) - \boldsymbol{A}(\boldsymbol{x}(s))]_j} \\
&= \int [\mathcal{D}\boldsymbol{x}(s)]\, e^{-A[\boldsymbol{x}(s)]}
\end{aligned}
\tag{3.26}
$$

with the action functional $A[\boldsymbol{x}(s)]$ and $D_{ij} = \frac{1}{2}\sum_k B_{ik}B_{jk}$.

The Onsager-Machlup [OM53] formalism allows us to write down the formal expression for the conditional path probability density

$$
\Pi\, [\boldsymbol{x}[s]|\boldsymbol{x}_0] \propto e^{-A[\boldsymbol{x}(s)]} \tag{3.27}
$$

3.4 Detailed balance and the Fluctuation Dissipation Theorem

A Fokker-Planck system with the steady state solution $p_{ss}(x) = e^{-\Phi(x)}$ is said to satisfy the detailed balance if

$$
p(x', t'|x, t) p_{ss}(x) = p(\epsilon x, t|\epsilon x', t') p_{ss}(\epsilon x') \tag{3.28}
$$

with the parity operator ϵ.

Please refer to the lecture note of Prof. Yeo of PSI 2014.

4 Stochastic Thermodynamics

We have studied the Langevin equation and the Forkker-Planck equation formalism for general stochastic systems. We are ready to study thermodynamics of such systems at the level of microscopic stochastic paths. We will learn how to define thermodynamic quantities such as heat, work, and entropy, and investigate some symmetry properties of thermodynamic systems. References for this chapter are Refs. [Sek10, Sei05, Kwo15].

4.1 Stochastic energetics

4.1.1 Underdamped Langevin system

Consider a particle (or a system of particles) in thermal contact with a heat bath of temperature T. The Langevin equation is given by

$$\begin{aligned} x &= v dt \\ m dv &= f_c(x)dt + f_{nc}(x)dt - \gamma v dt + \sqrt{2\gamma T} dW(t) \ , \end{aligned} \tag{4.1}$$

where $f_c(x) = -\frac{dV(x)}{dx}$ is the conservative force, and f_{nc} is a time-independent non-conservative force.

The internal energy of the system is given by

$$E = \frac{1}{2} m v^2 + V(x) \ . \tag{4.2}$$

It is a fluctuating variable since x and v are stochastic variables. During the infinitesimal time step dt, the energy changes by the amount of

$$dE = \frac{1}{2} m[(v + dv)^2 - v^2] + [V(x + dx) - V(x)] \tag{4.3}$$

Note that

$$dv^2 \equiv (v + dv)^2 - v^2 = 2v dv + (dv)^2 = 2\frac{v + (v + dv)}{2} dv = 2v \circ dv \tag{4.4}$$

One should not neglect the $(dv)^2$ term because dv involves $dW = \mathcal{O}(\sqrt{dt})$. We introduced the special multiplication rule denoted by $\circ$. It is defined as

$$X(t) \circ dY(t) = \frac{X(t) + X(t+dt)}{2} dY(t), \tag{4.5}$$

and called the Stratonovich calculus. In contrast, the usual multiplication $X(t)dY(t)$ is called the Ito calculus. One can use the normal calculus rule for the infinitesimal when all the multiplications are interpreted as the Stratonovich multiplication.

The energy change is then given by

$$dE = mv \circ dv + \frac{dV}{dx} \circ dx = mv \circ dv - f_c(x) \circ dx \ . \tag{4.6}$$

Elliminating $f_c = mdv/dt - f_{nc} + \gamma v dt - \sqrt{2\gamma T} dW/dt$, one obtains

$$\begin{aligned} dE &= mv \circ dv - v \circ \left[mdv - f_{nc}dt - (-\gamma v dt + \sqrt{2\gamma T} dW) \right] \\ &= f_{nc} \circ dx + v \circ (-\gamma v dt + \sqrt{2\gamma T} dW) \\ &= dW + dQ. \end{aligned} \tag{4.7}$$

This is the first law of thermodynamics for the Langiven system with the work and the heat

$$\begin{aligned} dW &= f_{nc} \circ dx \\ dQ &= v \circ \left(-\gamma v dt + \sqrt{2\gamma T}\, dW \right) = F_B \circ dx. \end{aligned} \tag{4.8}$$

The expression for the heat looks quite intuitive. It is the “work" done by the force F_B from the heat bath [Sek10].

4.1.2 Overdamped Langevin system

Langevin equation is given by

$$\gamma dx = f_c dt + f_{nc} dt + \sqrt{2\gamma T} dW = f_{tot} dt + \sqrt{2\gamma T} dW \ . \tag{4.9}$$

The first law of thermodynamics becomes as

$$dV = dW + dQ \tag{4.10}$$

where

$$\begin{aligned} dW &= f_{nc} \circ dx \\ dQ &= F_B \circ dx = -(f_c + f_{nc}) \circ dx \ . \end{aligned} \tag{4.11}$$

4.1.3 Overdamped Langevin system with time-dependent potential

Suppose that the potential energy includes a time dependence parameter

$$V = V(x, \lambda(t)) \ . \tag{4.12}$$

The parameter is called the protocol. You may think of a harmonic oscillator with a time dependent spring constant. The first law of thermodynamics becomes

$$dV = dW_{nc} + dW_J + dQ \tag{4.13}$$

where

$$dW_J = \frac{\partial V}{\partial \lambda}\frac{d\lambda}{dt}dt \tag{4.14}$$

is called the Jarzynski work [Jar97].

4.2 Nonequilibrium entropy

What is the entropy of the nonequilibrium system as a state function? Generalizing the equilibrium ensemble theory, we propose that a nonequilibrium state is specified by the probability distribution $p(q,t)$. Then, the Shannon's information entropy [Sha48] is a natural candidate as the thermodynamic entropy for nonequilibrium systems. It is defined as

$$\langle S_{sys}(t)\rangle = -\int dx p(q,t) \ln p(q,t) \ . \tag{4.15}$$

It is the ensemble averge of the instant entropy

$$S_{sys}(q(t),t) = -\ln p(q(t),t) \tag{4.16}$$

of a system being at $q(t)$ at time t.

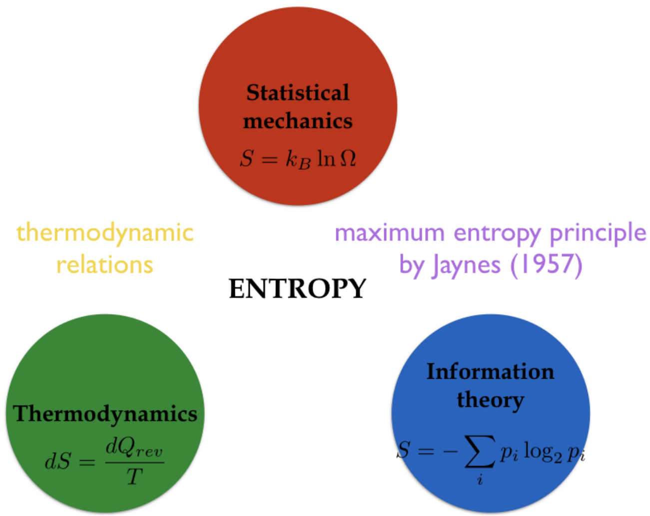

Figure 4.1: Entropy

Suppose that a system evolves in time following a stochastic path $[\boldsymbol{q}(t)]_{t_i}^{t_f}$ for $t_i \leq t \leq t_f$. The entropy change of the system is given by

$$\Delta S_{sys}[q] = -\ln \frac{p(q(t_f), t_f)}{p(q(t_i), t_i)} \ . \tag{4.17}$$

The entropy change of the heat bath is given by the Clausius form

$$\Delta S_B[q] = \frac{-\Delta Q}{T} \ . \tag{4.18}$$

The total entropy change is then given by $\Delta S_{tot} = \Delta S_{sys} + \Delta S_B$. Does it satisfy the second law of thermodynamics?

4.3 Time-irreversibility

We will show that the entropy is directed related to the **time-irreversibility**. Specifically, I explain the concept in the context of the overdamped Langevin system governed by (4.9). For simplicity, we consider the time irreversibility over the infinitesimal time interval between $t_i = t$ and $t_f = t + dt$. At time t, the system is in the state with the initial probability distribution $p(x, t_i) = p_i(x)$. The probability distribution at time t_f is determined by the Fokker-Planck equation. It will be denoted as $p(x, t_f) = p_f(x)$.

We want to ask the following question: How much is it more likely to observe a *forward path* $[\boldsymbol{x}_F] : (x \to x')$ than a *reverse path* $[\boldsymbol{x}_R] : (x' \to x)$?

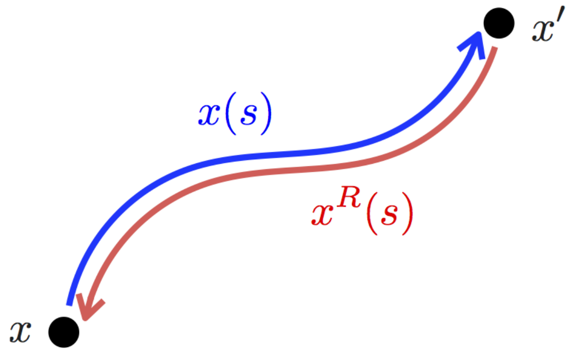

Figure 4.2: Forward and reverse paths

- **Forward path**
  The forward path probability is given by

$$\text{Prob}[\boldsymbol{x}_F] = p_i(x)\Pi_F[\boldsymbol{x}_F|x] \propto p_i(x)\exp\left[-\frac{\gamma dt}{4T}\left\{\frac{(x'-x)}{dt} - \frac{f_{tot}(x)}{\gamma}\right\}^2\right] , \tag{4.19}$$

  where $f_{tot}(x) = f_c(x) + f_{nc}(x)$ is the total force.

- **Reverse path**
  The reverse path probability is given by

$$\text{Prob}[\boldsymbol{x}_R] = p_f(x')\Pi_R[\boldsymbol{x}_R|x] \propto p_f(x')\exp\left[-\frac{\gamma dt}{4T}\left\{\frac{(x-x')}{dt} - \frac{f_{tot}(x')}{\gamma}\right\}^2\right] , \tag{4.20}$$

The irreversibility is quantified by the log ratio of the path probabilities:

$$\ln\frac{\text{Prob}[\boldsymbol{x}_F]}{\text{Prob}[\boldsymbol{x}_R]} = \ln\frac{p_i(x)}{p_f(x')} + \ln\frac{\Pi_F[\boldsymbol{x}_F]}{\Pi_F[\boldsymbol{x}_R]}. \tag{4.21}$$

The first term corresponds to the system entropy change

$$dS_{sys} = -\ln p_f(x') + \ln p_i(x). \tag{4.22}$$

The second term corresponds to the Clausius form for the entropy change of the heat bath

$$dS_B = \frac{dt}{4T}\left[2\frac{(x'-x)}{dt}(f(x)+f(x')) - \frac{f(x)^2 - f(x')^2}{\gamma}\right] = \frac{f\circ dx}{T} = \frac{-dQ}{T} . \tag{4.23}$$

Therefore, the total entropy change during a stochastic motion of the system along a path is equivalent to the time-irreversibility!

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_B = -\ln \frac{p_f(x')}{p_i(x)} - \frac{\Delta Q}{T} = \ln \frac{\text{Prob}[\boldsymbol{x}_F]}{\text{Prob}[\boldsymbol{x}_R]} \tag{4.24}$$

4.4 Fluctuation theorem for the entropy production

It is straightforward to show that

$$\left\langle e^{-\Delta S} \right\rangle = \int dSP(S)e^{-S} = 1 \tag{4.25}$$

for any Langevin system. This is called the integral fluctuation theorem (IFT). Applying the Jensen's inequality $\langle e^{-x} \rangle \geq e^{-\langle x \rangle}$, one can derive the second law of thermodynamics

$$\langle \Delta S \rangle \geq 0 \; . \tag{4.26}$$

When the system is in the steady state, we have more powerful fluctuation theorem for the probability distribution $P(S)$.

$$\frac{P(S)}{P(-S)} = e^S \; . \tag{4.27}$$

This is called the detailed fluctuation theorem (DFT). The DFT holds only when the system satisfies the involution property.

4.5 FT for the work

Consider a system with a time-dependent potential energy $V(x, \lambda(t))$. If it is in the thermal equilibrium state initially, then we have the IFT

$$\langle e^{-W/T} \rangle = e^{-\Delta F/T} \ . \tag{4.28}$$

This is called the Jarzynski equality [Jar97]. We also have the DFT

$$\frac{P_F(W)}{P_R(-W)} = e^{-\Delta(W-F/T)}. \tag{4.29}$$

which is called the Crooks fluctuation theorem [Cro99].

4.6 More

Maxwell's demon, heat engine, ...

5 Summary

- Langevin equation : stochastic processes, stochastic differential equation, numerical integration
- Fokker-Planck equation : Markov process, Chapmann-Kolmogorov equation, Ito and Stratonovich, Onsager-Machlup path integral formalism
- Stochastic thermodynamics : stochastic energetics, irreversibility, entropy production, fluctuation theorem, ...

Project I : Brownian motion in 1D

We consider the overdamped motion of a Brownian particle in one-dimensional space. The position of the particle is governed by the Langevin equation

$$\gamma \dot{x}(t) = f + \sqrt{2\gamma T}\xi(t) \text{ or } \gamma dx(t) = f dt + \sqrt{2\gamma T} dW(t). \tag{5.1}$$

The Brownian particle is driven by the constant force f. Initially, the Brownian particle is distributed according to the probability distribution function $P(x,0) = p_i(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}$ with a constant σ.

[1] Find the probability distribution function $P(x,t) = P_f(x)$ at time t. You may use the solution of the Langevin equation or solve the Fokker-Planck equation directly.
[2] We denote the stochastic path during the time interval $0 \le t \le \tau$ by $[\boldsymbol{x}]_0^\tau$. Show that the total entropy production is given by the simple form

$$\Delta S([\boldsymbol{x}]_0^\tau) = -\ln \frac{P_f(x(\tau))}{P_i(x(0))} + \frac{f\{x(\tau) - x(0)\}}{T}. \tag{5.2}$$

[3] You can solve numerically the Langevin equation to generate a stochastic path $[\boldsymbol{x}]_0^\tau$ and the entropy production using (5.2). By repeating the simulation over and over, you can generate the probability distribution function $P(S)$ for the entropy production. Confirm the integral fluctuation theorem $\langle e^{-\Delta S} \rangle = 1$ at several different values of τ. All the other parameters γ, T, and f may be set to unity.

Project II : Rotary motor

The motion of a rotary motor is described by the overdamped Langevin equation

$$\gamma d\theta(t) = -\frac{dV(\theta)}{d\theta}dt + f_0 dt + \sqrt{2\gamma k_B T}dW(t) \tag{5.3}$$

where $0 \leq \theta < 2\pi$ is the angular position of the motor, $V(\theta) = \cos\theta$ is the periodic potential, and f_0 is a constant applied torque, and $W(t)$ denotes the Wiener process. One can set $\gamma = k_B = T = 1$.

[1] Write down the corresponding Fokker-Planck equation for the probability distribution function $P(\theta, t)$ and solve it to find the stationary state distribution $P_{ss}(\theta)$. Compare it with the equilibrium Boltzmann distribution $P_{eq}(\theta) = \frac{1}{Z}e^{-\beta V(\theta)}$ without torque.
[2] The average angular velocity $\Omega = \lim_{t\to\infty} \frac{1}{t}\langle(\theta(t) - \theta(0))\rangle$ depends on the applied torque f_0. Draw the plot of Ω as a function of f_0. This can be done analycally or numerically.
[3] Initially $f_0 = 0$ and the system is prepared in the equilibrium state with $P_{eq}(\theta)$. At time $t = 0$, the torque is turned to take the value $f_0 = 1$. Solve the Langevin equation numerically up to time $t = \tau$ and measure the work done by the external torque $W(\tau) = \int_0^\tau f_0\dot{\theta}(t')dt'$. By performing the numerical simulations many times, you can construct the probability distribution function for the work $P(W)$. Test the integral and detailed fluctuation theorems by computing $\langle e^{-W}\rangle$ and $P(W)/P(-W)$.

Project III : Breathing harmonic oscillator

Consider the overdamped motion of a simple harmonic oscillator governed by

$$\gamma dx(t) = -k(t)x(t)dt + \sqrt{2\gamma k_B T}dW(t) \ . \tag{5.4}$$

The spring constant $k(t)$ is varied as a function of time.

$$k(t) = \begin{cases} k_0 & \text{for } t < 0 \\ k_0 + (k_1 - k_0)t/\tau & \text{for } 0 \le t < \tau \\ k_f & \text{for } t > \tau \end{cases} \tag{5.5}$$

The internal energy of the oscillator is given by $E(x, k(t)) = \frac{1}{2}k(t)x^2$. During the time interval $0 \le t \le \tau$, the work done on the harmonic oscillator is given by $W = \int_0^\tau dt \left(\frac{dk}{dt}\right)\left(\frac{\partial E(x,k)}{\partial k}\right) = \left(\frac{k_1 - k_0}{2\tau}\right)\int_0^\tau x(t)^2 dt$. Set $\gamma = k_B = T = 1$, $k_0 = 1$, $k_1 = 2$.

[1] Obtain the partition function $Z(k)$ and the free energy $F(k)$ for the equilibrium harmonic oscillator as a function of the spring constant k.

[2] Initially, the harmonic oscillator is in the thermal equilibrium state with the distribution function $P(x) = \frac{1}{Z(k_0)}e^{-\beta k_0 x^2/2}$. Perform the numerical simulations to obtain the probability distribution function of the work $P_F(W)$ during the time interval $0 \le t \le \tau$.

[3] Perform the similar simulations to obtain the distribution $P_R(W)$ in the reverse process.

[4] Test the fluctuation theorems $\langle e^{-\beta W}\rangle_F = e^{-\beta \Delta F}$ and $P_F(W)/P_R(-W) = e^{\beta(W - \Delta F)}$ with $\Delta F = F(k_1) - F(k_0)$.

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