Lecture Notes on Statistical Mechanics

based on course CHM427H1S, 2022 Spring

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Contents

Book List:

1. *Statistical Mechanics: Theory and Molecular Simulation* by Mark Tuckerman.
2. *Nonequilibrium Statistical Mechanics* by Robert Zwanzig.
3. *Introduction To Modern Statistical Mechanics* by David Chandler.

Lecture 1: Math Reviews

1.1 Taylor expansion

- Expand function $f(x+a)$ around x with $a \to 0$

$$\begin{aligned} f(x+a) &= f(x) + f'(x)a + \frac{1}{2}f''(x)a^2 + \cdots \\ &= \sum_{j=0}^{\infty} \frac{a^j}{j!}\frac{\mathrm{d}^j}{\mathrm{d}x^j} f(x+a)\bigg|_{a=0} \end{aligned} \tag{1.1}$$

- Since $e^{\lambda x} = \sum_{j=0}^{\infty} x^j \lambda^j / j!$

$$f(x+a) = \exp\left(a\frac{\mathrm{d}}{\mathrm{d}x}\right) f(x) \tag{1.2}$$

- Common Taylor series expansions. For $|x| < 1$,

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + \cdots = \sum_{j=0}^{\infty} (-1)^j x^j \tag{1.3}$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots = \sum_{j=0}^{\infty} x^j \tag{1.4}$$

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} + \cdots = \sum_{j=0}^{\infty} \frac{(-1)^j}{(2j+1)!} x^{2j+1} \tag{1.5}$$

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots = \sum_{j=0}^{\infty} \frac{(-1)^j}{(2j)!} x^{2j} \tag{1.6}$$

$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \cdots = \sum_{j=0}^{\infty} \frac{(-1)^{j+1}}{j+1} x^{(j+1)} \tag{1.7}$$

$$\ln(1-x) = x + \frac{1}{2}x^2 + \frac{1}{3}x^3 + \cdots = \sum_{j=0}^{\infty} \frac{1}{j+1} x^{(j+1)} \tag{1.8}$$

1.2 Probability theory

1.2.1 Discrete systems

Suppose measuring a property $\hat{E}$ results n discrete values $E_1, E_2, \ldots, E_n$. Let

$$\begin{aligned} N &= \text{number of measurements} \\ N_i &= \text{number of measurements of } E_i \end{aligned}$$

Then

$$P_i = \text{Probability to get } E_i = \lim_{N\to\infty} \frac{N_i}{N} \equiv P(E_i) \tag{1.9}$$

Properties of P_i:

1. $0 \leq P_i \leq 1$
2. $\sum_{i=1}^{n} P_i = 1$

Averages:

$$\overline{E} = \sum_{i=1}^{n} E_i P_i \tag{1.10}$$

$$\overline{E^2} = \sum_{i=1}^{n} E_i^2 P_i \tag{1.11}$$

$$\overline{f(E)} = \sum_{i=1}^{n} f(E_i) P_i \tag{1.12}$$

$$\tag{1.13}$$

Variance:

$$\sigma_E^2 = \overline{E^2} - \overline{E}^2 = \overline{(E - \overline{E})^2} \tag{1.14}$$

- σ_E^2 measures the dispersion of the probability distribution: how spread out the values are.

- In general, $\sigma_E^2 \neq 0$ unless $P_{ij} = \delta_{ij}$ for some certain j, where δ_{ij} is a *Kronecker delta* function:

$$P_i = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases} \Longrightarrow \overline{E} = E_j. \tag{1.15}$$

- Chebyshev's Inequality

$$\text{Prob}\left(\left|E - \overline{E}\right| \geq \lambda\right) \leq \frac{\sigma_E^2}{\lambda^2} \tag{1.16}$$

Joint Probability:

Now we are interested in two properties $\hat{E}$ and $\hat{G}$. Measuring $\hat{E}$ results in a set of values $\{E_i\}_{i=1,\dots,n_E}$, and measuring $\hat{G}$ results in a set of values $\{G_j\}_{j=1,\dots,n_G}$. Now we measure $\hat{E}$ and $\hat{G}$ simultaneously, and repeat the measurement N times, resulting in N pairs of values (E_i, G_j). Let

$$n_{ij} = \text{number of pairs of } (E_i, G_j)$$

Then

$$P_{ij} = \lim_{N\to\infty} \frac{n_{ij}}{N} \equiv P(E_i, G_j) \equiv \text{joint probability} \tag{1.17}$$

Properties of P_{ij}

1. $\sum_{i=1}^{n_E} \sum_{j=1}^{n_G} P(E_i, G_j) = 1$
2. $\sum_{i=1}^{n_E} P(E_i, G_j) = P(G_j)$
3. $\sum_{j=1}^{n_G} P(E_i, G_j) = P(E_i)$
4. If $\hat{E}$ and $\hat{G}$ are independent, then $P(E_i, G_j) = P(G_j)P(E_i)$

1.2.2 Combinatorics

In the following, we will assume that the objects are distinguishable objects.

- **Permutation**: The number of permutations of N objects is $N! = N(N-1)\cdots 1$. (Note: $0! = 1$)

- **Combination**: The number of ways of assigning N objects into r distinguishable containers is
$$t = \frac{N!}{\prod_{i=1}^{r} N_i!} \tag{1.18}$$
where N_i is the number of objects in the ith container.
  - *Example:* Number of ways of selecting k objects from a larger set of N objects is
$$\binom{N}{k} = \frac{N!}{k!(N-k)!} \tag{1.19}$$
where in this example we have two containers with size k and size $(N-k)$.

- **Coin Tossing:** Suppose we have an even coin. Let
$$\begin{aligned} N &= \text{Number of total tosses} \\ k &= \text{Number of heads} \end{aligned}$$
then the probability of having k heads in N tosses is
$$P(k,N) = \left(\frac{1}{2}\right)^N \binom{N}{k} \tag{1.20}$$

- **Coin Tossing (general case):** Suppose now the coin is uneven, and the probability of getting a head is p, and the probability of getting a tail is q, where $p+q=1$. What is the probability of getting k heads in N tosses? This is determined by the *Bernoulli* or *binomial* probability
$$P(k,N) = p^k q^{N-k} \binom{N}{k} \tag{1.21}$$
Note that
$$\sum_{k=0}^{N} P(k,N) = q^N + pq^{N-1}\binom{N}{1} + p^2 q^{N-2}\binom{N}{2} + \cdots + p^N = (p+q)^N = 1 \tag{1.22}$$
  - Statistical properties:
$$\begin{aligned} \overline{k} &= Np \\ \overline{k^2} &= Np + N(N-1)p^2 \\ \sigma_k^2 &= Npq \\ \text{Prob}\left(\left|k-\overline{k}\right| \geq \lambda\right) &\leq \frac{Npq}{\lambda^2} \end{aligned}$$

Note that the distribution narrows with N - typical behavior if $\overline{k} \sim n$.

- **Generating Function:** We define the generating function of a distribution $P(k,N)$ as

  $$F(x) = \sum_{k=0}^{N} P(k,N)x^k. \tag{1.23}$$

  Note that $F(1) = 1$ since the distribution is normalized. If

  $$P(k,N) = p^k q^{N-k} \binom{N}{k}$$

  then

  $$F(x) = (q+px)^N$$

  - Generating functions can be used for calculating the moments of the distribution:

    $$\overline{k} = \left(x\frac{\mathrm{d}}{\mathrm{d}x}F(x)\right)_{x=1} \tag{1.24}$$

    $$\overline{k^l} = \left[\left(x\frac{\mathrm{d}}{\mathrm{d}x}\right)^l F(x)\right]_{x=1} \tag{1.25}$$

    $$\tag{1.26}$$

1.2.3 Continuous systems

Suppose measuring an observable $\hat{X}$ results in a continuous value x. The probability of getting values between x and $x+\mathrm{d}x$ is $p(x)\mathrm{d}x$, where $p(x)$ is called the *probability density*.

Properties of $p(x)$:

1. Positive definite: $p(x) \geq 0$.
2. Normalized: $\int_{-\infty}^{\infty} \mathrm{d}x\ p(x) = 1$.

Averages:

$$\overline{x} = \int_{-\infty}^{\infty} \mathrm{d}x\ xp(x) \tag{1.27}$$

$$\overline{f(x)} = \int_{-\infty}^{\infty} \mathrm{d}x\ f(x)p(x) \tag{1.28}$$

$$\sigma_x^2 = \overline{x^2} - \overline{x}^2 = \int_{-\infty}^{\infty} \mathrm{d}x\ (x^2 - \overline{x}^2)p(x) \tag{1.29}$$

- *Example:* consider the probability density $p(x) = ce^{-\alpha x^2}$, we have

$$c = \sqrt{\frac{\alpha}{\pi}}$$
$$\sigma_x^2 = \frac{1}{2\alpha}$$

Therefore we get the Gaussian distribution:

$$p(x) = \frac{1}{\sqrt{2\pi\sigma_x^2}} e^{-\frac{x^2}{2\sigma_x^2}} \tag{1.30}$$

When $\sigma_x \to 0$, we get an infinitely narrow distribution, called *Dirac delta function*: the probability density has all weights on one value. We will talk more about the Dirac Delta function in the next section.

1.3 Delta function

The Dirac delta function can be seen as a special probability density where all the weights rest on one x value (usually on $x = 0$). The mathematical definition of the (Dirac) delta function is

$$\delta(x) = \begin{cases} \infty & x = 0 \\ 0 & x \neq 0 \end{cases} \tag{1.31}$$

Eq. (1.31) is rather abstract. We can see it in a limiting manner: consider a very small value $\epsilon \ll 1$,

$$\delta^{(\epsilon)}(x) = \begin{cases} \frac{1}{\epsilon} & -\frac{\epsilon}{2} \leq x \leq \frac{\epsilon}{2} \\ 0 & |x| > \frac{\epsilon}{2} \end{cases} \tag{1.32}$$

We can derive the following properties:

$$\int_{-\infty}^{\infty} \mathrm{d}x\, \delta^{(\epsilon)}(x) = \int_{-\frac{\epsilon}{2}}^{\frac{\epsilon}{2}} \mathrm{d}x \frac{1}{\epsilon} = 1 \tag{1.33}$$

$$\int_{-\infty}^{\infty} \mathrm{d}x\, f(x)\delta^{(\epsilon)}(x) = \int_{-\frac{\epsilon}{2}}^{\frac{\epsilon}{2}} \mathrm{d}x\, f(x)\delta^{(\epsilon)}(x) \approx \int_{-\frac{\epsilon}{2}}^{\frac{\epsilon}{2}} \mathrm{d}x\, f(0)\delta^{(\epsilon)}(x) = f(0) \tag{1.34}$$

The Delta function in Eq. (1.31) can be derived by $\delta(x) = \lim_{\epsilon \to 0} \delta^{(\epsilon)}(x)$.

Other representations of delta function in limit $\epsilon \to 0$:

$$\begin{aligned}
\delta^{(\epsilon)}(x) &= \frac{1}{2\epsilon} e^{-|x|/\epsilon} \\
\delta^{(\epsilon)}(x) &= \frac{1}{\pi} \frac{\epsilon}{x^2 + \epsilon^2} \\
\delta^{(\epsilon)}(x) &= \frac{1}{\epsilon\sqrt{\pi}} e^{-x^2/\epsilon^2} \\
\delta^{(\epsilon)}(x) &= \frac{1}{\pi} \frac{\sin(x/\epsilon)}{x}
\end{aligned}$$

The expectation value of a continuous function $f(x)$ under the above forms of probability density is

$$\lim_{\epsilon \to 0} \int_{-\infty}^{\infty} \mathrm{d}x\, f(x) \delta^{(\epsilon)}(x - x_0) = f(x_0) \tag{1.35}$$

Some properties of delta function

1. $\delta(-x) = \delta(x)$.
2. $\delta(cx) = \frac{1}{|c|}\delta(x)$.
3. $\delta(g(x)) = \sum_j \frac{\delta(x-x_j)}{|g'(x_j)|}$ where $g(x_j) = 0$ and $g'(x_j) \neq 0$.
4. $g(x)\delta(x - x_0) = g(x_0)\delta(x - x_0)$.
5. $\int_{-\infty}^{\infty} \mathrm{d}x\, \delta(x-y)\delta(x-z) = \delta(y-z)$.
6. $\int_{-\infty}^{\infty} \mathrm{d}x\, \frac{\mathrm{d}\delta(x-x_0)}{\mathrm{d}x} f(x) = -\int_{-\infty}^{\infty} \mathrm{d}x\, \delta(x-x_0) f'(x) = -f'(x_0)$

1.4 Matrix diagonalization

Given a square matrix $\mathbf{A}$, we are interested to find its eigenvalues λ and corresponding eigenvectors $\mathbf{v}$, which satisfy

$$\mathbf{A}\mathbf{v} = \lambda\mathbf{v} \tag{1.36}$$

Process

$$(1) \to (\mathbf{A} - \lambda\mathbf{I})\mathbf{v} = 0 \tag{1.37}$$

where $\mathbf{I}$ is the identity matrix. If (1.37) has a solution, then

$$\det(\mathbf{A} - \lambda\mathbf{I}) = 0 \tag{1.38}$$

$\det(\mathbf{A}\mathbf{v}_i - \lambda_i \mathbf{v}_i)$ results in a polynomial of λ_i, which is called the *characteristic polynomial* of **A**. If then (1.38) can be solved, then **A** is *diagonalizable*,

Hermitian Matrices

If **A** is a Hermitian matrix, then

$$\mathbf{A}^\dagger = \mathbf{A} \tag{1.39}$$

where $\mathbf{A}^\dagger$ is the complex conjugate transpose of **A** ($\mathbf{A}^\dagger = (\mathbf{A}^*)^T$).

Hermitian matrices are diagonalizable and the eigenvalues are real.

Example

$$\mathbf{A} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\mathbf{A} - \lambda \mathbf{I} = \begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix}$$

$$\det(\mathbf{A} - \lambda \mathbf{I}) = \lambda^2 - 1 = 0$$

The two eigenvalues are $\lambda_1 = 1$ and $\lambda_2 = -1$. Now let's compute the eigenvectors.

$$(\mathbf{A} - \lambda_1 \mathbf{I})\mathbf{v}_1 = 0 \Longrightarrow \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \mathbf{v}_1 = 0 \Longrightarrow \mathbf{v}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$(\mathbf{A} - \lambda_1 \mathbf{I})\mathbf{v}_2 = 0 \Longrightarrow \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \mathbf{v}_1 = 0 \Longrightarrow \mathbf{v}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Note that the pre-factor $1/\sqrt{2}$ is picked to *normalize* the eigenvectors.

One can organize the eigenvectors into a matrix

$$\mathbf{V} = [v_1 \quad v_2] = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

and define the diagonal matrix

$$\mathbf{D} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

then **A** is related to **D** by

$$\mathbf{AV} = \mathbf{DV} \quad \text{or} \quad \mathbf{A} = \mathbf{VDV}^{-1}$$

Lecture 2: Classical Mechanics

2.1 Newton's laws of motion

Newton's laws of motion are used to describe the *macroscopic world*, where the mass of an object is large enough that the quantum effect can be neglected. The three laws are summariezed as following:

1. In the absence of external forces, a body will either be at rest or execute motion along a straight line with a constant velocity $\mathbf{v}$.
2. The action of an external force $\mathbf{F}$ on a body produces an acceleration $\mathbf{a}$ equal to the force divided by the mass m of the body:
$$\mathbf{a} = \frac{\mathbf{F}}{m}, \qquad \mathbf{F} = m\mathbf{a}. \tag{2.1}$$
3. If body A exerts a force on body B $\mathbf{F}_{AB}$, then body B exerts an equal and opposite force on body A: $\mathbf{F}_{BA} = -\mathbf{F}_{AB}$.

Note that Newton's second law indicates the first law.

Some important concepts in Newtonian mechanics scheme are

$$\begin{aligned}
&\text{Time}: \quad t \\
&\text{Position}: \quad \mathbf{r}(t) = (x(t), y(t), z(t)) \\
&\text{Velocity}: \quad \mathbf{v}(t) = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \dot{\mathbf{r}} \\
&\text{Acceleration}: \quad \mathbf{a}(t) = \frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = \frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = \ddot{\mathbf{r}} \\
&\text{Momentum}: \quad \mathbf{p}(t) = m\mathbf{v}(t) = m\dot{\mathbf{r}} \\
&\text{Force}: \quad \mathbf{F} = m\mathbf{a} = m\ddot{\mathbf{r}} = m\dot{\mathbf{p}} \\
&\text{Work}: W_{AB}(\text{path}) = \int_A^B \mathbf{F}\cdot\mathrm{d}\mathbf{l} = \int_A^B F\cos(\theta)\mathrm{d}l
\end{aligned} \tag{2.2}$$

where θ is the angle between the force vector and the path.

A *trajectory* is a specification of the object's position as a function of time t and *initial conditions* $\mathbf{r}(0)$ and $\mathbf{v}(0)$.

$$\mathbf{r}(t) = \mathbf{r}(0) + \mathbf{v}t \tag{2.3}$$

2.1.1 Multiple objects

We have discussed the Newtonian mechanics for a single object. Now let's look into systems with multiple objects. The positions of N objects are specified by $\{\mathbf{r}_1(t),\dots,\mathbf{r}_N(t)\}$ and the velocities are $\{\mathbf{v}_1(t),\dots,\mathbf{v}_N(t)\}$. It is often preferred to work with the momenta instead of velocities: $\{\mathbf{p}_1(t),\dots,\mathbf{p}_N(t)\}$, where

$$\mathbf{p}_i = m_i\mathbf{v}_i = m_i\dot{\mathbf{r}}_i \tag{2.4}$$

The classical dynamics of an N-object system in three-dimension can be specified by $6N$ functions:

$$\{\mathbf{r}_1(t),\dots,\mathbf{r}_N(t),\mathbf{p}_1(t),\dots,\mathbf{p}_N(t)\} \tag{2.5}$$

The above $6N$ space is called *phase space*. We define a point in the phase space as the *phase space vector*

$$x = (\mathbf{r}_1(t),\dots,\mathbf{r}_N(t),\mathbf{p}_1(t),\dots,\mathbf{p}_N(t)) \tag{2.6}$$

Examples of phase diagrams can be found in Tuckerman $pp.6-9$.

One main difference between a system with multiple objects and a system with one single object is that there exist *interactions* among objects in a multi-object system. Usually an object i will experience a force $\mathbf{F}_i$ due to all the other objects:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r_1},\mathbf{r}_2,\dots,\mathbf{r}_N;\dot{\mathbf{r}}_i) \tag{2.7}$$

If the forces are *pairwise*, then

$$\mathbf{F}_i = \sum_{j\neq i}\mathbf{f}_{ji}(\mathbf{r}_i - \mathbf{r_j}) + \mathbf{f}^{\text{ext}}(\mathbf{r}_i,\dot{\mathbf{r}}_i) \tag{2.8}$$

The equation of motion of an N-object system is then

$$m_i\ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r_1},\mathbf{r}_2,\dots,\mathbf{r}_N;\dot{\mathbf{r}}_i),\ \text{ with } i = 1,\dots,N. \tag{2.9}$$

which can be solved given the initial conditions $\{\mathbf{r}_1(0),\dots,\mathbf{r}_N(0)\}$ and $\{\mathbf{v}_1(0),\dots,\mathbf{v}_N(0)\}$.

Discussion For a system consisting of microscopic particles (such as atoms), the number of particles $N \sim 10^{23}$, and the structure of the interactions $\mathbf{f}_{ji}(\mathbf{r}_i - \mathbf{r_j})$ is usually complicated. Solving Eq. (2.9) for all the N particles is basically impossible. The rules of statistical mechanics provide a connection between the microscopic laws and macroscopic laws, which can be used to alleviate the computational cost (or the curse of dimension). However, additional approximations are still necessary for practical simulations. For instance, instead of considering 10^{23} particles, one could consider a smaller number and extrapolate to the so-called *thermodynamic limit*; one could also introduce approximations to the interacting forces to reduce the complexity of the computation. This brings us to the research subject called *molecular dynamics*.

2.2 Lagrangian Formulation

We first introduce the concept of *conservative forces*. Conservative forces are defined as vector quantities that are derivable from a scalar function $U(\mathbf{r}_1,\ldots,\mathbf{r}_N)$, known as a *potential energy function*:

$$\mathbf{F}_i(\mathbf{r}_1,\ldots,\mathbf{r}_N) = -\nabla_i U(\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{2.10}$$

where $\nabla_i = \partial/\partial\mathbf{r}_i = (\partial/\partial x_i, \partial/\partial y_i, \partial/\partial z_i)$.

Next we define the *kinetic energy* due to the movement of the objects:

$$K(\dot{\mathbf{r}}_1,\ldots,\dot{\mathbf{r}}_N) = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i^2 = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} \tag{2.11}$$

Note that the potential energy U only depends on the positions while the kinetic energy K only depends on the velocities (or momenta).

The *Lagrangian* $\mathcal{L}$ is defined as the *difference* between the kinetic and potential energies:

$$\mathcal{L}(\mathbf{r}_1,\ldots,\mathbf{r}_N;\dot{\mathbf{r}}_1,\ldots,\dot{\mathbf{r}}_N) = K(\dot{\mathbf{r}}_1,\ldots,\dot{\mathbf{r}}_N) - U(\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{2.12}$$

The Lagrandian serves as the *generator* of the equation of motion (EOM) via the *Euler-Lagrange* equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial\mathcal{L}}{\partial\dot{\mathbf{r}}_i}\right) - \frac{\partial\mathcal{L}}{\partial\mathbf{r}_i} = 0 \tag{2.13}$$

Substituting Eq. (2.12) into Eq. (2.13), along with Eq. (2.10) and Eq. (2.11), one derives the Newton's second law:

$$m_i\ddot{\mathbf{r}}_i = \mathbf{F}_i \tag{2.14}$$

The reason why we introduce the Lagrangian is that the equation of motion that is hard to write down directly from Newton's second law can be derived from the Euler-Lagrange equation Eq. (2.13).

The *Hamiltonian* $\mathcal{H}$ corresponds to the total energy E of the system:

$$\mathcal{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N;\dot{\mathbf{r}}_1,\ldots,\dot{\mathbf{r}}_N) = K(\dot{\mathbf{r}}_1,\ldots,\dot{\mathbf{r}}_N) + U(\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{2.15}$$

It can be shown that the Hamiltonian and the Lagrangian are related by Legendre transforms (Tuckerman *pp.*16 – 17). Usually we use the momenta instead of velocity as the variables:

$$\mathcal{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N;\mathbf{p}_1,\ldots,\mathbf{p}_N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{2.16}$$

For a system with conservative forces, the equation of motion satisfies the *conservation of energy*, i.e. $\mathrm{d}E/\mathrm{d}t = 0$ or $\mathrm{d}\mathcal{H}/\mathrm{d}t = 0$.

Taking the derivatives of $\mathcal{H}$ with respect to $\mathbf{r}_i$ and $\mathbf{p}_i$, we derive the *Hamiltonian's equations of motion*:

$$\begin{aligned} \frac{\partial \mathcal{H}}{\partial \mathbf{r_i}} &= \frac{\partial U}{\partial \mathbf{r_i}} = -\mathbf{F}_i = -\dot{\mathbf{p}}_i \\ \frac{\partial \mathcal{H}}{\partial \mathbf{p_i}} &= \frac{\mathbf{p}_i}{m_i} = \dot{\mathbf{r}}_i \end{aligned} \tag{2.17}$$

which reproduces the Newton's second law and indicates the conservation of energy:

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} = \sum_i \left(\frac{\partial \mathcal{H}}{\partial \mathbf{r_i}} \dot{\mathbf{r}}_i + \frac{\partial \mathcal{H}}{\partial \mathbf{p_i}} \dot{\mathbf{p}}_i \right) = 0 \tag{2.18}$$

2.2.1 Generalized coordinates

In the above we used Cartesian coordinates $\{\mathbf{r}_i = (x_i, y_i, z_i)\}$, corresponding to $3N$ values. Here we introduce *generalized coordinates* $\{q_1, \ldots, q_{3N}\}$ which usually provide a more natural description of the particle locations. The generalized coordinates $\{q_1, \ldots, q_{3N}\}$ are related to the Cartesian coordinates via a reversible function

$$q_\alpha = f_\alpha(\mathbf{r}_1, \ldots, \mathbf{r}_N), \quad \alpha = 1, ..., 3N \tag{2.19}$$

The inverse of the transformation gives back the Cartesian coordinates:

$$\mathbf{r}_i = \mathbf{g}_i(q_1, \ldots, q_{3N}), \quad i = 1, ..., N \tag{2.20}$$

According to the chain rule,

$$\dot{\mathbf{r}}_i = \sum_{\alpha=1}^{3N} \frac{\partial \mathbf{r}_i}{\partial q_\alpha} \dot{q}_\alpha. \tag{2.21}$$

Therefore the kinetic energy in the new coordinate is

$$\begin{aligned} \tilde{K}(q, \dot{q}) &= \frac{1}{2} \sum_{\alpha=1}^{3N} \sum_{\beta=1}^{3N} \left(\sum_{i=1}^{N} m_i \frac{\partial \mathbf{r}_i}{\partial q_\alpha} \cdot \frac{\partial \mathbf{r}_i}{\partial q_\beta} \right) \dot{q}_\alpha \dot{q}_\beta \\ &= \frac{1}{2} \sum_{\alpha=1}^{3N} \sum_{\beta=1}^{3N} G_{\alpha\beta}(q_1, \ldots, q_{3N}) \dot{q}_\alpha \dot{q}_\beta \end{aligned} \tag{2.22}$$

where $G_{\alpha\beta}$ is a symmetric matrix called the *mass metric matrix*:

$$G_{\alpha\beta}(q_1, \ldots, q_{3N}) = \sum_{i=1}^{N} m_i \frac{\partial \mathbf{r}_i}{\partial q_\alpha} \cdot \frac{\partial \mathbf{r}_i}{\partial q_\beta} \tag{2.23}$$

Now we can express the concepts we learned in Section 2.2 in the generalized coordinates.

- Lagrangian:

$$\mathcal{L} = \frac{1}{2}\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N} G_{\alpha\beta}(q_1,\dots,q_{3N})\dot{q}_\alpha\dot{q}_\beta - U(\mathbf{r}_1(q_1,\cdots,q_{3N},\cdots,\mathbf{r}_N(q_1,\cdots,q_{3N})) \tag{2.24}$$

  where $U(\mathbf{r}_1(q_1,\cdots,q_{3N},\cdots,\mathbf{r}_N(q_1,\cdots,q_{3N}))$ is the potential energy as a function of $(q_1,\cdots,q_{3N})$.

- Euler-Lagrange equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{\beta=1}^{3N} G_{\alpha\beta}\dot{q}_\beta\right) - \left(\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N}\frac{\partial G_{\alpha\beta}}{\partial q_\gamma}\dot{q}_\alpha\dot{q}_\beta - \frac{\partial U}{\partial q_\gamma}\right) = 0 \tag{2.25}$$

- Generalized momenta $\{p_1,\cdots,p_{3N}\}$:

$$p_\alpha = \frac{\partial\mathcal{L}}{\partial\dot{q}_\alpha} = \sum_{\beta=1}^{3N} G_{\alpha\beta}\dot{q}_\beta \tag{2.26}$$

- Hamiltonian:

$$\mathcal{H} = \frac{1}{2}\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N} G^{-1}_{\alpha\beta}p_\alpha p_\beta + U(\mathbf{r}_1(q_1,\cdots,q_{3N},\cdots,\mathbf{r}_N(q_1,\cdots,q_{3N})) \tag{2.27}$$

  where G^{-1} is the inverse of the mass-metric matrix G, and

$$G^{-1}_{\alpha\beta} = \sum_{i=1}^{N}\frac{1}{m_i}\frac{\partial q_\alpha}{\partial\mathbf{r}_i}\cdot\frac{\partial q_\beta}{\partial\mathbf{r}_i} \tag{2.28}$$

- Hamiltonian's equations of motion:

$$\dot{q}_\alpha = \frac{\partial\mathcal{H}}{\partial p_\alpha}, \qquad \dot{p}_\alpha = -\frac{\partial\mathcal{H}}{\partial q_\alpha} \tag{2.29}$$

2.3 More about Hamiltonian

2.3.1 Time evolution of a general function

The *Poisson bracket* between two functions $f(x)$ and $g(x)$ is defined as

$$\{f(x), g(x)\} = \sum_{\alpha}^{3N}\left[\frac{\partial f(x)}{\partial q_\alpha}\frac{\partial g(x)}{\partial p_\alpha} - \frac{\partial f(x)}{\partial p_\alpha}\frac{\partial g(x)}{\partial q_\alpha}\right] \tag{2.30}$$

where $x = (q_1, \ldots, q_{3N}; p_1, \ldots, p_{3N})$ is the generalized vector.

The time evolution of a function $f(x)$ is then decided by the Poisson bracket $\{f(x), \mathcal{H}\}$:

$$\begin{aligned}\frac{\mathrm{d}f(x)}{\mathrm{d}t} &= \sum_{\alpha=1}^{3N}\left[\frac{\partial f(x)}{\partial q_\alpha}\dot{q}_\alpha + \frac{\partial f(x)}{\partial p_\alpha}\dot{p}_\alpha\right] \\ &= \sum_{\alpha=1}^{3N}\left[\frac{\partial f(x)}{\partial q_\alpha}\frac{\partial \mathcal{H}}{\partial p_\alpha} - \frac{\partial f(x)}{\partial p_\alpha}\frac{\partial \mathcal{H}}{\partial q_\alpha}\right] \\ &= \{f(x), \mathcal{H}\}\end{aligned} \tag{2.31}$$

If the Poisson bracket between an observable $f(x)$ and the Hamiltonian $\mathcal{H}$ is zero, i.e., $\{f(x), \mathcal{H}\} = 0$, then we say that $f(x)$ is *conserved*.

2.3.2 Phase space incompressibility

The term "incompressibility" in hydrodynamics (or fluid dynamics) means that there is no source or sinks in the flow, i.e., $\nabla \cdot \mathbf{v}(\mathbf{r}) = 0$. Consider the time derivative of the phase vector x and define

$$\eta(x) = \dot{x} \tag{2.32}$$

where we can consider η as a generalized velocity. η can be evaluated by

$$\begin{aligned}\eta(x) &= (\dot{q}_1, \ldots, \dot{q}_{3N}; \dot{p}_1, \ldots, \dot{p}_{3N}) \\ &= \left(\frac{\partial \mathcal{H}}{\partial p_1}, \ldots, \frac{\partial \mathcal{H}}{\partial p_{3N}}; -\frac{\partial \mathcal{H}}{\partial q_1}, \ldots, -\frac{\partial \mathcal{H}}{\partial q_{3N}}\right)\end{aligned} \tag{2.33}$$

We evaluate $\nabla_x \cdot \eta(x)$,

$$\begin{aligned}\nabla_x \cdot \eta(x) &= \sum_{\alpha=1}^{3N}\left[\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha}\right] \\ &= \sum_{\alpha=1}^{3N}\left[\frac{\partial}{\partial q_\alpha}\frac{\partial \mathcal{H}}{\partial p_\alpha} - \frac{\partial}{\partial p_\alpha}\frac{\partial \mathcal{H}}{\partial q_\alpha}\right] \\ &= \sum_{\alpha=1}^{3N}\left[\frac{\partial^2 \mathcal{H}}{\partial q_\alpha \partial p_\alpha} - \frac{\partial^2 \mathcal{H}}{\partial p_\alpha \partial q_\alpha}\right] \\ &= 0\end{aligned} \tag{2.34}$$

Therefore the Hamiltonian's equation of motion ensures the incompressibility condition in the phase space.

2.3.3 Symplectic structure

Eq. (2.33) can be rewritten in the following form

$$\eta(x) = \begin{pmatrix} \dot{\mathbf{q}} \\ \dot{\mathbf{p}} \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \mathbf{I} \\ -\mathbf{I} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial \mathbf{q}} \\ \frac{\partial \mathcal{H}}{\partial \mathbf{p}} \end{pmatrix} = M \frac{\partial \mathcal{H}}{\partial x} \tag{2.35}$$

where M is a $6N \times 6N$ matrix with the form

$$M = \begin{pmatrix} \mathbf{0} & \mathbf{I} \\ -\mathbf{I} & \mathbf{0} \end{pmatrix} \tag{2.36}$$

where $\mathbf{0}$ and $\mathbf{I}$ are $3N \times 3N$ zero and identity matrices, respectively.

A dynamical system expressible in the form of Eq. (2.35) is said to possess a *symplectic structure*.

Since the solution to the Hamiltonian's equation of motion is unique for each initial condition $x(0)$, one could say that $x(t)$ is a unique function of $x(0)$. Define the Jacobian matrix $J(t)$ with elements

$$J_{kl}(t) = \frac{\partial x_k(t)}{\partial x_l(0)}, \tag{2.37}$$

we have

$$M = J(t)^T M J(t) \tag{2.38}$$

where $J(t)^T$ is the transpose of $J(t)$. Eq. (2.38) is called the *sympletic property*.

Lecture 3: Thermodynamics and Ensemble Theory

3.1 Basic concepts of thermodynamics

- **Thermodynamic systems:** a *macroscopic* system. A thermodynamic system can be
  - *isolated*: there is no exchange of heat or material with surroundings;
  - *closed*: there is heat but no material exchange with surroundings;
  - *open*: there is both heat and material exchange with surroundings.
- **Thermodynamic state:** a thermodynamic state is characterized by a set of thermodynamic parameters (or state parameters) such as the pressure P, volume V, temperature T, and the number of moles n or the total mass M.
- **Thermodynamic equilibrium:** a system is in thermodynamic equilibrium if the thermodynamic states does not change with time, i.e., the thermodynamic parameters remain constant with time.
- **Equation of state (EOS):** Similar to the equation of motion (EOM), the EOS of a system describes the relationship among the thermodynamic parameters at equilibrium. When one parameter changes, the other parameters will respond according to the EOS to reach a new equilibrium.
  - Example 1: When P, V, T and n are the fundamental thermodynamic parameters, the *general* form of the EOS is

    $$g(n, P, V, T) = 0 \tag{3.1}$$

  - Example 2: EOS of an *ideal gas*

    $$PV - nRT = 0 \tag{3.2}$$

    where $R \approx 8.31446\ \mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$ is the *gas constant*. (Note that this number in the textbook is inaccurate.)
- **Thermodynamic transformation:** the system changes from one thermodynamic state to another. A thermodynamic transformation can be

  - *reversible*: the change is slow enough so that the system can evolve back to the initial state along the *same path*.
  - *irreversible*: the path of the transformation cannot be reversed.

- **State function**: a state function is any function $f(n, P, V, T)$ which *only* depends on the initial and final states, but irrelevant to the transformation paths.

3.2 Laws of thermodynamics

- **Zeroth law**
  If two thermodynamic systems $\mathcal{A}$ and $\mathcal{B}$ are each in thermal equilibrium with a third system $\mathcal{C}$, then $\mathcal{A}$ and $\mathcal{B}$ are in thermal equilibrium with each other.

- **First law**
  In any thermodynamic transformation, the change of the *internal energy* ΔE of a system equals to the heat ΔQ it absorbs and the amount of work ΔW performed on it:

  $$\Delta E = \Delta Q + \Delta W. \tag{3.3}$$

  Discussion:

  - Both ΔQ and ΔW are *not* state functions.
  - ΔE is a state function: $\Delta E = E_f - E_i$ (irrelevant of the path). For an isolated system, the energy is conserved.
  - In a reversible process, the changes of work and heat are

    $$\begin{aligned} \mathrm{d}W_{\mathrm{rev}} &= -P\mathrm{d}V + \mu \mathrm{d}n \\ \mathrm{d}Q_{\mathrm{rev}} &= C\mathrm{d}T \end{aligned} \tag{3.4}$$

    where μ is called the *chemical potential*, and C is called the *heat capacity*. Note that P is the *internal* pressure.

- **Second law**
  In any thermodynamic transformation, the *total entropy* S_{tot} of the universe must either increase or remain the same: $\mathrm{d}S_{\mathrm{tot}} \geq 0$.
  Two equivalent statements: there exists *no* thermodynamic transformation

  (1) whose sole effect is to extract a quantity of heat from a high-temperature source and convert it entirely into work; or

  (2) whose sole effect is to transfer heat from a cold source to a hot source.

- **Third law**
  The entropy of a system at the absolute zero of temperature $T = 0$ is a universal constant, which can be taken to be zero.

Discussion

In the first chapter, we studied the classical mechanics of individual particles (atoms, molecules, etc.) in a *microscopic* picture. The thermodynamic concepts and laws in this chapter are concerned with the *macroscopic* behaviors of a large number ($\sim 10^{23}$) of the microscopic particles.

In Chapter 1 we mentioned two practical difficulties of applying the Newton's laws to the particles directly: (1) the number of particles is enormous; and (2) the interactions (forces) among the particles are complicated. After learning/reviewing the laws of thermodynamics, another problem raises: the second law of thermodynamics decides the direction of time, i.e., the direction in which the entropy S increases. But in the mechanical laws, the "arrow" of time does not exist. The above paradox is known as *Loschmidt's paradox*. The reconciliation of this paradox relies on statistical mechanics.

3.3 Ensemble theory

There exist many microscopic configurations of a system that lead to the same macroscopic properties (e.g., P, T, V, n, E), since the macroscopic properties are generally connected to summations or averages of microscopic values. Therefore the macroscopic observables of a system are not sensitive to precise microscopic details. This leads to the concept of *ensemble*.

- **Ensemble**: a collection of systems described by the same set of microscopic interactions and sharing a common set of macroscopic properties.[1] These systems have distinguished microscopic states $x = (q_1, ..., q_{3N}; p_1, ..., p_{3N})$.
- **Ensemble average:** suppose $a(x)$ is a microscopic phase space function that can be used to calculate the macroscopic equilibrium observable A, then

$$\begin{aligned} \text{Discrete case :} \quad & A = \frac{1}{\mathcal{N}} \sum_{\lambda=1}^{\mathcal{N}} a(x_\lambda) \equiv \langle a \rangle, \\ \text{Continuous case :} \quad & A = \int \mathrm{d}x \; a(x) f(x) \equiv \langle a \rangle, \end{aligned} \tag{3.5}$$

  where for discrete ensembles: $\mathcal{N}$ is the number of systems in the ensemble, and x_λ is the microscopic state of the λth system; and for continuous ensembles: $f(x)$ is a normalized distribution function of the systems.

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[1] In the rest of the course, we will assume the systems in an ensemble are at equilibrium → equilibrium ensembles.

3.4 Time evolution of ensembles

Recall that the phase space is a $6N$ dimensional space, and a point in the phase space corresponds to a phase space vector $x = (q_1, ..., q_{3N}; p_1, ..., p_{3N})$, where $\{q_i\}_{i=1,...,3N}$ are generalized coordinates and $\{p_i\}_{i=1,...,3N}$ are the conjugate momenta. The *Liouville's theorem* and *Liouville's equation* describe the time evolution of an ensemble in the phase space.

We first introduce two concepts: phase space volume element $\mathrm{d}x$ and phase space distribution function (or ensemble distribution function) $f(x,t)$.

- **Phase space volume element:** $\mathrm{d}x = (\mathrm{d}q_1, \ldots, \mathrm{d}q_{3N}; \mathrm{d}p_q, \ldots, \mathrm{d}p_{3N})$ is a small volume centered at x.
- **Phase space distribution function:** $f(x,t)$ is the distribution of the systems in the ensemble at point x and time t, which satisfies:

$$\begin{aligned} f(x,t) &\geq 0 \\ \int \mathrm{d}x\, f(x,t) &= 1 \end{aligned} \tag{3.6}$$

Here we give the conclusions of how the above two values evolve with time, and the derivations/proofs can be found in the Tuckerman book *pp*.63 – 68.

- **Liouville's theorem**

$$\mathrm{d}x_0 = \mathrm{d}x_t \tag{3.7}$$

  where x_0 is the phase space vector at $t = 0$ and x_t at time t. This theorem states that even though the shape of the volume element can change with time, but the total volume is conserved.

- **Liouville's equation**

$$\boxed{\frac{\partial}{\partial t} f(x,t) = -\{f(x,t), \mathcal{H}(x,t)\}} \tag{3.8}$$

  where $\mathcal{H}(x,t)$ is the Hamiltonian, and $\{\cdot,\cdot\}$ is the Poisson bracket.

  At equilibrium, $\partial f / \partial t = 0$, therefore,

$$\{f(x), \mathcal{H}(x)\} = 0. \tag{3.9}$$

  A general solution to Eq. (3.9) is that f is a function of $\mathcal{H}$ (this can be proved straightforwardly), i.e.,

$$f(x) \propto \mathcal{F}(\mathcal{H}(x)). \tag{3.10}$$

  Therefore one can define $f(x)$ as

$$f(x) = \frac{1}{\mathcal{Z}} \mathcal{F}(\mathcal{H}(x)), \tag{3.11}$$

where the normalization factor $\mathcal{Z}$ is called the *partition function*

$$\mathcal{Z} = \int \mathrm{d}x \, \mathcal{F}(\mathcal{H}(x)). \tag{3.12}$$

The continuous ensemble average in Eq. (3.5) can also be written as

$$A = \langle a(x) \rangle = \frac{1}{\mathcal{Z}} \int \mathrm{d}x \, a(x)\mathcal{F}(\mathcal{H}(x)). \tag{3.13}$$

Lecture 4: Microcanonical Ensemble

In the previous lecture, we learned the concept of ensemble – *a collection of systems described by the same Hamiltonian with each system in a unique microscopic state at any given instant in time*. We also introduced three types of thermodynamic systems: isolated systems, closed systems and open systems. They correspond to three types of ensembles: microcanonical ensembles, canonical ensembles and grand canonical ensembles. The type of an ensemble is decided by fixing certain *control variables*, which are the macroscopic values of a thermodynamic systems (e.g. N, V, P, T, E...). Below is the summary of the three common ensembles (N-total number of particles, V-volume, E-total energy, T-temperature, μ-chemical potential).

Ensemble Names	Fixed Control Variables	Thermodynamic systems
Microcanonical	N, V, E	Isolated systems
Canonical	N, V, T	Closed systems
Grand canonical	μ, V, T	Open systems

Table 4.1: A summary of the three common types of ensembles.

Note that there are also other types of ensembles. For instance, in Gibbs ensembles, the pressure P is fixed while V can vary. We will focus on the above three ensembles for this course.

To understand the statistical properties of an ensemble, it is important to know the distribution of the microstates. For a microcanonical ensemble, it is possible to figure out the total number of systems, and the distribution can be straightforwardly calculated. We use $\Omega(N, V, E)$ to represent the total number of microstates.

For canonical ensembles and grand canonical ensembles, we will introduce the concept of *partition function*, which has a similar role as Ω. We will leave this part for future lectures. In fact, one can treat $\Omega(N, V, E)$ as the partition function of the microcanonical ensemble.

4.1 Boltzmann Entropy

The Boltzmann entropy is defined as

$$S = k_B \ln \Omega(N, V, E) \tag{4.1}$$

where $k_B \approx 1.38 \times 10^{-23} \mathrm{J} \cdot \mathrm{K}^{-1}$ is the Boltzmann's constant.

Eq. (4.1) indicates that S is also a function of N, V and E, therefore

$$\mathrm{d}S = \left(\frac{\partial S}{\partial E}\right)_{N,V} \mathrm{d}E + \left(\frac{\partial S}{\partial V}\right)_{N,E} \mathrm{d}V + \left(\frac{\partial S}{\partial N}\right)_{V,E} \mathrm{d}N \tag{4.2}$$

Recall from the thermodynamics that

$$\mathrm{d}E = \mathrm{d}Q_{\mathrm{rev}} + \mathrm{d}W_{\mathrm{rev}} \tag{4.3}$$

where $\mathrm{d}Q_{\mathrm{rev}}$ is the heat that the system absorbed at a reversible process, and $\mathrm{d}W_{\mathrm{rev}}$ is the work done to the system at a reversible process. We have

$$\begin{aligned} \mathrm{d}Q_{\mathrm{rev}} &= T\mathrm{d}S \\ \mathrm{d}W_{\mathrm{rev}} &= \mathrm{d}W_{\mathrm{rev}}^{\mathrm{mech}} + \mathrm{d}W_{\mathrm{rev}}^{\mathrm{chem}} \\ &= -P\mathrm{d}V + \mu\mathrm{d}N \end{aligned} \tag{4.4}$$

Therefore

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \tag{4.5}$$

and

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + \frac{P}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N = \frac{k_B}{\Omega}\mathrm{d}\Omega. \tag{4.6}$$

The relationships between the intensive properties T, P, μ and Ω are

$$\begin{aligned} \frac{1}{T} &= \frac{k_B}{\Omega}\left(\frac{\partial \Omega}{\partial E}\right)_{N,V} \\ P &= \frac{k_B T}{\Omega}\left(\frac{\partial \Omega}{\partial V}\right)_{N,E} \\ \mu &= -\frac{k_B T}{\Omega}\left(\frac{\partial \Omega}{\partial N}\right)_{V,E} \end{aligned} \tag{4.7}$$

Eq. (4.7) conveys an important information: the thermal properties of a system is closely related to the size of the ensemble it belongs to, or more precisely, the partition function of the ensemble.

4.2 $\Omega(N,V,E)$ for the microcanonical ensemble

In order to calculate $\Omega(N,V,E)$, we start from the equilibrium Liouville equation

$$\{f(x),\mathcal{H}(x)\}=0 \tag{4.8}$$

where $f(x)$ is the ensemble distribution function at phase vector x, $\mathcal{H}(x)$ is the Hamiltonian of the ensemble at x, and $\{\ldots,\ldots\}$ is the Poisson bracket. Eq. (4.8) leads to $f(x)=F(\mathcal{H}(x))$.

For a microcanonical ensemble, the energy E is conserved, therefore

$$\mathcal{H}(x)=E \tag{4.9}$$

which means that $F(\mathcal{H}(x))=0$ unless $\mathcal{H}(x)=E$. Therefore

$$F(\mathcal{H}(x))=\mathcal{N}\delta(\mathcal{H}(x)-E) \tag{4.10}$$

where $\delta(\ldots)$ is the Dirac delta function (see Math Reviews), and $\mathcal{N}$ is the normalization factor to ensure that $\int \mathrm{d}x\, F=1$.

For an ensemble in the continuous $6N$ dimensional phase space, Ω is the amount of space available to the systems. However, due to the properties of Delta function, the space that is available is actually a $(6N-1)$ dimensional hypersurface (only $(6N-1)$ degrees of freedom). How do we evaluate the volume of this hypersurface?

A clever way to bypass evaluating the volume of a "surface" is to consider a thin shell between $[E,E+\Delta E]$, called the *energy shell*, where ΔE is a very small value, as shown in Fig. 4.1. All points inside the energy shell should be equally weighted, and our goal is to count the number of distinguished microstates inside the shell, i.e., $\Omega(N,V,E)$. Heisenberg's uncertainty principle tells us that $\Delta q_i \Delta p_i \geq h/4\pi$, where h is called the Planck's

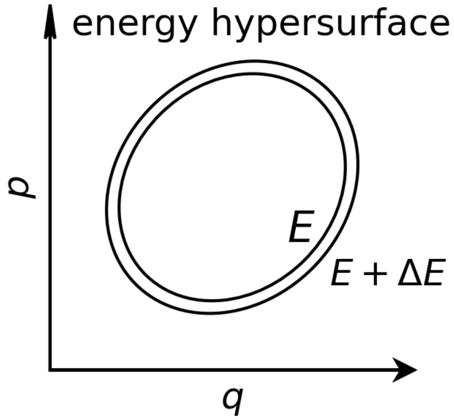


Figure 4.1: Energy shell in the phase space.

constant. We can assume that points inside a cube within the volume $\Delta x \sim h^{3N}$ are indistinguishable. Therefore, counting the number of distinguishable microstates is reduced to counting how many $\Delta x \sim h^{3N}$ cubes that the shell contains:

$$\Omega(N,V,E) = \frac{\text{volume of the energy shell}}{h^{3N}} \tag{4.11}$$

The volume of the shell can be approximated by the area of the hypersurface times the thickness ΔE: $\Delta E \int \mathrm{d}x\ \delta(\mathcal{H} - E)$.

The above derivation, however, is not enough. Because in quantum mechanical world, the N particles are indistinguishable. But in the classical world, particles are distinguishable. Therefore, there are $N!$ classical systems that will share the same microstates, where $N!$ comes from the number of permutations of N particles. To avoid overcounting, we need to divide the above Ω by $N!$. The final form of $\Omega(N,V,E)$ is thus

$$\boxed{\Omega(N,V,E) = \frac{\Delta E}{h^{3N} N!} \int \mathrm{d}x\ \delta(\mathcal{H}(x) - E)} \tag{4.12}$$

Comments

1. The value of $\delta(\mathcal{H}(x)-E)$ depends on the specific Hamiltonian.
2. The constant ΔE does not affect the statistical properties, since it cancels out in Eq. (4.7).

4.3 Example: The Classical Ideal Gas

The Hamiltonian of the ideal gas in a container is

$$\begin{aligned}\mathcal{H}(x) &= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + V_{\text{wall}}(x) \\ V_{\text{wall}}(x) &= \begin{cases} 0, & x \in \text{container}; \\ \infty & x \notin \text{container}. \end{cases}\end{aligned} \tag{4.13}$$

Suppose the volumn of the container is V, then Eq. (4.12) becomes

$$\begin{aligned}\Omega(N,V,E) &= \frac{\Delta E}{h^{3N}N!}\int_V \mathrm{d}\mathbf{q}_1 \cdots \int_V \mathrm{d}\mathbf{q}_N \int \mathrm{d}\mathbf{p}_1 \cdots \int \mathrm{d}\mathbf{p}_N \; \delta\left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - E\right) \\ &= \frac{\Delta E V^N}{h^{3N}N!}\int \mathrm{d}\mathbf{p}_1 \cdots \int \mathrm{d}\mathbf{p}_N \; \delta\left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - E\right)\end{aligned} \tag{4.14}$$

Let $\mathbf{y}_i = \mathbf{p}_i/\sqrt{2m}$, and $\mathrm{d}\mathbf{p}_i = \sqrt{2m}\,\mathrm{d}\mathbf{y}_i$, the integration becomes

$$\int \mathrm{d}\mathbf{p}_1 \cdots \int \mathrm{d}\mathbf{p}_N \; \delta\left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - E\right) = (2m)^{3N/2} \int \mathrm{d}\mathbf{y}_1 \cdots \int \mathrm{d}\mathbf{y}_N \; \delta\left(\sum_{i=1}^{N} \mathbf{y}_i^2 - E\right) \tag{4.15}$$

$\delta\left(\sum_{i=1}^{N} \mathbf{y}_i^2 - E\right)$ defines a $(3N-1)$-dimensional hypersphere with radius $\sqrt{E}$. We make a coordinate transformation to the hyperspherical coordinates:

$$\int \mathrm{d}p_1 \cdots \int \mathrm{d}p_{3N} = \underbrace{\int \mathrm{d}\theta_1 \cdots \int \mathrm{d}\theta_{3N-1}}_{\text{integration over angles}} \int \mathrm{d}r\, r^{3N-1} \tag{4.16}$$

where

$$\begin{aligned}\int \mathrm{d}\theta_1 \cdots \int \mathrm{d}\theta_{3N-1} &= \frac{2\pi^{3N/2}}{\Gamma(3N/2)} \\ \sum_{i=1}^{N} \mathbf{y}_i^2 &= r^2\end{aligned} \tag{4.17}$$

$\Gamma(x)$ is the Gamma function. Therefore the integral becomes

$$\Omega(N,V,E) = \frac{\Delta E V^N (2m)^{3N/2}}{h^{3N} N!} \frac{\pi^{3N/2}}{\Gamma(3N/2)} E^{3N/2-1} \tag{4.18}$$

In the above we used two properties of Delta function:

- $\int \mathrm{d}x\, f(x)\delta(x-a) = f(a)$.
- $\delta(x^2 - a^2) = \frac{1}{2|a|}[\delta(x-a) + \delta(x+a)]$.

Lecture 5: Canonical Ensemble I

In the last lecture, we discussed the microcanonical ensemble - a collection of isolated systems that conserves (N, V, E). In real life, however, it is nearly impossible to find a truly isolated system (the whole universe could be an exception). Most systems in the experimental setups exchange energy or even particles with the surrounding environment.

In this lecture, we introduce another type of ensembles: *canonical ensembles*, which are collections of systems that conserve (N, V, T) and exchange energy E with the surrounding environment, as shown in Fig. 5.1.

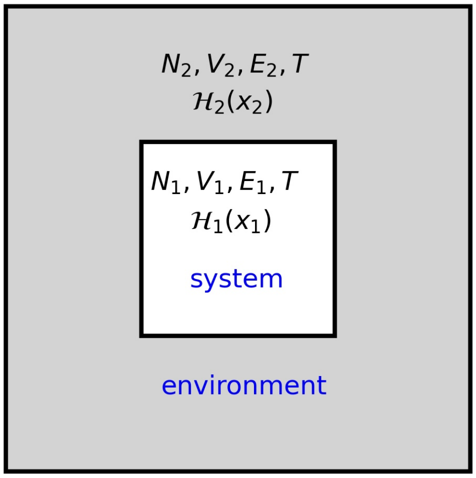


Figure 5.1: A system in contact with the environment (thermal reservoir).

In Fig. 5.1, the system of interest is embedded in a large environment (or thermal reservoir, thermal bath), with $E_2 \gg E_1$. The system has a fixed volume V_1 and can *only exchange heat* with the environment. Both the system and environment are at equilibrium. According to the first law of thermodynamics, $T_1 = T_2 = T$. This system obeys the laws of canonical ensemble. The whole system (system + environment) is an isolated system and obeys the laws of microcanonical ensemble.

5.1 Partition function

In the previous lecture, we learned that the number of microstates of a microcanonical ensemble $\Omega(N,V,E)$ is the key to connect the microscopic distribution with the macroscopic thermal properties. For canonical and grand canonical ensembles, there exists a more general concept called the *partition function*, which plays the same role as $\Omega(N,V,E)$ in microcanonical ensembles. We use $\mathcal{Q}(N,V,T)$ to represent the partition function for canonical ensembles.

One can interpret the partition function as the normalization factor for the ensemble distribution:

$$f(x) = \frac{F(x)}{\mathcal{Q}(N,V,T)}, \tag{5.1}$$

where $f(x)$ satisfies $f(x) \geq 0$ and $\int \mathrm{d}x\ f(x) = 1$. Then the partition function can be evaluated by

$$\mathcal{Q}(N,V,T) = \int \mathrm{d}x\ F(x). \tag{5.2}$$

Again, one can multiply $F(x)$ with a constant and $f(x)$ will remain unchanged.

In the following, we evaluate $F(x)$ and hence $\mathcal{Q}(N,V,T)$. We start from what we know already: *(system + environment) belongs to a microcanonical ensemble*. (**Note**: this strategy of starting from the whole system and trace the environment out is a very important trick and we will run into it again!)

We use the index 1 for the system, 2 for the environment, while the total system properties have no indices.

Before we jump to the derivation of $F(x)$, let's look at the basic properties of this bipartitioned problem at equilibrium. Suppose the total system is bipartitioned into System-1 and System-2.

- **Phase space:** The dimension of the phase space of system-1 is $6N_1$ and that of system-2 is $6N_2$, then the dimension of the total system is $6(N_1+N_2)$, with

$$x = \left(q_1^1, \cdots, q_{3N_1}^1, q_1^2, \cdots, q_{3N_2}^2;\ p_1^1, \cdots, p_{3N_1}^1, p_1^2, \cdots, p_{3N_2}^2\right). \tag{5.3}$$

- **Distribution function:** if $f(x) = f(x_1, x_2)$ is the distribution of the microstates in the whole system, then the distribution function $f_1(x_1)$ in System-1 is evaluated by integrating out System-2 from $f(x)$, vice versa.

$$\begin{aligned} f_1(x_1) &= \int \mathrm{d}x_2\ f(x_1, x_2) \\ f_2(x_2) &= \int \mathrm{d}x_1\ f(x_1, x_2) \end{aligned} \tag{5.4}$$

5.1.1 Derivation of $\mathcal{Q}(N,V,E)$

We will mainly follow the steps in the Tuckerman book ($pp.135-138$). However, there are several places in the book that are not mathematically rigid, and we will make some modifications in the following derivation. Suppose the coupling between the system and environment can be neglected, then the total Hamiltonian is

$$\mathcal{H}(x) = \mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) \tag{5.5}$$

Since the total system is an isolated system, $\mathcal{H}(x) = E$ is constant, and

$$\begin{aligned}\Omega(N,V,E) &\propto \int \mathrm{d}x\ \delta(\mathcal{H}(x) - E)\\ &= \int \mathrm{d}x_1 \mathrm{d}x_2\ \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E)\\ &= \int \mathrm{d}x_1 \mathrm{d}x_2\ F(x_1, x_2)\end{aligned} \tag{5.6}$$

where $F(x_1,x_2)$ is an unnormalized distribution of the total system depending on x_1 and x_2. To get the (unnormalized) distribution function that only depends on x_1, we integrate x_2 out:

$$\begin{aligned}F(x_1) &= \int \mathrm{d}x_2\ F(x_1, x_2)\\ &= \int \mathrm{d}x_2\ \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E)\end{aligned} \tag{5.7}$$

In the previous lecture we saw that the thermal properties depends on the logarithm of the partition function, so in the following we work with $\ln F(x_1)$:

$$\ln F(x_1) = \ln \int \mathrm{d}x_2\ \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E). \tag{5.8}$$

Since $E_2 \gg E_1$, $\mathcal{H}_2(x_2) \gg \mathcal{H}_1(x_1)$, and $|\mathcal{H}_1(x_1)/E| \ll 1$. Therefore we can do Taylor expansion around $\mathcal{H}_1(x_1)/E = 0$. Using $\delta(ax) = \delta(x)/|a|$,

$$\begin{aligned}\ln F(x_1) =&\ \ln \int \mathrm{d}x_2\ \frac{1}{|E|}\delta(\frac{\mathcal{H}_1(x_1)}{E} + \frac{\mathcal{H}_2(x_2)}{E} - 1)\\ &\approx \frac{1}{|E|}\ln \int \mathrm{d}x_2\ \delta(0 + \frac{\mathcal{H}_2(x_2)}{E} - 1)\\ &+ \frac{1}{|E|}\left(\frac{\partial}{\partial(\mathcal{H}_1(x_1)/E)}\ln \int \mathrm{d}x_2\ \delta(\frac{\mathcal{H}_1(x_1)}{E} + \frac{\mathcal{H}_2(x_2)}{E} - 1)\right)\Bigg|_{\mathcal{H}_1(x_1)/E=0} \frac{\mathcal{H}_1(x_1)}{E}\\ &= \ln \int \mathrm{d}x_2\ \delta(\mathcal{H}_2(x_2) - E)\\ &+ \left(\frac{\partial}{\partial \mathcal{H}_1(x_1)}\ln \int \mathrm{d}x_2\ \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E)\right)\Bigg|_{\mathcal{H}_1(x_1)/E=0} \mathcal{H}_1(x_1).\end{aligned} \tag{5.9}$$

Due to the δ-function $\delta(\mathcal{H}_1(x_1)+\mathcal{H}_2(x_2)-E)$, where the total energy E is constant, we have

$$\begin{aligned} \mathcal{H}_1(x_1) &= E-\mathcal{H}_2(x_2), \\ \mathrm{d}\mathcal{H}_1(x_1) &= -\mathrm{d}\mathcal{H}_2(x_2). \end{aligned} \tag{5.10}$$

Eq. (5.9) can be rewritten as

$$\begin{aligned} \ln F(x_1) &= \ln\int \mathrm{d}x_2\ \delta(\mathcal{H}_2(x_2)-E) \\ &\quad -\left(\frac{\partial}{\partial\mathcal{H}_2(x_2)}\ln\int \mathrm{d}x_2\ \delta(\mathcal{H}_1(x_1)+\mathcal{H}_2(x_2)-E)\right)\Bigg|_{\mathcal{H}_1(x_1)=0}\mathcal{H}_1(x_1) \\ &= \ln\int \mathrm{d}x_2\ \delta(\mathcal{H}_2(x_2)-E)-\left(\frac{\partial}{\partial\mathcal{H}_2(x_2)}\ln\int \mathrm{d}x_2\ \delta(\mathcal{H}_2(x_2)-E)\right)\mathcal{H}_1(x_1). \end{aligned} \tag{5.11}$$

We notice that both two terms in Eq. (5.11) has $\int \mathrm{d}x_2\ \delta(\mathcal{H}_2(x_2)-E)$, which is the form of the partition function for the microcanonical ensemble. In fact, because the environment (System-2) is much larger than the system, we can assume that the energy of the environment E_2 fluctuates inside a small energy shell around E, then

$$\int \mathrm{d}x_2\ \delta(\mathcal{H}_2(x_2)-E) \propto \Omega_2(N_2,V_2,E_2) \tag{5.12}$$

Recall the definition of the Boltzmann entropy in the last lecture

$$S_2(N_2,V_2,E_2) = k_B\ln\Omega_2(N_2,V_2,E_2). \tag{5.13}$$

Eq. (5.11) becomes

$$\begin{aligned} \ln F(x_1) &= \frac{S_2(N_2,V_2,E_2)}{k_B}-\mathcal{H}_1(x_1)\frac{\partial}{\partial E_2}\frac{S_2(N_2,V_2,E_2)}{k_B} \\ &= \frac{S_2(N_2,V_2,E_2)}{k_B}-\frac{\mathcal{H}_1(x_1)}{k_BT}, \end{aligned} \tag{5.14}$$

where we used $\partial S_2/\partial E_2 = T_2$ and $T_1 = T_2 = T$. Again, since the environment is large, S_2 can also be taken as a constant, and

$$F(x_1) \propto e^{-\mathcal{H}_1(x_1)/k_BT}. \tag{5.15}$$

As we have already discussed in the microcanonical ensemble part, there are two coefficients come from the *quantum effect*:

1. The resolution of the phase space due to Heisenberg's uncertainty principle → $\frac{1}{h^{3N_1}}$.
2. The indistinguishable property of particles → $\frac{1}{N_1!}$

For the sake of simplicity, we drop the index '1' and

$$F(x) = \frac{1}{N!h^{3N}} e^{-\mathcal{H}(x)/k_B T} = C_N e^{-\mathcal{H}(x)/k_B T} \tag{5.16}$$

The normalized distribution function is

$$\boxed{f(x) = \frac{C_N e^{-\mathcal{H}(x)/k_B T}}{\mathcal{Q}(N,V,T)}} \tag{5.17}$$

where $\mathcal{Q}(N,V,T)$ is the *partition function* of the canonical ensemble:

$$\boxed{\mathcal{Q}(N,V,T) = C_N \int \mathrm{d}x \; e^{-\beta \mathcal{H}(x)}} \tag{5.18}$$

5.1.2 Evaluating a thermal observable

Now we have the distribution function $f(x)$, we can evaluate any thermal observables by $B(N,V,T) = \langle b(x) \rangle$, where $b(x)$ is the microscopic function corresponding to B:

$$B(N,V,T) = \langle b(x) \rangle = \int \mathrm{d}x \; f(x) b(x). \tag{5.19}$$

Eq. (5.19) connects a microscopic property $b(x)$ with a macroscopic property B. Substituting Eq. (5.17) into Eq. (5.19), we derive the formula of thermal observables under the canonical statistics:

$$\boxed{B(N,V,T) = \frac{C_N \int b(x) e^{-\mathcal{H}(x)/k_B T}}{\mathcal{Q}(N,V,T)} = \frac{\int b(x) e^{-\mathcal{H}(x)/k_B T}}{\int \mathrm{d}x \; e^{-\beta \mathcal{H}(x)}},} \tag{5.20}$$

where the factor C_N canceled out.

Example: energy evaluation

$$\begin{aligned} E = \langle \mathcal{H}(x) \rangle &= \frac{\int \mathcal{H}(x) e^{-\mathcal{H}(x)/k_B T}}{\int \mathrm{d}x \; e^{-\beta \mathcal{H}(x)}} \\ &= -\frac{1}{\mathcal{Q}(N,V,T)} \frac{\partial \mathcal{Q}(N,V,T)}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta} \ln \mathcal{Q}(N,V,T). \end{aligned} \tag{5.21}$$

We see that E has a simpler form which relies on the partial derivative of $\ln \mathcal{Q}(N,V,T)$. In fact, we can also evaluate other common thermal properties (such as S and P) from $\ln \mathcal{Q}(N,V,T)$, avoiding the integration. However, Eq. (5.19) is still useful as the general form to evaluate any thermal observables. In the next lecture, we will see how to relate the common thermal properties to $\ln \mathcal{Q}(N,V,T)$.

Lecture 6: Canonical Ensemble II

6.1 Thermal properties

In the last lecture, we introduced the general form to evaluate a thermal property under canonical statistics Eq. (5.19). In this section, we start the discussion from the thermodynamic point of view, and connect the macroscopic properties to the microscopic partition function.

For the microcanonical ensemble with (N, V, E) as control variables, we introduced relationships of state functions as

$$\begin{aligned} \mathrm{d}S &= \frac{1}{T}\mathrm{d}E + \frac{P}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N, \\ \text{or } \mathrm{d}E &= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N. \end{aligned} \tag{6.1}$$

Since for canonical ensemble, we prefer to use (N, V, T) as control variables. In order to move T to the variables in Eq. (6.1), we perform *Legrendre transformation*:

$$\begin{aligned} \mathrm{d}(TS) &= T\mathrm{d}S + S\mathrm{d}T, \\ \mathrm{d}(E - TS) &= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N - (T\mathrm{d}S + S\mathrm{d}T) \\ &= -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N. \end{aligned} \tag{6.2}$$

Therefore the value $(E - TS)$ is a state function that uses (N, V, T) as variables, and we call it *Helmholtz free energy*:

$$\boxed{A(N, V, T) = E(N, V, S) - TS(N, V, E)}, \tag{6.3}$$

and

$$dA = -SdT - PdV + \mu dN. \tag{6.4}$$

Comments
According to the second law of thermodynamics, the *total entropy* of the universe (or an isolated system) must increase or remain the same: $S_{tot} \geq 0$. Since a microcanonical ensemble is composed of isolated systems, the entropy $S(N, V, E)$ is a natural value to determine whether a process is thermodynamically favorable. The *Helmholtz free energy* $A(N, V, T)$ for the canonical ensemble plays the same role:

A thermodynamic process in the canonical ensemble is favorable if $A(N,V,T)$ decreases.

(Decreasing $A(N,V,T)$ corresponds to increasing S or decreasing E.)

Aside from being the indicator of thermodynamical processes, $A(N,V,T)$ is also directly related to the canonical partition function $\mathcal{Q}(N,V,T)$:

$$\boxed{A(N,V,T) = -k_B T \ln \mathcal{Q}(N,V,T) = -\frac{1}{\beta}\ln \mathcal{Q}(N,V,T)} \tag{6.5}$$

where $\beta = 1/k_B T$. The proof of Eq. (6.5) can be found in the Tuckerman book *p.*139.

With Eq. (6.5), we can connect the macroscopic thermal properties to the microscopic partition function:

$$\begin{aligned} \mu &= \left(\frac{\partial A}{\partial N}\right)_{V,T} = -k_B T\left(\frac{\partial \ln \mathcal{Q}}{\partial N}\right)_{V,T}, \quad P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = k_B T\left(\frac{\partial \ln \mathcal{Q}}{\partial V}\right)_{N,T}, \\ S &= -\left(\frac{\partial A}{\partial T}\right)_{N,V} = k_B \ln \mathcal{Q} + k_B T\left(\frac{\partial \ln \mathcal{Q}}{\partial T}\right)_{N,V}, \quad E = A + TS = -\left(\frac{\partial \ln \mathcal{Q}}{\partial \beta}\right)_{N,V}. \end{aligned} \tag{6.6}$$

One can evaluate other thermal properties (such as heat capacity C_V) in the similar way.

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = k_B \beta^2 \frac{\partial^2 \ln \mathcal{Q}}{\partial \beta^2.} \tag{6.7}$$

It seems that Eq. (6.5) comes from intuition. However, we can validate it by proving that Eq. (6.5) is the solution to Eq. (6.3). Knowing $E = -\partial \ln \mathcal{Q}/\partial \beta$ from last lecture, Eq. (6.3) becomes

$$A + TS - E = A - T\frac{\partial A}{\partial T} + \frac{\partial \ln \mathcal{Q}}{\partial \beta} = 0. \tag{6.8}$$

Replacing T with $T = 1/k_B \beta$, Eq. (6.8) becomes

$$A + \beta\frac{\partial A}{\partial \beta} + \frac{\partial \ln \mathcal{Q}}{\partial \beta} = 0. \tag{6.9}$$

The easiest way to solve Eq. (6.9) is to substitute Eq. (6.5) into it and prove that it's the solution. We provide a general way to solve a differential equation with the form of Eq. (6.9) in the end of this lecture, in case you are interested.

6.2 Energy fluctuation

The fluctuation of a thermal property B is defined as

$$\Delta B = \sqrt{\langle (b(x) - B)^2 \rangle} = \sqrt{\langle b(x)^2 \rangle - B^2}, \tag{6.10}$$

where $B = \langle b(x) \rangle$. We examine the thermal fluctuation of the energy

$$\Delta E = \sqrt{\langle \mathcal{H}(x)^2 \rangle - E^2}. \tag{6.11}$$

First we need to calculate $\langle \mathcal{H}(x)^2 \rangle$ by

$$\langle \mathcal{H}(x)^2 \rangle = \frac{\int \mathrm{d}x\ \mathcal{H}(x)^2 e^{-\beta \mathcal{H}(x)}}{\int \mathrm{d}x\ e^{-\beta \mathcal{H}(x)}} = \frac{1}{\mathcal{Q}} \frac{\partial^2 \mathcal{Q}}{\partial \beta^2}. \tag{6.12}$$

Therefore

$$(\Delta E)^2 = \langle \mathcal{H}(x)^2 \rangle - E^2 = \frac{1}{\mathcal{Q}} \frac{\partial^2 \mathcal{Q}}{\partial \beta^2} - \frac{1}{\mathcal{Q}^2} \left(\frac{\partial Q}{\partial \beta} \right)^2 = \frac{\partial^2 \ln \mathcal{Q}}{\partial \beta^2}. \tag{6.13}$$

Since $C_V = k_B \beta^2 (\partial^2 \mathcal{Q} / \partial \beta^2)$, we get

$$\Delta E = \sqrt{k_B T^2 C_V}. \tag{6.14}$$

Discussion
If a thermal property B is proportional to the number of particles N, then B is *extensive*; if a thermal property B is irrelevant to the total particle number N, then B is *intensive*. Some useful rules:

$$\frac{\text{extensive}}{\text{intensive}} \to \text{extensive}, \quad \frac{\text{extensive}}{\text{extensive}} \to \text{intensive}, \quad \frac{\text{intensive}}{\text{intensive}} \to \text{intensive}. \tag{6.15}$$

Therefore, $\ln \mathcal{Q} = -\beta A(N, V, T)$ is an extensive property, and $\partial^n \ln \mathcal{Q} / \partial \beta^n$ is extensive → C_V is extensive, which leads to

$$\Delta E \propto \sqrt{N}. \tag{6.16}$$

The relative energy fluctuation is

$$\frac{\Delta E}{E} = \frac{\sqrt{k_B T^2 C_V}}{E} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}. \tag{6.17}$$

At the thermodynamic limit (TDL) where $N \to \infty$, $\frac{\Delta E}{E} \to 0$. Therefore, *at the TDL, the canonical ensemble becomes equivalent to the microcanonical ensemble.*

6.3 Examples

6.3.1 Ideal gas

We first consider the simplest case: a free particle of mass m in a one-dimensional box of length L, with Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + V(r), \quad \text{where } V(r) = \begin{cases} 0, & 0 < r < L; \\ \infty, & r \leq 0 \text{ or } r \geq L. \end{cases} \tag{6.18}$$

The above potential $V(r)$ guarantees that the particle is only in the box $(0 < r < L)$. In the following, we drop the potential $V(r)$ and instead confine the integration of r in the box. The canonical partition function is

$$\mathcal{Q} = \frac{1}{h}\int_0^L \mathrm{d}r \int_{-\infty}^{\infty} \mathrm{d}p\, e^{-\beta\mathcal{H}} = \frac{1}{h}\int_0^L \mathrm{d}r \int_{-\infty}^{\infty} \mathrm{d}p\, e^{-\beta p^2/2m}. \tag{6.19}$$

Using the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} = \sqrt{\pi/\alpha}, \tag{6.20}$$

we derive the final form of $\mathcal{Q}$:

$$\mathcal{Q} = L\sqrt{\frac{2\pi m}{\beta h^2}} = L\sqrt{\frac{2\pi m k_B T}{h^2}}. \tag{6.21}$$

Define the *thermal wavelength* of a particle $\lambda = \sqrt{\beta h^2/2\pi m}$, then

$$\mathcal{Q} = \frac{L}{\lambda}. \tag{6.22}$$

Eq. (6.22) shows that the partition function of a particle in a box equal the ratio of the box length L to the thermal wavelength of the particle λ.

Next we look at N free particles in a three dimensional box with volume $V = L^3$. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^{N} V(\mathbf{r}_i), \quad \text{where } V(\mathbf{r}_i) = \begin{cases} 0, & \mathbf{r} \in \text{ box ;} \\ \infty, & \mathbf{r} \notin \text{ box .} \end{cases} \tag{6.23}$$

The partition function is given by

$$\mathcal{Q}(N,V,T) = \frac{1}{N!h^{3N}} \int_{\text{box}} \mathrm{d}^N\mathbf{r} \int \mathrm{d}^N\mathbf{p}\ \exp\left(-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}\right), \tag{6.24}$$

where $\int \mathrm{d}^N\mathbf{p} = \int \mathrm{d}\mathbf{p}_1 \cdots \int \mathrm{d}\mathbf{p}_N$. Since there are no interactions among the particles, we can safely write Eq. (6.24) as

$$\mathcal{Q}(N,V,T) = \frac{1}{N!}\left[\frac{1}{h^3}\int_{\text{box}} \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{p}\ \exp\left(-\beta\frac{\mathbf{p}^2}{2m}\right)\right]^N, \tag{6.25}$$

where the partition function of N free particles reduced to the product of N partition functions of a single particle times a factor $1/N!$. Now we only need to calculate the partition function of a single particle in a three-dimensional box.

$$\begin{aligned}
&\frac{1}{h^3}\int_{\text{box}} \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{p}\ \exp\left(-\beta\frac{\mathbf{p}^2}{2m}\right)\\
&= \frac{1}{h^3}\int_0^L \mathrm{d}r_x \int_0^L \mathrm{d}r_y \int_0^L \mathrm{d}r_z \int_{-\infty}^{\infty} \mathrm{d}p_x\ e^{-\frac{\beta p_x^2}{2m}} \int_{-\infty}^{\infty} \mathrm{d}p_y\ e^{-\frac{\beta p_y^2}{2m}} \int_{-\infty}^{\infty} \mathrm{d}p_z\ e^{-\frac{\beta p_z^2}{2m}}\\
&= \left[\frac{1}{h}\int_0^L \mathrm{d}r \int_{-\infty}^{\infty} \mathrm{d}p\ e^{-\frac{\beta p^2}{2m}}\right]^3\\
&= \left(\frac{L}{\lambda}\right)^3.
\end{aligned} \tag{6.26}$$

Therefore the partition function of N free particles in a three-dimensional box is

$$\mathcal{Q}(N,V,T) = \frac{V^N}{N!\lambda^{3N}}. \tag{6.27}$$

Knowing the partition function, we can evaluate thermal properties using the equations in Section 6.1, for example,

$$\begin{aligned}
E &= -\frac{\partial \ln \mathcal{Q}}{\partial \beta} = \frac{3}{2}Nk_BT;\\
P &= k_BT\frac{\partial \ln \mathcal{Q}}{\partial V} = \frac{Nk_BT}{V};\\
C_V &= \frac{\partial E}{\partial T} = \frac{3}{2}Nk_B.
\end{aligned} \tag{6.28}$$

6.3.2 Harmonic Oscillator (HO)

Again we start with the simplest form: a one-dimensional HO of mass m and frequency ω. The Hamiltonian is

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2. \tag{6.29}$$

The canonical partition function is

$$\begin{aligned}
\mathcal{Q}(\beta) &= \frac{1}{h}\int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}p\ e^{-\beta\left(\frac{p^2}{2m}+\frac{1}{2}m\omega^2x^2\right)}\\
&= \frac{1}{h}\int_{-\infty}^{\infty} \mathrm{d}x\ e^{-\beta m\omega^2x^2/2} \int_{-\infty}^{\infty} \mathrm{d}p\ e^{-\beta p^2/2m}\\
&= \frac{1}{h}\sqrt{\frac{2\pi m}{\beta}}\sqrt{\frac{2\pi}{m\omega^2}}\\
&= \frac{2\pi}{\beta h\omega} = \frac{1}{\beta\hbar\omega}.
\end{aligned} \tag{6.30}$$

where $\hbar = h/2\pi$.

For N indistinguishable three-dimensional harmonic oscillators, the partition function can be easily evaluated: $\mathcal{Q}(N,\beta) = 1/[N!(\beta\hbar\omega)^{3N}]$.

6.3.3 Discrete energy spectrum

Now suppose we have a system of M energy levels with energy ε_i and degeneracy g_i. The degeneracy g_i is the number of states that correspond to energy ε_i. Fig. 6.1 provides an example to understand the this setup.

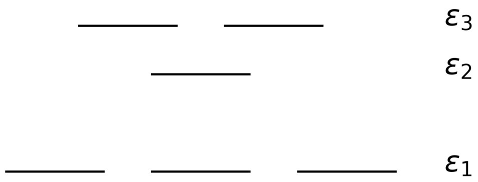


Figure 6.1: Example of a discrete energy spectrum. In this spectrum, there are three energy levels: the first level has energy ε_1 and degeneracy $g_1 = 3$, the second level has energy ε_2 and degeneracy $g_2 = 1$ and the third level has energy ε_3 and degeneracy $g_3 = 2$.

The general form of the canonical partition function of an M energy level system is

$$\mathcal{Q} = \sum_{i=1}^{M} g_i e^{-\beta\varepsilon_i} \tag{6.31}$$

Note that here we ignored the pre-factor $\frac{1}{h^{3N}N!}$ as in the previous integrals. In fact, since for the canonical ensemble, the particle number N is fixed, this pre-factor does not affect the distribution function and hence the values of thermal properties or

The expectation value of the energy is

$$E(\beta) = -\frac{\partial \ln \mathcal{Q}}{\partial \beta} = \frac{\sum_{i=1}^{M} g_i e^{-\beta\varepsilon_i}\varepsilon_i}{\mathcal{Q}} = \sum_{i=1}^{M} \varepsilon_i f_i, \tag{6.32}$$

where f_i is the distribution function over the energy spectrum

$$f_i = \frac{g_i e^{-\beta\varepsilon_i}}{\mathcal{Q}}. \tag{6.33}$$

6.4 Nosé-Hoover thermostat

The last part of this lecture is to introduce a numerical tool to simulate molecular dynamics in the canonical ensemble. Let's recall the definition of the canonical ensemble from last lecture: the canonical ensemble can be seen as a subsystem embedded in a thermal bath (environment), as shown in Fig. 6.2. The thermal bath is used to make sure that T for the system is constant.

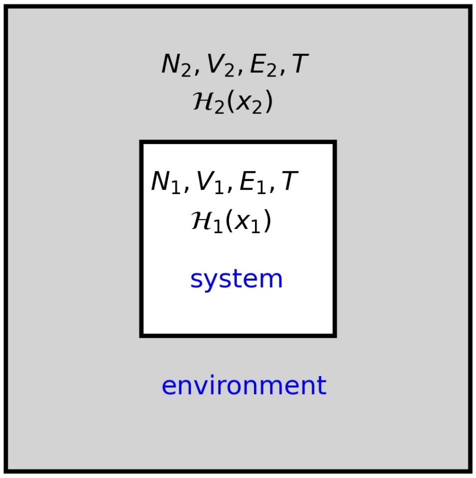


Figure 6.2: A system in contact with the environment (thermal reservoir).

Idealy (or physically) the bath should contain a large number of particles to serve as the reservoir. However we can make up a bath with a single pseudo-particle that is "powerful" enough to control the temperature of the system (like a Maxwell daemon). We use s and p_s as the generalized coordinates of this particle, where s is a dimensionless variable, and p_s has units of energy × time. Now the phase space of the total system has dimension $2dN+2$ for a d-dimensional system. The total system has a microcanonical distribution.

The temperature T corresponds to the average behavior of the kinetic energy of the system. In order to control the temperature, we *rescale* the kinetic energy. A perfect rescaling factor is the dimensionless s. We also add the kinetic energy and potential energy of this bath particle, which gives us the formulation of the *Nosê Hamiltonian*:

$$\mathcal{H}_N = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) + \frac{p_s^2}{2\mathcal{M}_s} + g k_B T \ln s, \tag{6.34}$$

where the first two terms are the Hamiltonian of the system with kinetic energy rescaled, and the last two terms are the Hamiltonian of the bath particle. The generalized mass of the bath particle $\mathcal{M}_s$ has units of energy × time^2 to make sure that the Hamiltonian has units of energy[1]. The parameter g is determined by ensuring the canonical distribution of the system.

---

[1] In the Tuckermann book, Q is used instead of $\mathcal{M}_s$, we are using $\mathcal{M}_s$ here so we don't mix it with the canonical partition function symbol.

The microcanonical partition function is

$$\Omega = \int \mathrm{d}^N \mathbf{r} \mathrm{d}^N \mathbf{p}\ \mathrm{d}s \mathrm{d}p_s\ \delta(\mathcal{H}_N - E) \tag{6.35}$$

where E is the energy of the enlarged system. We make the following substitution

$$\tilde{\mathbf{p}}_i = \frac{\mathbf{p}_i}{s}, \tag{6.36}$$

then $\mathcal{H}_N$ becomes

$$\begin{aligned} \mathcal{H}_N &= \sum_{i=1}^{N} \frac{\tilde{\mathbf{p}}_i^2}{2m_i} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) + \frac{p_s^2}{2\mathcal{M}_s} + g k_B T \ln s \\ &= \mathcal{H}(\mathbf{r}, \tilde{\mathbf{p}}) + \frac{p_s^2}{2\mathcal{M}_s} + g k_B T \ln s. \end{aligned} \tag{6.37}$$

The partition function becomes

$$\Omega = \int \mathrm{d}^N \mathbf{r} \mathrm{d}^N \tilde{\mathbf{p}}\ \mathrm{d}s \mathrm{d}p_s\ s^{dN}\ \delta\left(\mathcal{H}(\mathbf{r}, \tilde{\mathbf{p}}) + \frac{p_s^2}{2\mathcal{M}_s} + g k_B T \ln s - E\right). \tag{6.38}$$

We first integrate over s. Let $f(s) = \mathcal{H}(\mathbf{r}, \tilde{\mathbf{p}}) + p_s^2/2\mathcal{M}_s + g k_B T \ln s - E$, we integrate

$$\int \mathrm{d}s\ s^{dN} \delta(f(s)). \tag{6.39}$$

Knowing the trick

$$\delta(f(s)) = \frac{\delta(s - s_0)}{|f'(s_0)|} \tag{6.40}$$

where $f(s_0) = 0$, we get

$$\begin{aligned} & s_0 = \exp\Big[(E - \mathcal{H}(\mathbf{r}, \tilde{\mathbf{p}}) - p_s^2/2\mathcal{M}_s)/g k_B T\Big], \\ & \frac{1}{|f'(s_0)|} = \frac{s_0}{g k_B T}. \end{aligned} \tag{6.41}$$

Therefore

$$\begin{aligned} \int \mathrm{d}s\ s^{dN} \delta(f(s)) &= \int \mathrm{d}s\ s^{dN} \frac{\delta(s - s_0)}{|f'(s_0)|} \\ &= \frac{s_0^{dN}}{|f'(s_0)|} = \frac{s_0^{dN+1}}{g k_B T}. \end{aligned} \tag{6.42}$$

The partition function is

$$\begin{aligned} \Omega &= \frac{1}{g k_B T} \int \mathrm{d}^N \mathbf{r} \mathrm{d}^N \tilde{\mathbf{p}} \mathrm{d}p_s\ s_0^{dN+1} \\ &= \frac{1}{g k_B T} \int \mathrm{d}^N \mathbf{r} \mathrm{d}^N \tilde{\mathbf{p}} \mathrm{d}p_s\ \exp\Big((dN+1)\Big(E - \mathcal{H}(\mathbf{r}, \tilde{\mathbf{p}}) - p_s^2/2\mathcal{M}_s\Big)/g k_B T\Big). \end{aligned} \tag{6.43}$$

Next we integrate with p_s:

$$\begin{aligned}\Omega &= \frac{e^{(dN+1)E/gk_BT}}{gk_BT}\int \mathrm{d}^N\mathbf{r}\mathrm{d}^N\tilde{\mathbf{p}}\exp\left(-\frac{dN+1}{g}\beta\mathcal{H}(\mathbf{r},\tilde{\mathbf{p}})\right)\\ &\quad\times\int \mathrm{d}p_s\ \exp\left(-\frac{dN+1}{2\mathcal{M}_sgk_BT}p_s^2\right)\\ &= \frac{e^{(dN+1)E/gk_BT}}{gk_BT}\sqrt{\frac{2\mathcal{M}_s\pi gk_BT}{dN+1}}\int \mathrm{d}^N\mathbf{r}\mathrm{d}^N\ \tilde{\mathbf{p}}\exp\left(-\frac{dN+1}{g}\beta\mathcal{H}(\mathbf{r},\tilde{\mathbf{p}})\right).\end{aligned} \tag{6.44}$$

If we choose $g = dN + 1$, then Eq. (6.44) has the canonical partition function form:

$$\Omega = \frac{e^{E/k_BT}\sqrt{2\mathcal{M}_s\pi k_BT}}{(dN+1)k_BT}\int \mathrm{d}^N\mathbf{r}\mathrm{d}^N\tilde{\mathbf{p}}\exp\left(-\frac{dN+1}{g}\beta\mathcal{H}(\mathbf{r},\tilde{\mathbf{p}})\right). \tag{6.45}$$

Therefore, we derived a canonical partition function form with a prefactor due to the bath-particle.

Now we proved that the Nosé Hamiltonian provides the microcanonical distribution of the total system (system + bath) and a canonical distribution of the system, we can simulate the $2dN + 2$ coordinates according to the Hamilton's equations of motion:

$$\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\partial\mathcal{H}_N}{\partial\mathbf{p}_i} = \frac{\mathbf{p}_i}{m_is^2}\\ \dot{\mathbf{p}}_i &= -\frac{\partial\mathcal{H}_N}{\partial\mathbf{r}_i} = \mathbf{F}_i\\ \dot{s} &= \frac{\partial\mathcal{H}_N}{\partial p_s} = \frac{p_s}{\mathcal{M}_s}\\ \dot{p}_s &= -\frac{\partial\mathcal{H}_N}{\partial s} = \frac{1}{s}\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_is^2} - gk_BT\right].\end{aligned} \tag{6.46}$$

A more convenient expression is to change the variables:

$$\tilde{\mathbf{p}}_i = \frac{\mathbf{p}_i}{s}, \qquad \tilde{p}_s = \frac{p_s}{s}, \qquad ,\mathrm{d}\tilde{t} = \frac{\mathrm{d}t}{s} \tag{6.47}$$

and another set of equations can be derived from Eq. (6.46). Note that the system and the bath are coupled in Eq. (6.46), so one has to time evolve all the $2dN + 2$ variables to get the correct behavior of the system ($2dN$-dimension phase space).

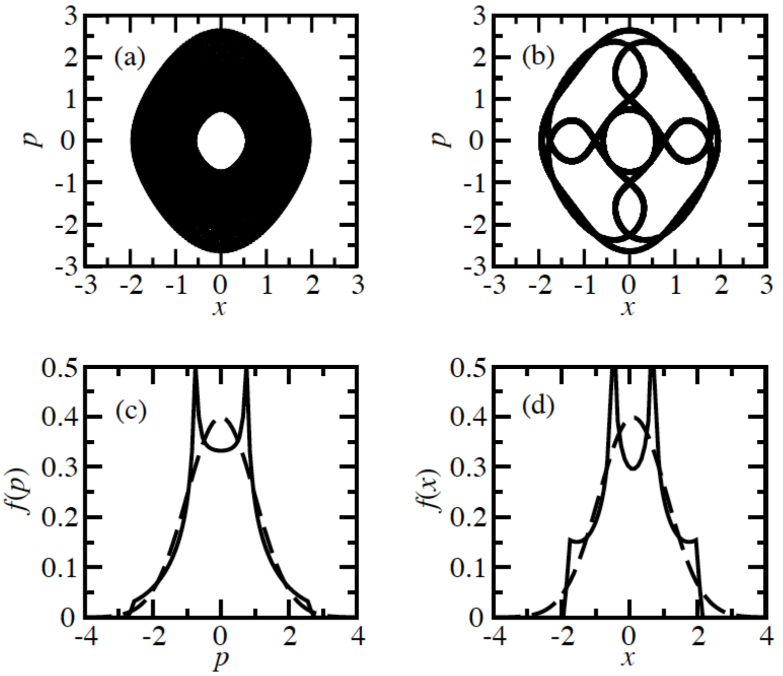


Figure 6.3: Phase space and distribution functions obtained by integrating the Nosé–Hoover equations for harmonic oscillator. (a) shows the phase space p vs. x independent of η and p_η, (b) shows the phase space for $p_\eta = \pm 0.001$; (c) and (d) show distributions $f(p)$ and $f(x)$ obtained from the simulation (solid line) compared with the correct canonical distributions (dashed line).

6.4.1 Nosé-Hoover equations

In 1985, Hoover introduced a reformulation of the Nosé equations Eq. (6.46), with the non-canonical change of variables[2]

$$\tilde{\mathbf{p}}_i = \frac{\mathbf{p}_i}{s}, \qquad \mathrm{d}\tilde{t} = \frac{\mathrm{d}t}{s}, \qquad \frac{1}{s}\frac{\mathrm{d}s}{\mathrm{d}\tilde{t}} = \frac{\mathrm{d}\eta}{\mathrm{d}\tilde{t}}, \qquad \tilde{p}_s = p_\eta, \qquad g = dN. \tag{6.48}$$

---

[2] Non-canonical change of variables means the new variables introduce a non-Hamiltonian system and do not preserve the Hamilton's equation of motion. It is hard to substitute s in Eq. (6.34) with the above change of variables.

The equations of motion then becomes

$$\begin{aligned}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - \frac{p_\eta}{\mathcal{M}_s}\mathbf{p}_i \\
\dot{\eta} &= \frac{p_\eta}{\mathcal{M}_s} \\
\dot{p}_\eta &= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - g k_B T.
\end{aligned} \tag{6.49}$$

6.4.2 Discussion on ergodicity

The term *ergodicity* is an important concept for many numerical methods related to ensemble simulations. If a method is *ergodic*, then it visits all the microstates in the ensemble (i.e., all the points in the phase space that the ensemble allows). Fig. 6.3 shows an example of simulating a harmonic oscillator with Nosé-Hoover equations. From Fig. 6.3 (*Tuckermann Fig. 4.10*) we see that the Nosé-Hoover equations are not ergodic, thus do no provide the correct distribution functions.

One way to fix the non-ergodicity of the Nosé-Hoover equations is to use the method called Nosé-Hoover chains (*Tuckermann Chapter 4.10*), and we will leave this to the students to read.

Appendix Solving Eq. (6.9)

We solve $y(x)$ from the following differential equation, with $g(x)$ given.

$$y + x\frac{\mathrm{d}y}{\mathrm{d}x} + \frac{\mathrm{d}g(x)}{\mathrm{d}x} = 0. \tag{6.50}$$

We integrate both sides w.r.t. x:

$$\begin{aligned}
&\int \mathrm{d}x\, y + \int \mathrm{d}x\, x\frac{\mathrm{d}y}{\mathrm{d}x} + \int \mathrm{d}x\, \frac{\mathrm{d}g(x)}{\mathrm{d}x} \\
&= \int \mathrm{d}x\, y + \int x\mathrm{d}y + \int \mathrm{d}g(x) \\
&= \int \mathrm{d}x\, y + \left(xy - \int \mathrm{d}x\, y\right) + g(x) \\
&= xy + g(x) = 0.
\end{aligned} \tag{6.51}$$

where we used integration by parts for $\int x\mathrm{d}y$. The solution to Eq. (6.51) is

$$y = -\frac{g(x)}{x}. \tag{6.52}$$

Lecture 7: Real Gases and Liquids

In the previous examples, we studied systems of particles without particle-particle iteractions (non-interaction systems). These systems are considered simple and can usually be solved analytically. However, systems without interactions are boring, because they can only have one *phase* (e.g. the ideal gas can only exist in the gas phase).

In this lecture, we study systems where the particle-particle interaction exists. These complicated systems can undergo *phase transitions* between different phases (e.g. solid, liquid, gas, ...). We assume that the systems we study have *canonical distribution*.

7.1 Spatial distribution function

In this section, we study the spatial distribution functions of particles, which will be useful to know the relative distribution of particles, the coordination numbers, and to evaluate thermal properties. In most realistic systems, the two-body interaction is the leading interacting term, thus we emphasize the pair-correlation function and the radial distribution function.

7.1.1 Joint probability distribution

Before we start, we review the basics of joint probability distribution. Suppose $f(x_1, x_2)$ is a distribution of variable x_1 and variable x_2, and $\int \mathrm{d}x_1 \int \mathrm{d}x_2\, f(x_1, x_2) = 1$. The value of $f(x_1, x_2)\mathrm{d}x_1\mathrm{d}x_2$ denotes the probability of the first variable being in the small volume $\mathrm{d}x_1$ around x_1 while the second variable being in the small volume $\mathrm{d}x_2$ around x_2.

We can derive the distribution of x_1 by

$$f(x_1) = \int \mathrm{d}x_2\, f(x_1, x_2). \tag{7.1}$$

Now lets consider the distribution function of N variables $f(x_1, \ldots, x_N)$. The distribution function of the first $k \le N$ variables $(x_1, \ldots, x_k)$ is

$$f(x_1, \ldots, x_k) = \int \mathrm{d}x_{k+1} \ldots \mathrm{d}x_N f(x_1, \ldots, x_k, x_{k+1}, \ldots, x_N). \tag{7.2}$$

7.1.2 Multi-particle correlation function

The general form of a Hamiltonian of a system of N indistinguishable particles is

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{7.3}$$

The kinetic term is universal for any systems, and the many-body interaction is included in the potential term $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$.

The canonical partition function is

$$\begin{aligned} \mathcal{Q}(N,V,T) &= \frac{1}{N!h^{3N}} \int \mathrm{d}^N\mathbf{p} \int \mathrm{d}^N\mathbf{r}\ e^{-\beta\mathcal{H}} \\ &= \frac{1}{N!h^{3N}} \int \mathrm{d}^N\mathbf{p}\ \exp\left(-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}\right) \times \int \mathrm{d}^N\mathbf{r}\ e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\ &= \frac{1}{N!h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}} \int \mathrm{d}^N\mathbf{r}\ e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}. \end{aligned} \tag{7.4}$$

In the last lecture, we defined the *thermal wavelength* $\lambda = \sqrt{\beta h^2/2\pi m}$, and the partition function can be expressed as

$$\mathcal{Q}(N,V,T) = \frac{1}{N!\lambda^{3N}} \int \mathrm{d}^N\mathbf{r}\ e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}. \tag{7.5}$$

We introduce the *configurational partition function*:

$$Z(N,V,T) = \int \mathrm{d}^N\mathbf{r}\ \exp[-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)], \tag{7.6}$$

then $\mathcal{Q}(N,V,T) = Z(N,V,T)/(N!\lambda^{3N})$. We have divided the partition function into the contributions from the kinetic term $1/\lambda^{3N})$ and the potential term $Z(N,V,T)$.

In the following, we will focus on phase space functions that only depends on the positions. Let $a(x) = a(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ be such a function, then

$$\begin{aligned} \langle a \rangle &= \frac{1}{\mathcal{Q}} \left[\frac{1}{N!h^{3N}} \int \mathrm{d}^N\mathbf{p} \int \mathrm{d}^N\mathbf{r}\ a(\mathbf{r}_1, \ldots, \mathbf{r}_N) e^{-\beta\mathcal{H}} \right] \\ &= \frac{1}{\mathcal{Q}} \frac{1}{N!h^{3N}} \int \mathrm{d}^N\mathbf{p}\ \exp\left(-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}\right) \times \int \mathrm{d}^N\mathbf{r}\ a(\mathbf{r}_1, \ldots, \mathbf{r}_N) e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\ &= \frac{1}{Z} \int \mathrm{d}^N\mathbf{r}\ a(\mathbf{r}_1, \ldots, \mathbf{r}_N) e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}. \end{aligned} \tag{7.7}$$

The spatial distribution function of the N particles is

$$P^{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{Z} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}. \tag{7.8}$$

One could interpret $P^{(N)}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\mathrm{d}\mathbf{r}_1\cdots\mathrm{d}\mathbf{r}_N$ as the probability of finding one particle in a small volume element $\mathrm{d}\mathbf{r}_1$ around r_1, one particle in a small volume element $\mathrm{d}\mathbf{r}_2$ around r_2, ..., and one particle in a small volume element $\mathrm{d}\mathbf{r}_N$ around r_N. An example is shown in Fig. 7.1 Now suppose we only care about the distribution of the first $k \le N$ particles,

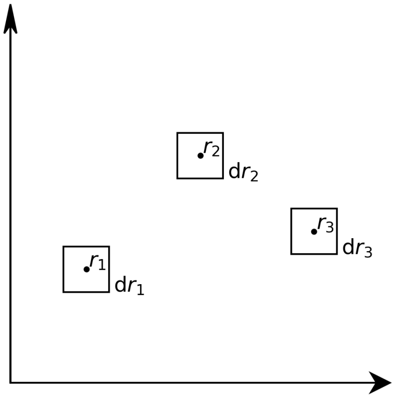


Figure 7.1: Interpretation of $P^{(N)}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\mathrm{d}\mathbf{r}_1\cdots\mathrm{d}\mathbf{r}_N$ with $N = 3$ in a two-dimensional space. $P^{(3)}(\mathbf{r}_1,\mathbf{r}_2),\mathbf{r}_3)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\mathrm{d}\mathbf{r}_3$ is the probability of each volume element ($\mathrm{d}\mathbf{r}_i$) containing one particle.

where we can get probability function by integrating the rest of the $N-k$ coordinates out:

$$P^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k)\mathrm{d}\mathbf{r}_1\cdots\mathbf{r}_k = \left[\int \mathrm{d}\mathbf{r}_{k+1}\cdots\mathrm{d}\mathbf{r}_N\ P^{(N)}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right]\mathrm{d}\mathbf{r}_1\cdots\mathrm{d}\mathbf{r}_k. \tag{7.9}$$

Since the particles are indistringuishable, we can define the distribution density of k particles as

$$\rho^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k) = k!\binom{N}{k}P^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k) \tag{7.10}$$

where the prefactor $k!\binom{N}{k} = N!/(N-k)!$ comes from the indistinguishability of the particles: $\binom{N}{k}$ is the number of combinations of choosing k particles from the N particles, and $k!$ is the number of permutations among these k particles.

Suppose the particles are evenly distributed in the space, and $\rho = N/V$ is the number density, then we can define the *k-particle correlation function as*

$$g^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k) = \frac{\rho^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k)}{\rho^k} \tag{7.11}$$

Note that when $(\mathbf{r}_1,\ldots,\mathbf{r}_k)$ is fixed,

$$\int \mathrm{d}\mathbf{r}_{k+1}\cdots\mathrm{d}\mathbf{r}_N = \int \mathrm{d}^N\mathbf{r}' \prod_{i=1}^{k}\delta(\mathbf{r}'_i - \mathbf{r}_i). \tag{7.12}$$

where $\mathrm{d}^N\mathbf{r}' = \mathrm{d}\mathbf{r}_1' \cdots \mathrm{d}\mathbf{r}_N'$. Therefore we can rewrite $g^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_k)$ as

$$\begin{aligned} g^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_k) &= \frac{N!}{(N-k)!\rho^k} \frac{1}{Z} \int \mathrm{d}^N\mathbf{r}'\, e^{-\beta U(\mathbf{r}_1', \ldots, \mathbf{r}_N')} \prod_{i=1}^{k} \delta(\mathbf{r}_i' - \mathbf{r}_i) \\ &= \frac{N!}{(N-k)!\rho^k} \left\langle \prod_{i=1}^{k} \delta(\mathbf{r}_i' - \mathbf{r}_i) \right\rangle_{\mathbf{r}_1', \ldots, \mathbf{r}_N'} \end{aligned} \tag{7.13}$$

When $k = 1$, $\rho^1(\mathbf{r})$ means the probability density of having one particle at the position $\mathbf{r}$, and since the system is homogeneous, we have

$$\rho^1(\mathbf{r}) = \frac{N}{V} = \rho, \tag{7.14}$$

therefore $g^1(\mathbf{r}) = \rho^1(\mathbf{r})/\rho = 1$. Therefore, $g^1(\mathbf{r})$ provides the information of the single particle distribution, and when $g^1(\mathbf{r}) = 1$, the system is homogeneous.

7.1.3 Radial distribution function

The pair-wise (or two-body) interaction plays an important role in determining the physics of a realistic system. In this subsection, we consider the situation where $k = 2$.

Following Eq. (7.13), the *pair correlation function* is

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{\rho^2} \langle \delta(\mathbf{r}_1' - \mathbf{r}_1)\delta(\mathbf{r}_2' - \mathbf{r}_2) \rangle_{\mathbf{r}_1', \ldots, \mathbf{r}_N'}. \tag{7.15}$$

In a homogeneous system, the $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ should not depend on the absolute positions $\mathbf{r}_1$ and $\mathbf{r}_2$. In fact, $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ should only depend on the distance between the two particles.

We introduce the *center-of-mass* coordinate with the following substitution:

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{7.16}$$

Then we can rewrite Eq. (7.15) as a function of $r = |\mathbf{r}|$:

$$\boxed{g(r) = \frac{N-1}{4\pi\rho r^2} \langle \delta(r - r') \rangle_{r', \theta, \phi, \mathbf{R}', \mathbf{r}_3', \ldots \mathbf{r}_N'}} \tag{7.17}$$

where $1/4\pi r^2$ comes from changing to the spherical coordinate for $\mathbf{r}$, i.e., (r, θ, ϕ). $g(r)$ is called the radial distribution function[1].

Picking one particle as the center, $g(r)$ denotes the likelihood of finding another particle at the distance r from the center particle, and

---

[1] We will save our time from the derivation, which can be found in Tuckerman *pp.*154 – 155.

$\rho g(r)$ = average density of particles at distance r given that a tagged particle is at the origin.

Integrating $\rho g(r)$ over the space we should find exactly $N-1$ particles,

$$\int_0^\infty 4\pi r^2 \, \rho g(r) \, \mathrm{d}r = N - 1. \tag{7.18}$$

Example 1: simple liquid structure[2]

First we see a simple atomic liquid and it's radial distribution function, as in Fig. 7.2. The particles have the so called van der Waals diameter σ. The particles can be seen as hard spheres, and the potential is simply:

$$V(r) = \begin{cases} \infty, & r \leq \sigma, \\ 0, & r > \sigma. \end{cases} \tag{7.19}$$

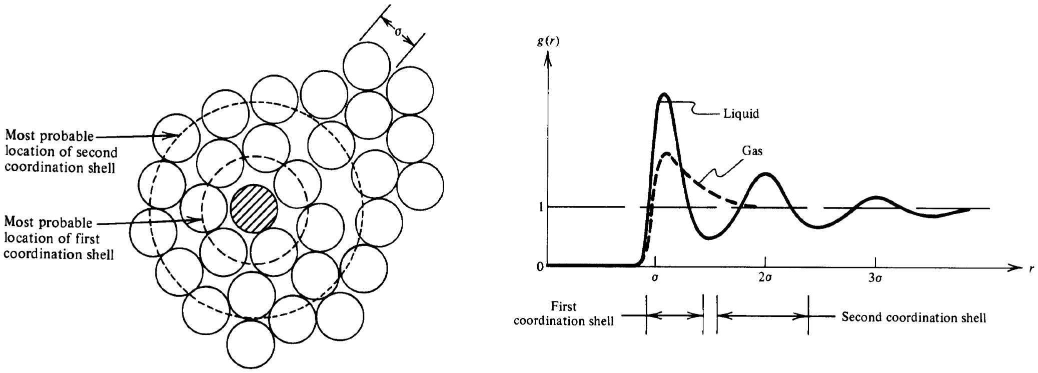


Figure 7.2: A simple liquid structure (left) and the corresponding radial distribution function $g(r)$ (left).

Example 2: Lennard-Jones potential

The Lennard-Jones potential has the form

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{7.20}$$

where ϵ is the depth of the well and when $r = \sigma$, the potential is zero.

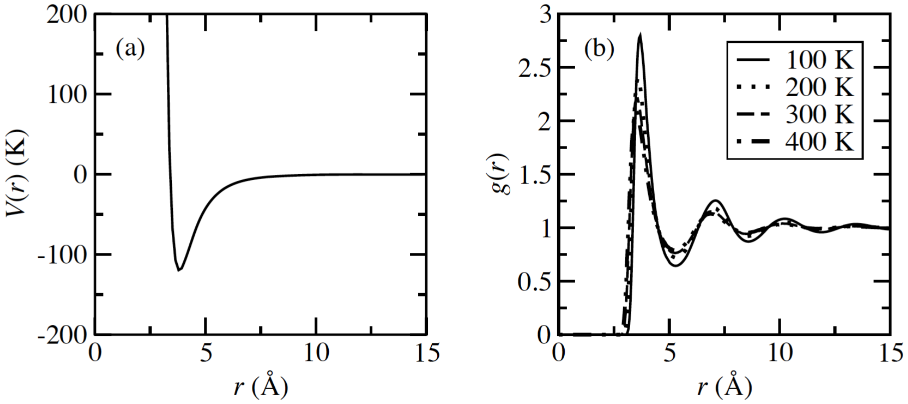


Figure 7.3: (Tuckerman Fig. 4.2) (a) Lennard-Jones potential with $\sigma = 3.405$Å and $\epsilon = 119.8K$. (b) The radial distribution funtion $g(r)$.

Fig. 7.3 shows the shape of the Lennard-Jones potential and the radial distribution function $g(r)$.[3]

Observations

1. The first (and highest) peak of $g(r)$ is close to the well of the Lennard-Jones potential, the second peak corresponds to the second layer of particle, and so on.
2. As the temperature is raised, $g(r)$ becomes flatter. Recall that temperature is related to the kinetic energy. When the kinetic energy becomes large enough, the potential energy becomes negligible, and we get the ideal gas.
3. The integration of $\rho g(r)$ up to the first peak gives the *coordination number*

$$N_1 = 4\pi\rho \int_0^{r_{\text{peak}}} r^2 g(r) \mathrm{d}r \tag{7.21}$$

7.2 Thermodynamic quantities from the spatial distribution function

In this section, we show the application of spatial distribution functions in evaluating thermodynamic quantities.

We start from the energy

$$E = \langle \mathcal{H} \rangle = \langle K(\mathbf{p}_1, \ldots, \mathbf{p}_N) \rangle + \langle U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \rangle \tag{7.22}$$

---

[2] Figures from the book *Introduction to Modern Statistical Mechanics* by David Chandler.

[3] $V(r)$ shown in this figure from Tuckerman is shifted compared to Eq. (7.18).

The integration of the first term is the kinetic energy $\langle K\rangle = \frac{3}{2}Nk_BT$; since the potential is a function of positions, we can use Eq. (7.7) to derive:

$$\langle U\rangle = \frac{1}{Z}\int \mathrm{d}^N\mathbf{r}\; U(\mathbf{r}_1,\ldots,\mathbf{r}_N)e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}. \tag{7.23}$$

Now let's consider a pair potential

$$U_{\text{pair}} = \sum_{i=1}^{N}\sum_{j>i}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|). \tag{7.24}$$

The expectation value is

$$\langle U_{\text{pair}}\rangle = \frac{1}{Z}\sum_{i=1}^{N}\sum_{j>i}^{N}\int \mathrm{d}^N\mathbf{r}\; u(|\mathbf{r}_i - \mathbf{r}_j|)e^{-\beta U_{\text{pair}}} \tag{7.25}$$

Since U_{pair} is homogeneous, the integration in Eq. (7.25) is equivalent to replacing the $N(N-1)/2$ pairs of (i,j) with $(1,2)$:

$$\begin{aligned}\langle U_{\text{pair}}\rangle &= \frac{1}{Z}\sum_{i=1}^{N}\sum_{j>i}^{N}\int \mathrm{d}^N\mathbf{r}\; u(|\mathbf{r}_1 - \mathbf{r}_2|)e^{-\beta U_{\text{pair}}}\\ &= \frac{N(N-1)}{2Z}\int \mathrm{d}^N\mathbf{r}\; u(|\mathbf{r}_1 - \mathbf{r}_2|)e^{-\beta U_{\text{pair}}}.\end{aligned} \tag{7.26}$$

Since $u(|\mathbf{r}_1 - \mathbf{r}_2|)$ only depends on $\mathbf{r}_1$ and $\mathbf{r}_2$, we can integrate the rest of position vectors first:

$$\langle U_{\text{pair}}\rangle = \frac{N(N-1)}{2Z}\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|)\left[\int \mathrm{d}\mathbf{r}_3\cdots\mathrm{d}\mathbf{r}_N\; e^{-\beta U_{\text{pair}}}\right]. \tag{7.27}$$

Substituting the expression of $g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ in Eq. (7.15) into Eq. (7.27), we get

$$\boxed{\langle U_{\text{pair}}\rangle = \frac{\rho^2}{2}\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\; u(|\mathbf{r}_1 - \mathbf{r}_2|)g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)} \tag{7.28}$$

Significance of Eq. (7.28)

1. If a Hamiltonian only contains two-particle interactions, one only needs the information of the two-particle correlation function $g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$, and the computation involves the integration of only two position variables (i.e., $\mathbf{r}_1$ and $\mathbf{r}_2$.
2. One could generalize Eq. (7.28) to the k-particle interaction case:

$$\langle U^{(k)}\rangle = \frac{\rho^k}{k!}\int \mathrm{d}\mathbf{r}_1\cdots\mathrm{d}\mathbf{r}_k\; u(\mathbf{r}_1,\ldots,\mathbf{r}_k)g^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k) \tag{7.29}$$

We can again rewrite Eq. (7.28) with radial distribution function $g(r)$, and the trick is to first transform to the center-of-mass coordinate, and then transform to the spherical coordinate,

$$\langle U_{\text{pair}}\rangle = \frac{N\rho}{2}\int_0^\infty \mathrm{d}r 4\pi r^2 u(r)g(r) = 2\pi N\rho\int_0^\infty \mathrm{d}r\ r^2 u(r)g(r). \tag{7.30}$$

With the similar procedure (Tuckerman *pp.*$162-165$), one could evaluate the pressure from

$$P = k_B T\frac{\partial}{\partial V}\ln \mathcal{Q}(N,V,T) = \frac{k_B T}{Z(N,V,T)}\frac{\partial Z(N,V,T)}{\partial V} \tag{7.31}$$

and arrive at

$$PV = Nk_B T - \frac{2\pi\rho N}{3}\int_0^\infty \mathrm{d}r\ r^3\frac{\mathrm{d}u}{\mathrm{d}r}g(r), \tag{7.32}$$

which can be seen as the state function of a two-particle interaction Hamiltonian. The first term is from the kinetic energy, and the second term is from the pair potential.

Comments

The evaluation of a Hamiltonian in quantum chemistry methods follows the similar idea. The equivalence to the k-particle correlation functions in quantum chemistry is the k-particle reduced density matrix. As you take more and more courses, you will find the similarities of some approaches. When you see a completely new problem, hopefully the basic courses you learn will provide you insights to find potential solutions.

7.3 Perturbation theory

In the previous sections, we simplified the computation of quantities related to the many-particle interaction by introducing the multi-particle correlation function. However, it is still complicated to evaluate the quantities related to the potential part.

In this section, we introduce a very useful tool: *the perturbation theory* (PT). Taylor expansion is one example of perturbation methods, where we keep the leading terms and discard the higher orders. Similarly, we can write the potential energy as

$$U = U_0 + U_1 \tag{7.33}$$

where U_0 is the leading term (also easier to compute), and U_1 is considered as a small *perturbation*.

Let's look at the configurational partition function

$$Z(N,V,T) = \int \mathrm{d}^N\mathbf{r}e^{-\beta U} = \int \mathrm{d}^N\mathbf{r}e^{-\beta(U_0+U_1)} = \int \mathrm{d}^N\mathbf{r}e^{-\beta U_0}e^{-\beta U_1} \tag{7.34}$$

We define the first order of the configurational partition function

$$Z_0(N,V,T) = \int \mathrm{d}^N\mathbf{r} e^{-\beta U_0}, \tag{7.35}$$

then

$$\begin{aligned} Z(N,V,T) &= \frac{Z_0(N,V,T)}{Z_0(N,V,T)} \int \mathrm{d}^N\mathbf{r} e^{-\beta U_0} e^{-\beta U_1} \\ &= Z_0(N,V,T)\langle e^{-\beta U_1}\rangle_0, \end{aligned} \tag{7.36}$$

where $\langle\cdots\rangle_0$ is the expectation value under the first order configurational distribution function, e.g.,

$$\langle a\rangle_0 = \int \mathrm{d}^N\mathbf{r}\; a(\mathbf{r}^N) e^{-\beta U_0}, \tag{7.37}$$

where we used $\mathbf{r}^N$ to represent $(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ for a concise expression.

Since U_1 is a small perturbation, we can expand $e^{-\beta U_1}$ with Taylor expansion,

$$\begin{aligned} \langle e^{-\beta U_1}\rangle_0 &= 1 - \beta\langle U_1\rangle_0 + \frac{\beta^2}{2!}\beta\langle U_1^2\rangle_0 - \cdots \\ &= \sum_{l=1}^{\infty} \frac{(-\beta)^l}{l!}\langle U_1^l\rangle_0. \end{aligned} \tag{7.38}$$

To show how perturbation theory works, let's keep the first order:

$$\langle e^{-\beta U_1}\rangle_0 \approx 1 - \beta\langle U_1\rangle_0. \tag{7.39}$$

We evaluate the Helmholtz free energy, which is the key to evaluate other thermodynamic quantities.

$$\begin{aligned} A = -\frac{1}{\beta}\ln\mathcal{Q} &= -\frac{1}{\beta}\ln\frac{Z}{N!\lambda^{3N}} \\ &= -\frac{1}{\beta}\ln\frac{Z_0}{N!\lambda^{3N}} - \frac{1}{\beta}\ln\langle e^{-\beta U_1}\rangle_0. \end{aligned} \tag{7.40}$$

Let

$$A = A^{(0)} + A^{(1)}, \tag{7.41}$$

then the zeroth order of A is simply

$$A^{(0)} = -\frac{1}{\beta}\ln\frac{Z_0}{N!\lambda^{3N}}. \tag{7.42}$$

For the perturbation part

$$\begin{aligned} A^{(1)} &= -\frac{1}{\beta}\ln\langle e^{-\beta U_1}\rangle_0 \\ &\approx -\frac{1}{\beta}\ln(1-\beta\langle U_1\rangle_0) \end{aligned} \tag{7.43}$$

Using the Taylor expansion of $\ln(1-x)\approx -x$, we get

$$A^{(1)} = \langle U_1\rangle_0 + \cdots. \tag{7.44}$$

A more rigorous way to find the whole expansion is provided in the Tuckerman book *pp.*167 – 170 called *cumulant expansion*, which gives

$$A^{(1)} = \langle U_1\rangle_0 + \sum_{l=2}^{\infty}\frac{(-\beta)^{l-1}}{l!}\langle (U_1-\langle U_1\rangle_0)^l\rangle. \tag{7.45}$$

For a pair-wise potential, following Eq. (7.30),

$$\langle U_1\rangle_0 = 2\pi N\rho\int_0^{\infty}\mathrm{d}\, r r^2 u_1(r) g_0(r), \tag{7.46}$$

where $g_0(r)$ is the zeroth order of the radial distribution function.

Example: van der Waals equation of state (EOS)

We consider the zeroth order of the potential energy to be the hard sphere potential

$$u(r) = \begin{cases} \infty, & r\le\sigma, \\ 0, & r>\sigma. \end{cases}, \tag{7.47}$$

and

$$g_0(r) \approx e^{-\beta r_0(r)} = \begin{cases} 0, & r\le\sigma, \\ 1, & r>\sigma. \end{cases} = \theta(r-\sigma). \tag{7.48}$$

where $\theta(r-\sigma)$ is called a step function.

We evaluate Z_0 first

$$\begin{aligned} Z_0 &= \int \mathrm{d}^N\mathbf{r}e^{-\beta U_0} \\ &= \int \mathrm{d}^N\ \mathbf{r}e^{-\beta\sum_{j>i=1}^N u_0(|\mathbf{r}_i-\mathbf{r}_j|)} \\ &= \int \mathrm{d}^N\ \mathbf{r}\prod_{j>i=1}^{N} e^{-\beta u_0(|\mathbf{r}_i-\mathbf{r}_j|)}. \end{aligned} \tag{7.49}$$

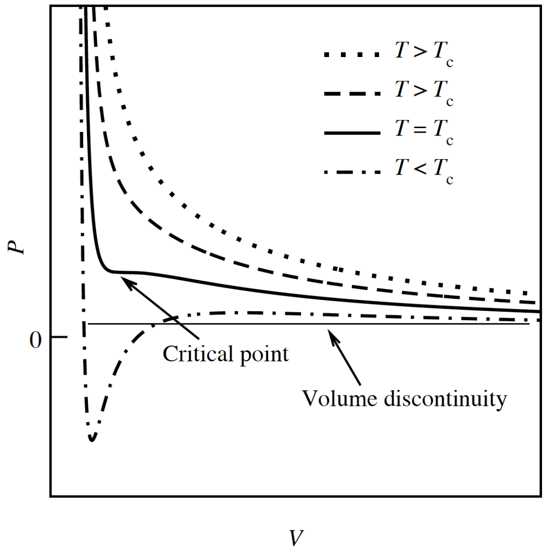


Figure 7.4: (Tuckerman Fig. 4.8) Isotherms of the van der Waals equation of state for four different temperatures.

If $|\mathbf{r}_i - \mathbf{r}_j| < \sigma$ for any (i, j) pair, then the integral is zero, therefore, we should integrate all $\mathbf{r}^N$ in the available volume:

$$\begin{aligned} Z_0 &= \int_{D(V_{\text{avail}})} \mathrm{d}^N\, \mathbf{r} \times 1 = V_{\text{avail}}^N \\ &= \left(V - \frac{2N\pi\sigma^3}{3}\right)^N \\ &= (V - Nb)^N. \end{aligned} \tag{7.50}$$

Next we evaluate $A^{(1)}$,

$$\begin{aligned} A^{(1)} &= 2\pi N\rho \int_0^\infty \mathrm{d}r\, r^2 u_1(r) g_0(r) \\ &= 2\pi N\rho \int_0^\infty \mathrm{d}r\, r^2 u_1(r)\theta(r-\sigma) \\ &= 2\pi N\rho \int_\sigma^\infty \mathrm{d}r\, r^2 u_1(r) \\ &\equiv -aN\rho, \end{aligned} \tag{7.51}$$

where

$$a = -2\pi \int_\sigma^\infty \mathrm{d}r\, r^2 u_1(r) > 0 \tag{7.52}$$

is a parameter depending on the specific potential form. Therefore,

$$A \approx -\frac{1}{\beta} \ln\left[\frac{(V-Nb)^N}{N!\lambda^3}\right] - \frac{aN^2}{V}. \tag{7.53}$$

The pressure is

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2}, \tag{7.54}$$

which turns into

$$\boxed{(P + \frac{aN^2}{V^2})(V - Nb) = Nk_BT = nRT}, \tag{7.55}$$

where R is the Avogadro's number, and n is the number of mols. We see that the van der Waals EOS modified the potential and volume in the ideal gase EOS based on the real potential.

Finally we see how this U_1 brings phase transition by analyzing a isotherm plot of the van der Waals equation of state in Fig. 7.4.

The critical temperature T_c is a important value in which:

1. $T < T_c$: liquid-gas phase transition exists.
2. $T > T_c$: there is only one phase (gas phase for this example).

Lecture 8: Grand Canonical Ensemble

In the previous lectures, we discussed the microcanonical ensemble (or the NVE ensemble) and canonical ensemble (or the NVT ensemble). One should expect other types of ensembles depending on the specific problem of interest. Here is a list of common ensembles:

- Microcanonical ensemble - NVE
- Canonical ensemble - NVT
- Grand canonical ensemble - μVT
- Isoenthalpic-isobaric ensemble - NPH ($H = E + PV$ is the enthalpy.)
- Isothermal-isobaric ensemble - NPT

The key property of an ensemble is the *partition function*, which connects the distribution of microstates and the thermodynamic quantities. In the following, we will discuss the grand canonical ensemble, which is the last classical ensemble we will cover in this class.

8.1 Partition function of the grand canonical ensemble

A direct derivation of the grand canonical partition function $\mathcal{Z}(\mu, V, T)$ can be found in Tuckerman $pp.264-268$, here we introduce an intuitive approach to get the expression of $\mathcal{Z}(\mu, V, T)$.

In the previous lectures, we found that the natural thermodynamic quantities for the microcanonical ensemble and the canonical ensemble are,

$$\begin{aligned} &\text{microcanonical ensemble - entropy} \quad S(N,V,E) = k_B \ln \Omega, \\ &\text{canonical ensemble - Helmholtz free energy} \quad A(N,V,T) = E - TS = -\frac{1}{\beta}\ln Q. \end{aligned} \tag{8.1}$$

We can assume that the natural quantity[1], say $\tilde{A}(\mu, V, T)$, for the grand canonical ensemble has a similar connection to $\mathcal{Z}(\mu, V, T)$ as Eq. (8.1).

---

[1] One could prove that $\tilde{A} = -PV$ using Euler's theorem (Tuckerman 6.2).

First we find out the expression of $\tilde{A}(\mu, V, T)$ with Legendre transformation. Starting from the Helmholtz free energy

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N, \tag{8.2}$$

we replace $\mu\mathrm{d}N$ with $N\mathrm{d}\mu$:

$$\mathrm{d}\tilde{A} = \mathrm{d}(A - \mu N) = -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu. \tag{8.3}$$

where $\tilde{A} = A - \mu N = E - TS - \mu N$, and

$$\tilde{A} = -\frac{1}{\beta}\ln\mathcal{Z}. \tag{8.4}$$

Given a fixed particle number N_i, we have

$$-\frac{1}{\beta}\ln\mathcal{Z}(\mu, V, T; N_i) = A(N_i, V, T) - \mu N_i = -\frac{1}{\beta}\ln\mathcal{Q}(N_i, V, T) - \mu N_i, \tag{8.5}$$

which gives

$$\mathcal{Z}(\mu, V, T; N_i) = e^{\beta\mu N_i}\mathcal{Q}(N_i, V, T). \tag{8.6}$$

Since the particle number N_i can fluctuate from 0 to ∞, we need to sum over all possible N_i values

$$\mathcal{Z}(\mu, V, T) = \sum_{N_i=0}^{\infty}\mathcal{Z}(\mu, V, T; N_i). \tag{8.7}$$

Thus we get the final expression of $\mathcal{Z}(\mu, V, T)$:

$$\boxed{\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta\mu N}\mathcal{Q}(N, V, T)}, \tag{8.8}$$

where $\mathcal{Q}(N, V, T)$ is the canonical partition function

$$\mathcal{Q}(N, V, T) = \frac{1}{N!h^{3N}}\int \mathrm{d}x\, e^{-\beta\mathcal{H}(x,N)}. \tag{8.9}$$

8.2 Thermodynamic quantities

$$
\begin{aligned}
\langle N\rangle(\mu,V,T) &= -\left(\frac{\partial \tilde{A}}{\partial \mu}\right)_{V,T} = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{V,T} = \frac{1}{\mathcal{Z}}\sum_{N=0}^{\infty} N e^{\beta\mu N}\mathcal{Q}, \\
E(\mu,V,T) &= -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{\mu,V} = \frac{1}{\mathcal{Z}}\sum_{N=0}^{\infty}\left[-\left(\frac{\partial \ln \mathcal{Q}}{\partial \beta}\right)_{N,V} - \mu N\right] e^{\beta\mu N}\mathcal{Q} \\
P(\mu,V,T) &= -\left(\frac{\partial \tilde{A}}{\partial V}\right)_{\mu,T} = \frac{1}{\mathcal{Z}}\sum_{N=0}^{\infty}\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Q}}{\partial V}\right)_{N,T} e^{\beta\mu N}\mathcal{Q}, \\
S(\mu,V,T) &= -\left(\frac{\partial \tilde{A}}{\partial T}\right)_{\mu,V} = k_B \ln \mathcal{Z} + \frac{1}{\mathcal{Z}}\sum_{N=0}^{\infty}\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Q}}{\partial T}\right)_{N,V} e^{\beta\mu N}\mathcal{Q}.
\end{aligned}
\tag{8.10}
$$

where $\langle N\rangle$ denotes the average of the particle numbers.

Recall that for the canonical ensemble, we had

$$
\begin{aligned}
E(N,V,T) &= -\left(\frac{\partial \ln \mathcal{Q}}{\partial \beta}\right)_{N,V}, \\
P(N,V,T) &= \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Q}}{\partial V}\right)_{N,T}, \\
S(N,V,T) &= k_B \ln \mathcal{Q} + \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Q}}{\partial T}\right)_{N,V}.
\end{aligned}
\tag{8.11}
$$

We can see the connection between quantities of canonical ensembles and quantities of grand canonical ensembles.

Example: ideal gas

For ideal gas, we know that the canonical partition function is

$$
\mathcal{Q}(N,V,T) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N. \tag{8.12}
$$

where $\lambda = \sqrt{\beta h^2/2\pi m}$ is the thermal wavelength. Therefore the grand canonical partition function is

$$
\mathcal{Z}(\mu,V,T) = \sum_{N=0}^{\infty} e^{\beta\mu N}\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N = \sum_{N=0}^{\infty}\frac{1}{N!}\left(\frac{V e^{\beta\mu}}{\lambda^3}\right)^N = e^{V e^{\beta\mu}/\lambda^3}, \tag{8.13}
$$

where we used $e^x = \sum_{k=0}^{\infty} x^k/k!$.

We evaluate the thermal quantities in Eq. (8.10).

$$\langle N\rangle = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{V,T} = PV/k_B T \tag{8.14}$$

Therefore we get the equation of state for ideal gas:

$$PV = \langle N\rangle k_B T. \tag{8.15}$$

We can also evaluate the energy

$$E = -\frac{\partial}{\partial \beta}\ln \mathcal{Z} = \frac{3}{2}\langle N\rangle k_B T. \tag{8.16}$$

The entropy is

$$S = \frac{5}{2}\langle N\rangle k_B + \langle N\rangle k_B \ln\left(\frac{V}{\langle N\rangle \lambda^3}\right). \tag{8.17}$$

8.3 Particle number fluctuation

The particle number fluctuation is defined as

$$\Delta N = \sqrt{\langle N^2\rangle - \langle N\rangle^2}. \tag{8.18}$$

We will skip the calculation of ΔN (see Tuckerman Chapter 6.6) and give the conclusion here

$$\begin{aligned} \Delta N &\propto \sqrt{\langle N\rangle} \\ \frac{\Delta N}{\langle N\rangle} &\propto \frac{1}{\sqrt{\langle N\rangle}}. \end{aligned} \tag{8.19}$$

Therefore, at thermodynamic limit, where $\langle N\rangle \to \infty$, the grand canonical ensemble is equivalent to the canonical ensemble and the microcanonical ensemble.

Lecture 9: Monte Carlo

The Monte Carlo methods are introduced as *sampling techniques* to reproduce certain distributions or perform integrations. As a warm-up, we see an example of evaluating the area of a circle with random sampling.

Example: area of a circle

Suppose we do not know the formula of the area of a circle, but we know the formula of the area of a square. We can set up the following experiment (Fig. 9.1): prepare a square with side length $2r$, and fit the circle with radius r into it; then we randomly throw N balls into the square, and the position where a ball lands is uniformly distributed; we count the number of balls that fall into the circle N_c (pink dots in Fig. 9.1), and the area of the circle is approximated by

$$\text{Area of the circle} \approx 4r^2 \frac{N_c}{N}. \tag{9.1}$$

We can also evaluate the value of $\pi \approx 4N_c/N$.

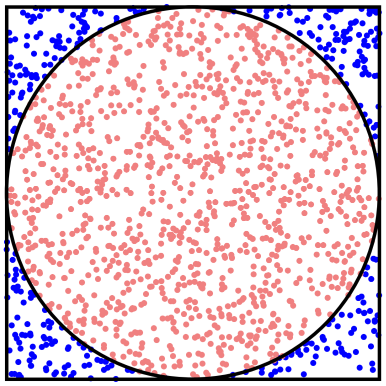


Figure 9.1: Evaluating the area of a circle by random sampling.

9.1 Calculating observables with random sampling

One essential task of the Monte Carlo methods in statistical mechanics is to evaluate the expectation values of physical observables at equilibrium, with the general formula

$$\langle a \rangle = \int \mathrm{d}x \; a(x) f(x), \tag{9.2}$$

where x is an n-dimensional vector, $a(x)$ is the value of the observable at x, and $f(x)$ is the probability distribution function satisfying

$$\begin{aligned} f(x) &\geq 0, \\ \int \mathrm{d}x \; f(x) &= 1. \end{aligned} \tag{9.3}$$

The integration in Eq. (9.2) is usually expensive to evaluate, and the numerical integration methods can sometimes perform poorly depending on the shape of $f(x)$.

The random sampling approach provides an efficient and accurate way to estimate Eq. (9.2), described as following: randomly sample M points from the distribution $f(x)$: $\{x_1, ..., x_M\}$, then Eq. (9.2) can be estimated by

$$\langle a \rangle = \int \mathrm{d}x \; a(x) f(x) \approx \frac{1}{M} \sum_{i=1}^{M} a(x_i) = \bar{a}. \tag{9.4}$$

Note that on the right hand side of Eq. (9.4), we do not have $f(x_i)$, because $f(x)$ is already encoded in the process of sampling $\{x_1, ..., x_M\}$.

The law of large numbers

The *law of large numbers* guarantees that as $M \to \infty$, the random sampling result becomes exact:

$$\int \mathrm{d}x \; a(x) f(x) \overset{M\to\infty}{=} \frac{1}{M} \sum_{i=1}^{M} a(x_i). \tag{9.5}$$

or $\langle a \rangle \overset{M\to\infty}{=} \bar{a}$.

Central limit theorem

The central limit theorem (CLT)[1] describes the behavior of *the mean* of a set of randomly sampled data. Suppose now we have N sets of random variables drawn from the distri-

---

[1] The derivation can be found in Tuckerman 7.2.

bution $f(x)$ with different means of $a(x)$:

$$\begin{gathered}
\text{Set 1: } \{x_{1,i}, ..., x_{1,M}\} \rightarrow \bar{a}_1 \\
\cdots \\
\text{Set N: } \{x_{N,i}, ..., x_{N,M}\} \rightarrow \bar{a}_N
\end{gathered}$$

Then no matter what $f(x)$ is, the means $\bar{a}_1, \ldots, \bar{a}_N$ tend to display a *normal distribution*

$$g(\bar{a}) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\bar{a}-\mu}{\sigma}\right)^2} \tag{9.6}$$

with

$$\begin{aligned}
\mu &= \langle a \rangle \\
\sigma &= \frac{\sigma_a}{\sqrt{M}}.
\end{aligned} \tag{9.7}$$

where σ_a is the standard deviation of $a(x)$ under the distribution of $f(x)$.

The central limit theorem leads to the law of large numbers.

9.2 Markov chain Monte Carlo (MCMC)

This section provides an algorithm to draw samples from any distribution functions and evaluate observables. For common distribution functions, such as the uniform distribution and the normal distribution, they can be simply generated by a module from programming packages. For instance, with PYTHON, one could call `numpy.random.uniform()` to draw one or multiple samples from a uniform distribution, or `numpy.random.normal()` for a normal distribution. But what if the distribution is arbitrary?

In this section, we introduce an *acceptance-rejection* procedure to generate a sequence of samples $x_1 \rightarrow x_2 \rightarrow \cdots \rightarrow x_M$, called a *Markov chain*. $x_i \rightarrow x_j$ means that x_j is generated based on x_i. We first give the algorithm to generate a Markov Chain, called the *Metropolis* algorithm, see Algorithm 1. Then we prove that the samples generated from this algorithm display the correct probability distribution.

9.2.1 Metropolis algorithm

We define the following important concepts in the algorithm:

- *Candidate-generating probability*

  $T(y|x)$ is a rule of generating a trial (proposed move) to y from x. $T(y|x)$ does not depend on the distribution $f(x)$, but depends on the nature of x. For instance, if x

denotes a spatial position, then jumping to a closer point is easier than jumping to a farther point. $T(x_j|x_i)$ satisfies

$$\int \mathrm{d}y\, T(y|x) = 1. \tag{9.8}$$

For many cases, we have $T(y|x) = T(x|y)$.

- *Acceptance ratio*

  $$r(y|x) = \frac{T(y|x)f(x)}{T(x|y)f(y)}. \tag{9.9}$$

  Note that $r(y|x)$ can be greater than 1. If $T(y|x) = T(x|y)$, then we simply have $r(y|x) = f(y)/f(x)$.

- *Acceptance probability*

  $$A(y|x) = \min[1, r(y|x)]. \tag{9.10}$$

- *Transition probability*

  $$R(y|x) = A(y|x)T(y|x). \tag{9.11}$$

  $R(y|x)$ depends on both the distribution $f(x)$ and the nature of x.

- *Detailed balance*

  $$R(y|x)f(x) = R(y|x)f(x). \tag{9.12}$$

  The detailed balance states that at equilibrium, each elementary process is at equilibrium, and the transitions are *reversible*.

Note: the rejection step is important to fulfill ergodicity.

9.2.2 Proof of the correct distribution

Let $\pi_M(x)$ be the probability distribution generated by the Metropolis algorithm, where M is the number of samples. We prove that

$$\lim_{M\to\infty} \pi_M(x) = f(x) \tag{9.13}$$

We use the mathematical induction:

- Since x_0 is a single point, we can say that it is under any distribution.

Algorithm 1 Metropolis Algorithm

```
Input: $f(x)$, $T(y|x)$, number of samples $M$.
  Generate an arbitrary starting point $x_0$
  i = 0
  while i < $M-1$ do
      Evaluate the observable at $x_i$: $a_i = a(x_i)$.
      Pick the next trial point $x_{\text{new}}$.                    ▷ Explained later.
      Calculate the acceptance ratio $r(x_{\text{new}}|x_i) = \frac{T(x_i|x_{\text{new}})f(x_{\text{new}})}{T(x_{\text{new}}|x_i)f(x_i)}$.
      if $r(x_{\text{new}}|x_i) \geq 1$ then
          Accept the move and $x_{i+1} = x_{\text{new}}$.
      else
          Generate a random number $\xi$ from the uniform distribution between $[0,1)$.
          if $r(x_{\text{new}}|x_i) > \xi$ then
              Accept the move and $x_{i+1} = x_{\text{new}}$.
          else
              Reject the move and $x_{i+1} = x_i$.                   ▷ $x_{i+1}$ is a copy of $x_i$
          end if
      end if
      i = i + 1
  end while
  Evaluate the approximated expectation value $\bar{a} = \sum_{i=1}^{M} a_i$.
Output: $\{x_0, ..., x_{M-1}\}$, $\bar{a}$.
```

- We assume $\pi_k(x) = f(x)$, and prove that $\pi_{k+1}(x) = f(x)$. The probability distribution of a point x is composed of two parts: (1) probability of transition from another point y to x; (2) probability of getting rejected to move from x to another point y.

$$\begin{aligned} p_1 &= \int A(x|y)T(x|y)\pi_k(y)\mathrm{d}y = \int A(y|x)T(y|x)\pi_k(x)\mathrm{d}y \\ p_2 &= \int [1 - A(y|x)]T(y|x)\pi_k(x)\mathrm{d}y \end{aligned} \tag{9.14}$$

  where the second equal sign for p_1 is due to the detailed balance. Therefore

$$\pi_{k+1}(x) = (1) + (2) = \pi_k(x) = f(x) \tag{9.15}$$

- Therefore the Markov chain drawn with the Metropolis has the correct distribution.

9.2.3 Picking the next trial point

We discuss how to pick the next trial point. Since the Markov Chain Monte Carlo method is based on detailed balance, one usually chooses a small change at each step.

In the following, we assume $T(x|y)$ has the following uniform form

$$T(x|y) = \begin{cases} \frac{1}{\Delta}, & |x-y| < \Delta/2, \\ 0, & \text{otherwise.} \end{cases} \tag{9.16}$$

which leads to $T(x|y) = T(y|x)$.

For an N-particle d-dimensional homogeneous system, the procedure is

- Choose a step size Δ.
- Generate a uniform random integer $n \in [1, N]$ as the index of the chosen particle.
- Generate d uniform random real numbers $\{\xi_1, ..., \xi_d\} \in [-0.5, 0.5]$.
- Move the position of the nth particle:

$$r_{n,\alpha} \to r_{n,\alpha} + \frac{1}{\sqrt{d}}\xi_\alpha \Delta, \quad \alpha = 1, ..., d. \tag{9.17}$$

9.2.4 Discussion

The Monte Carlo methods form a big family, and there are so many more aspects to be included in order to improve the performance of the MC code, for instance

- Convergence. The error is proportional to $1/\sqrt{M}$.
- Parallelization. Once could start with many different x_0 values, and perform MC simulations parallelly. The final result will be the mean of the results from all the MC simulations.
- Warm-up. To make sure that the MC result is not biased due to the initial value x_0, one usually discards the first several values (~ 10), which are called the warm-up steps.
- Time correlation. Since a new MC sample is generated from the last one, therefore the samples are not fully independent. The real error is generally larger than the error calculated from all the samples. One can use the batching (or blocking) strategy to evaluate the correct error.

Lecture 10: Quantum Gases

10.1 Basics of quantum mechanics

As the word *quantum* suggests, when going from classical to quantum, one moves from a continuous picture to a *quantized* picture.

$$\int \mathrm{d}x \rightarrow \sum_{v} \tag{10.1}$$

In the following, we will introduce/review the basic concepts in quantum mechanics in this quantized picture.

Hamiltonian

We learned that the classical Hamiltonian is the key to (1) guide the time evolution of microstates via the Hamilton's EOM and to (2) provide the statistical behavior via the partition functions. The *quantum Hamiltonian* plays similar roles and has the same significance as the classical one - an operator related to the total energy of the system.

$$\hat{H} = \hat{K} + \hat{V}, \tag{10.2}$$

where $\hat{K}$ is the kinetic energy operator, and $\hat{V}$ is the potential energy operator. The hat sign is used to denote a *quantum operator*. Any observable has a corresponding quantum operator, e.g., the position operator $\hat{\mathbf{r}}$ and the momentum operator $\hat{\mathbf{p}}$.

Quantum states

Another important concept is the *quantum state*, which can be represented by a *ket* $|\psi\rangle$, whose complex conjugate transpose is $\langle\psi|$ - called a *bra*. A quantum state can be seen as an analog to the microstate. One main difference compared to a classical microstate is that a quantum state can be a *superposition* of other quantum states

$$|\Psi\rangle = \sum_{v} c_v |\psi_v\rangle, \tag{10.3}$$

where $\{|\psi_i\rangle\}$ is called a basis set, and $\{c_i\}$ are the linear combination coefficients. On the contrary, a classical system can only be at one microstate at a time.

The overlap of two quantum states is evaluated by $\langle\psi|\phi\rangle$. If a state $|\psi\rangle$ is *normalized*, then $\langle\psi|\psi\rangle = 1$; if two states $|\psi\rangle$ and $|\phi\rangle$ are orthogonal to each other, then $\langle\psi|\phi\rangle = 0$.

Eigenstates and eigen-energies

For a given Hamiltonian $\hat{H}$, there exists a set of multi-particle quantum states $\{|\psi_v\rangle\}$ that satisfy

$$\hat{H}|\psi_v\rangle = E_v|\psi_v\rangle, \tag{10.4}$$

where $\{|\psi_v\rangle\}$ are called the eigenstates of the Hamiltonian, and $\{E_v\}$ are the corresponding eigen-energies. The set $\{|\psi_v\rangle\}$ forms an orthonormal basis set[1] for the Hilbert space of the $\hat{H}$, and

$$\hat{H} = \sum_v E_v|\psi_v\rangle\langle\psi_v|. \tag{10.5}$$

Expectation values

The expectation value of a quantum operator $\hat{O}$ at state $|\Psi\rangle$ is evaluate by

$$\langle\Psi|\hat{O}|\Psi\rangle. \tag{10.6}$$

e.g., $E_v = \langle\psi_v|\hat{H}|\psi_v\rangle$.

The trace of an operator can be evaluated by

$$\mathrm{Tr}[\hat{O}] = \sum_v \langle\psi_v|\hat{O}|\psi_v\rangle, \tag{10.7}$$

where $\{|\psi_v\rangle\}$ is an orthonormal basis set, such as the eigenstates of the Hamiltonian.

10.2 Quantum statistical mechanics

Canonical ensemble

We start from the *canonical* quantum ensemble, and provide the following comparison between classical and quantum pictures.

---

[1] Orthonormal: $\langle\psi_v|\psi_w\rangle = \delta_{vw}$.

Classical	**Quantum**
Distribution function $f(x) = \frac{e^{-\beta\mathcal{H}}}{\int \mathrm{d}x\, e^{-\beta\mathcal{H}}}$	Density matrix $\hat{\rho} = \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}[e^{-\beta\hat{H}}]}$
Partition function $Q(N,V,T) = c\int \mathrm{d}x\, e^{-\beta\mathcal{H}}$	$Q = \mathrm{Tr}[e^{-\beta\hat{H}}]$
Thermal average $\langle A(x)\rangle = \frac{\int \mathrm{d}x\, f(x)A(x)}{\int \mathrm{d}x\, f(x)}$	$\langle\hat{A}\rangle = \mathrm{Tr}[\hat{\rho}\hat{A}]$
Time evolution $\frac{\partial f}{\partial t} = \{\mathcal{H}, f\}$	$\frac{\partial\hat{\rho}}{\partial t} = -i[\hat{H},\hat{\rho}] = -i(\hat{H}\hat{\rho} - \hat{\rho}\hat{H})$

In the above table, the *density matrix* $\hat{\rho}$ is a new concept. It plays the same role as the distribution function $f(x)$ - telling the probability distribution of the quantum states.

If the eigen-energies $\{E_v\}$ and eigenstates $\{|\psi_v\rangle\}$ of the Hamiltonian are known, we can rewrite the above quantities by

$$\begin{aligned}
\hat{\rho} &= \frac{1}{Q}\sum_v e^{-\beta E_v}|\psi_v\rangle\langle\psi_v| \\
Q &= \mathrm{Tr}[e^{-\beta\hat{H}}] = \sum_v \langle\psi_v|e^{-\beta\hat{H}}|\psi_v\rangle = \sum_v e^{-\beta E_v} \\
\langle\hat{A}\rangle &= \mathrm{Tr}[\hat{\rho}\hat{A}] = \frac{1}{Q}\sum_v \langle\psi_v|\hat{A}e^{-\beta\hat{H}}|\psi_v\rangle = \frac{\sum_v e^{-\beta E_v}\langle\psi_v|\hat{A}|\psi_v\rangle}{\sum_v e^{-\beta E_v}}.
\end{aligned} \tag{10.8}$$

Grand canonical ensemble

For the grand canonical ensemble, we need to consider the fluctuation of the particle number, and the corresponding statistical quantities are

$$\begin{aligned}
\text{Density matrix: } \hat{\rho} &= \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathrm{Tr}[e^{-\beta(\hat{H}-\mu\hat{N})}]} \\
\text{Partition function: } Z &= \mathrm{Tr}[e^{-\beta(\hat{H}-\mu\hat{N})}] \\
\text{Thermal average: } \langle\hat{A}\rangle &= \mathrm{Tr}[\hat{\rho}\hat{A}]
\end{aligned} \tag{10.9}$$

where $\hat{N}$ is the particle number operator. When rewriting the trace with summation, one needs to consider the summation of all possible particle numbers, from 0 to the maximum possible number N_{max}.

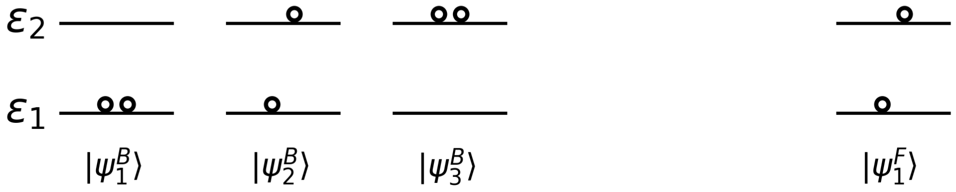
10.3 Ideal gas of indistinguishable quantum particles

In this section, we will derive the distributions of real particles, *bosons* and *fermions*, in a *non-interacting picture*. Examples of bosons and fermions: photons and gluons are bosons, while electrons and protons are fermions. We will also learn the corresponding statistical distributions: the *Bose-Einstein distribution* for bosons, and the *Fermi-Dirac distribution* for fermions. We will then go to the classical limit and derive the *Boltzman distribution*.

We start from the discussion of the properties of bosons and fermions.

10.3.1 Occupation numbers

Bosons are particles with integer spins (1, 2, . . .), and fermions with odd half-integer spins (1/2, 3/2,. . .). This leads to different parity symmetries[2] and thus different occupation patterns: *there can be an arbitrary number of bosons on a single-particle state, while no two fermions can occupy the same single-particle state*[3] Note that the term *single-particle state* doesn't mean that only one particle can occupy this state; rather it describes a state of one particle. In chemistry, we call a single-particle state an *orbital*. We illustrate the above difference in an example of putting two particles in two single-particle states, shown in Fig. 10.1. In Fig. 10.1, bosons can have three different arrangements, while fermions only have one valid arrangement due to the Pauli exclusion principle.



(a) Possible configurations of two bosons. (b) Possible configurations of two fermions.

Figure 10.1: Possible configurations of putting two particles onto two single-particle states. (a) there are three configurations for bosons; (b) there is only one configuration for fermions.

We call an arrangement of occupations a *multi-particle state*, or a *configuration* $|\psi\rangle$. Note that we use E for energies of multi-particle states, and ε for energies of single-particle states. Suppose the occupation number of level-ε_j is n_j, then we can simply use the occupation numbers to specify a configuration:

$$\text{configuration } |\psi_v\rangle : (n_1^v, n_2^v, \dots, n_j^v, \dots). \tag{10.10}$$

The total particle number and total energy of $|\psi_v\rangle$ are

$$\begin{aligned} N_v &= \sum_j n_j^v, \\ E_v &= \sum_j \varepsilon_j n_j^v. \end{aligned} \tag{10.11}$$

---

[2] A result from quantum field theory. We won't discuss the parity here.

[3] This is called the Pauli exclusion principle for fermions.

In the following, we will derive the corresponding distributions under the *grand canonical ensemble*. As the particle number is large enough, the different ensembles are equivalent.

10.3.2 Bosons: Bose-Einstein Distribution

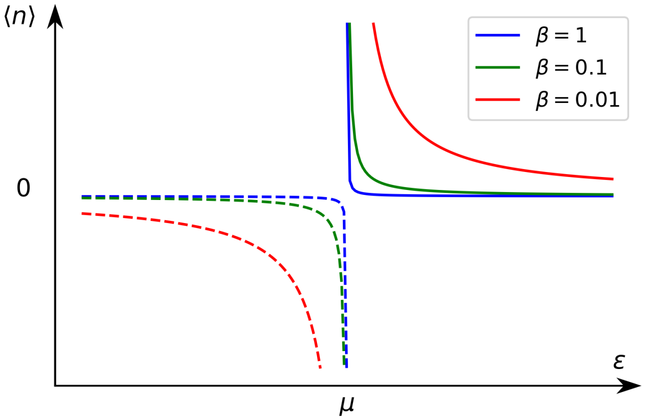


Figure 10.2: Bose-Einstein distribution (choosing $\mu = 1$). The dashed lines are non-physical, corresponding to zero occupations.

For a multi-particle system, the partition funciton is

$$Z = \sum_{v} e^{-\beta(E_v - \mu N_v)} \tag{10.12}$$

where we sum over all possible configurations $|\psi_v\rangle : (n_1^v, n_2^v, \ldots, n_j^v, \ldots) \in [0, \infty)$.

For bosons, Eq. (10.12) can be rewritten as

$$\begin{aligned} Z &= \sum_{\{n_1, n_2, \ldots\}=0}^{\infty} \exp\left[-\beta \sum_j (\varepsilon_j - \mu) n_j\right] \\ &= \sum_{\{n_1, n_2, \ldots\}=0}^{\infty} \prod_j \exp\left[-\beta(\varepsilon_j - \mu) n_j\right] \\ &= \prod_j \left(\sum_{n_j=0}^{\infty} \exp[-\beta(\varepsilon_j - \mu) n_j] \right) \\ &= \prod_j \frac{1}{1 - e^{-\beta(\varepsilon_j - \mu)}}. \end{aligned} \tag{10.13}$$

We evaluate the average occupation number on level-ε_j

$$\begin{aligned}\langle n_j\rangle &= \frac{\sum_v n_j e^{-\beta(E_v-\mu N_v)}}{Z}\\ &= -\frac{1}{\beta}\frac{\partial Z/\partial(\varepsilon_j)}{Z}\\ &= -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_j},\end{aligned} \tag{10.14}$$

which leads to the *Bose-Einstein distribution*

$$\boxed{\langle n_j\rangle_{\text{B.E.}} = \frac{1}{e^{\beta(\varepsilon_j-\mu)}-1}} \tag{10.15}$$

where B.E. stands for Bose-Einstein.

The plot of Eq. (10.15) is shown in Fig. 10.2. Eq. (10.15) diverges at $\varepsilon_j = \mu$. Only when $\varepsilon > \mu$, the distribution is physical. One could see that as the temperature T decreases (β increases), the distribution at $\varepsilon \to \mu$ goes to infinity, which means all the particles tends to occupy the lowest possible state $\varepsilon = \mu$. This leads to the famous *Bose-Einstein condensation* (BEC)[4], which is believed to be the mechanism for superfluidity (zero viscosity and zero entropy). There are many videos online of the superfluid helium, look them up if you are curious about superfluidity!

10.3.3 Fermions: Fermi-Dirac distribution

We start from the same partition function

$$Z = \sum_v e^{-\beta(E_v-\mu N_v)}. \tag{10.16}$$

For fermions, the possible occupation numbers are 0 and 1. Therefore Eq. (10.16) can be rewritten as

$$\begin{aligned}Z &= \sum_{\{n_1,n_2,\dots\}=0}^{1} \exp\left[-\beta\sum_j(\varepsilon_j-\mu)n_j\right]\\ &= \sum_{\{n_1,n_2,\dots\}=0}^{1} \prod_j \exp\left[-\beta(\varepsilon_j-\mu)n_j\right]\\ &= \prod_j\left(\sum_{n_j=0}^{1}\exp[-\beta(\varepsilon_j-\mu)n_j]\right)\\ &= \prod_j\left(1+e^{-\beta(\varepsilon_j-\mu)}\right).\end{aligned} \tag{10.17}$$

---

[4] One of your classmates will talk more about BEC in the final presentation!

The average occupation number of level-ε_j is again evaluated by

$$\langle n_j \rangle = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_j}, \tag{10.18}$$

which leads to the *Fermi-Dirac distribution*,

$$\boxed{\langle n_j \rangle_{\text{F.D.}} = \frac{1}{e^{\beta(\varepsilon_j-\mu)}+1}.} \tag{10.19}$$

where F.D. stands for Fermi-Dirac.

Eq. (10.19) is plotted in Fig. 10.3. We again expect a smoother curve at higher temperature, and as $T \to 0$, the fermions tends to stay on energy levels lower than μ. We call the energy levels with fermions the *occupied orbitals*, and the empty levels are called *unoccupied orbitals*. The hypersurface that separates the occupied and unoccupied orbitals is called the *Fermi-surface*. In this example, the Fermi-surface is simply defined by the chemical potential μ, which is equal to *the Fermi energy* ε_F. Electrons in metals can usually be approximated as non-interacting fermions.

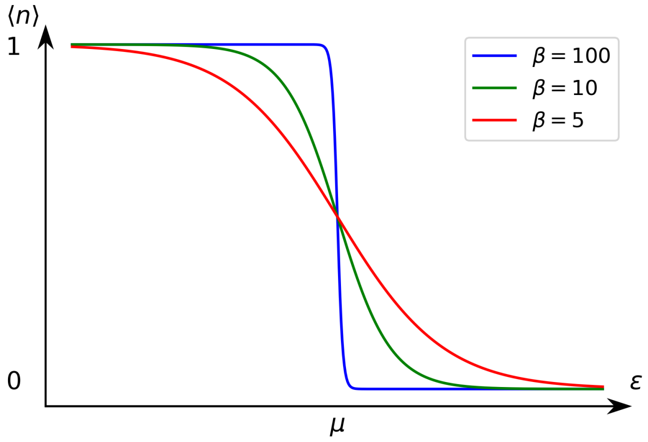


Figure 10.3: Fermi-Dirac distribution (choosing $\mu = 1$).

In summary:

$$\boxed{\langle n_j \rangle_{\substack{\text{F.D.}\\ \text{B.E.}}} = \frac{1}{e^{\beta(\varepsilon_j-\mu)}\pm 1}.} \tag{10.20}$$

where + corresponds to the Fermi-Dirac distribution and − corresponds to the Bose-Einstein distribution. At zero temperature $T = 0$, we have

$$\begin{aligned} \langle n_j \rangle_{\text{F.D.}} &= \begin{cases} 1, & \varepsilon < \mu; \\ 0, & \varepsilon > \mu. \end{cases} \\ \langle n_j \rangle_{\text{B.E.}} &= \begin{cases} N_{\text{max}}, & \varepsilon = \mu; \\ 0, & \varepsilon > \mu. \end{cases} \end{aligned} \tag{10.21}$$

10.3.4 Classical limit: Boltzmann distribution

The classical limit happens at $T \to \infty$ and $\rho \to 0$, i.e. the high temperature and low density limit. When the temperature T is high, the distributions of different particles are all flat, so there is no difference between the distribution patterns of fermions and bosons. When the particle density ρ is low, it is hard for a particle to meet other particles, so we won't see the effect of different parity symmetries, thus no difference between fermions and bosons.

At the high-T low-ρ limit, the occupation number of each single-particle state ε_j must be very small: $\langle n_j \rangle << 1$, which leads to $e^{\beta(\varepsilon_j - \mu)} \pm 1 >> 1$, i.e.

$$e^{\beta(\varepsilon_j - \mu)} >> 1. \tag{10.22}$$

Therefore, $\langle n_j \rangle$ becomes

$$\langle n_j \rangle_{\mathrm{cl}} = e^{-\beta(\varepsilon_j - \mu)} \tag{10.23}$$

which agrees with the classical grand canonical distribution.

The average of the total particle number is

$$\langle N \rangle = \sum_j \langle n_j \rangle = \sum_j e^{-\beta(\varepsilon_j - \mu)} = e^{\beta\mu} \sum_j e^{-\beta\varepsilon_j}. \tag{10.24}$$

So

$$\langle n_j \rangle_{\mathrm{cl}} = \langle N \rangle \frac{e^{-\beta\epsilon_j}}{\sum_j e^{-\beta\epsilon_j}} \tag{10.25}$$

which gives the *Boltzmann distribution*.

Lecture 11: Langevin Equation I

11.1 Non-equilibrium phenomena

In the previous lectures, we discussed thermodynamical and statistical properties of equilibrium systems, where the macroscopic observables remain invariant with respect to time. The behavior of a system at equilibrium is governed by the ensemble theory, where the key quantity is the *partition function*.

However, an equilibrium system is rather ideal. The real-life systems or processes are mostly non-equilibrium. A non-equilibrium system usually experiences a flow of *energy or matter*. Therefore, the non-equilibrium macroscopic properties are *time-dependent*. Here are some examples of non-equilibrium phenomena: heat transport, charge transfer, chemical reactions, etc.

Fig. 11.1 shows an example of a non-equilibrium process caused by the external disturbance. At equilibrium, there is no flow of charge in the electrolyte solution, and the average current $\langle j \rangle$ is zero. At time t_1, an electric field $\mathcal{E}$ is applied, and the charge ions begin to flow, and the charge current $\langle j(t) \rangle$ reaches to the maximum proportional to $\mathcal{E}$ within a relaxation time τ_{relax}. At time t_2, $\mathcal{E}$ is turned off, and the electric current $\langle j(t) \rangle$ drops to zero within a relaxation time τ_{relax}.

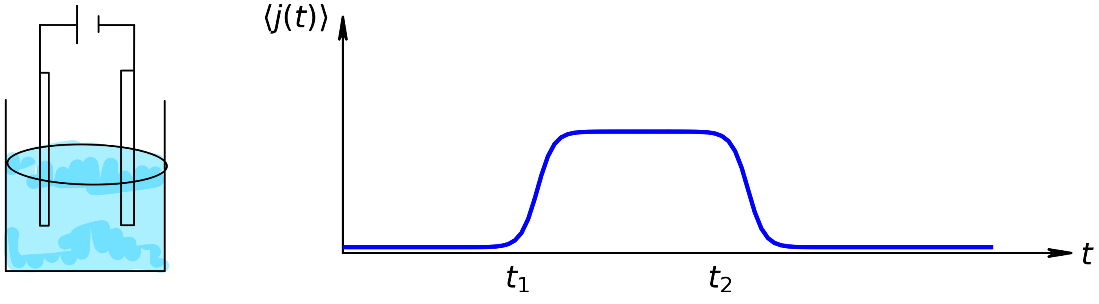


Figure 11.1: Non-equilibrium current produced by a electric field between t_1 and t_2.

We should interpret $\langle j(t) \rangle$ as the non-equilibrium ensemble average. Once the initial condition x_0 is specified, the profile of $j(t; x_0)$ is fixed [1]. Therefore the non-equilibrium en-

---

[1] The initial condition here plays a similar role as the *seed* of a random number generator.

semble average is the average over all initial conditions according to the distribution of the system [2], i.e.,

$$\langle j(t)\rangle = \int \mathrm{d}x_0 f(x_0) j(t;x_0). \tag{11.1}$$

where $f(x_0)$ is the ensemble distribution that the system obeys.

Onsager's regression hypothesis

When left undisturbed, a non-equilibrium system will relax to the equilibrium state. Onsager's regression hypothesis relates the macroscopic relaxation to the microscopic fluctuation process:

> *The relaxation of macroscopic non-equilibrium disturbances is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium system.*

This hypothesis can be proved by the *linear response theory*, which requires the knowledge of the *time correlation function* (TCF). We will leave the Onsager's regression hypothesis unproved for now, and change gear to quantitative description and modeling of non-equilibrium systems.

11.2 Time correlation function

In the equilibrium statistical mechanics, the partition function is key to evaluating the time-independent thermal properties. Away from equilibrium, the *time correlation function* is used in describing the dynamics of the thermal properties. A general form of the time correlation function of dynamical variables A and B is defined as

$$C_{AB}(t,t') = \langle A(t)B(t')\rangle, \tag{11.2}$$

which is the non-equilibrium ensemble average of the product of two variables at different times. $C_{AB}(t,t')$ tells us the the correlation of two variables with respect to time. The average $\langle\cdot\rangle$ can be interpreted as the average over all initial conditions x_0, or the average over a long period of time, and the two are equivalent assuming the system is ergodic:

$$\begin{aligned} \langle A(t)B(t')\rangle &= \int \mathrm{d}x_0 f(x_0) A(t;x_0) B(t';x_0), \\ \text{or } \langle A(t)B(t')\rangle &= \lim_{s\to\infty} \frac{1}{s}\int_0^s \mathrm{d}s A(t+s)B(t'+s). \end{aligned} \tag{11.3}$$

---

[2] In the Zwanzig book, the average is over a long period of time, which is equivalent to the average of initial conditions with the assumption that the system is *ergodic*.

If $A(t)$ and $B(t')$ are *uncorrelated*, then

$$\langle A(t)B(t')\rangle = \langle A(t)\rangle\langle B(t')\rangle \tag{11.4}$$

.

In this lecture, we are interested in the *autocorrelation function*, which is a time correlation function of a variable with itself:

$$C_{AA}(t,t') = \langle A(t)A(t')\rangle. \tag{11.5}$$

The autocorrelation function $C_{AA}(t,t')$ tells us how fast the system "forgets" its past. In fact, for time-invariant systems (e.g., when there is no driving force), only the difference $t'-t$ matters. Therefore, we can simplify Eq. (11.5) as

$$C_A(t) = \langle A(0)A(t)\rangle. \tag{11.6}$$

One important time correlation function is the *velocity correlation function*

$$\langle v_\alpha(0)v_\alpha(t)\rangle, \quad \alpha = x,y,z, \tag{11.7}$$

which is related to the self-diffusion coefficient of the Einstein's equation of diffusion. In the following, we drop the subscript α for simplicity. Fig. 11.2 shows a qualititive sketch of the velocity correlation function of liquid[3]. The correlation time is of the scale of picosecond.

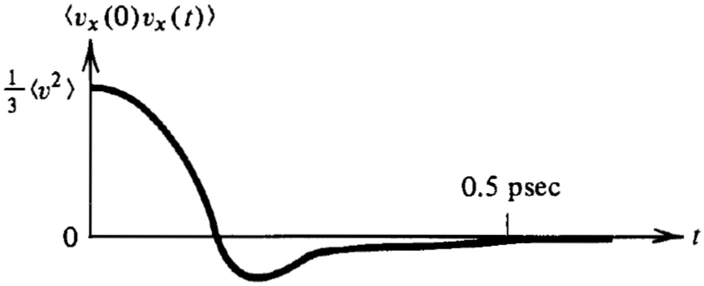


Figure 11.2: Velocity correlation function for a liquid.

Another example is the correlation function for instantaneous fluctuations. Let $A(t)$ be a thermal property if the system, and $\langle A\rangle$ be the time-independent equilibrium average, the fluctuation is defined as

$$\delta A(t) = A(t) - \langle A\rangle. \tag{11.8}$$

---

[3] *Introduction to Modern Statistical Mechanics* by David Chandler, p240.

The correlation funciton of $\delta A(t)$ is

$$C_{\delta A}(t) = \langle \delta A(0)\delta A(t)\rangle = \langle A(0)A(t)\rangle - \langle A\rangle^2. \tag{11.9}$$

We examine Eq. (11.9) at $t \to 0$ and $t \to \infty$:

$$\begin{aligned} C_{\delta A}(0) &= \langle \delta A(0)\delta A(0)\rangle = \langle (\delta A)^2\rangle \\ \lim_{t\to\infty} C_{\delta A}(t) &= \langle \delta A(0)\rangle\langle \delta A(t)\rangle = 0 \end{aligned} \tag{11.10}$$

where we used the fact that at long time, the system will forget its past and $\delta A(t)$ becomes uncorrelated to $\delta A(0)$. Since the average fluctuation should be zero, i.e., $\langle \delta A(t)\rangle = 0$, $\lim_{t\to\infty} C_{\delta A}(t) = 0$.

Now that we have learned the concept if the time correlation function, we are going to introduce a widely used framework to describe non-equilibrium dynamics based on the Langevin equation.

11.3 Brownian motion

The Brownian motion describes the *random* motion of a small particle in a fluid. The fluctuations of the molecules in the fluid kick or pull the particle, causing the particle to move randomly. Fig. 11.3 illustrates a two-dimensional Brownian motion of a particle (the big yellow dot) in a medium (blue dots). The irregular black line indicates the path of the Brownian particle, and the red arrow indicates the instantaneous force the Brownian particle experiences. The spatial distribution of the Brownian particle is described by *Einstein's diffusion equation*. We will skip the discussion of the diffusion equation and focus on the time-dependent motion of the Brownian particle.

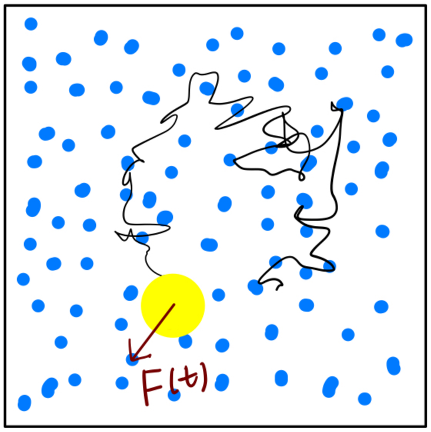


Figure 11.3: Two-dimensional Brownian motion.

Although describing the force that the particle experiences is complicated, the motion still obeys Newton's laws. Consider a one-dimensional motion of a particle with mass m, position x and velocity v. Let $F(t)$ denote the total instantaneous force that the particle experiences at time t, then

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = F(t). \tag{11.11}$$

While we cannot get the exact form of $F(t)$, we can find an approximation that contains the leading components of $F(t)$. In a real liquid with viscosity, $F(t)$ is dominated by the *friction force*

$$\text{friction force } = -\zeta v.$$

This friction force is caused by the movement of the particle, and reduces its velocity v until it becomes zero. We know that this is not the case since the particle keeps on moving for a long enough time. At thermal equilibrium, $\langle v^2\rangle_{\mathrm{eq}} = k_B T/m \neq 0$. There must be another component in $F(t)$ that drives the particle, and this component is due to the kicks of the medium (also called a *heat bath*), denoted by $\delta F(t)$. Therefore, the instantaneous force can be approximated by the sum of friction term due to the motion in the medium and the instantaneous (seemingly random) forces exerted on the particle from the molecules in the medium

$$F(t) = -\zeta v + \delta F(t). \tag{11.12}$$

Eq. (11.12) is an example of the *fluctuation-dissipation theorem*, and leads to the famous *Langevin equation*.

11.4 Langevin equation

The Langevin equation for a Brownian particle is

$$\boxed{m\frac{\mathrm{d}v}{\mathrm{d}t} = -\zeta v + \delta F(t)} \tag{11.13}$$

where the total force has been partitioned into a systematic part (the friction) and a fluctuating part (noise).

Remarks
Since the Langevin equation controls the velocity of a particle, and the velocity is related to the kinetic energy, and hence the *temperature* of the system, we can treat the Langevin equation as a *thermostat* for equilibrium systems. We have seen the Nosé-Hoover thermostat in our previous lectures. In this lecture, we will not talk about the equilibrium thermostat, but use the Langevin equation as a equation of motion at non-equilibrium.

Let's now take a closer look at the noise $\delta F(t)$. In a time-invariant medium, the average of the noise must be zero, i.e., $\langle \delta F(t)\rangle = 0$. We can assume that $\delta F(t)$ has a *Gaussian* *distribution*. Moreover, the noise should be uncorrelated at different times: $\langle \delta F(t)\delta F(t')\rangle \propto \delta(t-t')$. In summary,

$$\langle \delta F(t)\rangle = 0, \quad \langle \delta F(t)\delta F(t')\rangle = 2B\delta(t-t'), \tag{11.14}$$

where B measures the strength of the fluctuating force.

11.4.1 Solving the Lagevin equation

The Langevin equation in Eq. (11.13) is a first-order linear inhomogeneous differential equation, the solution of which can be found at the end of this lecture. The solution is

$$v(t) = e^{-\zeta t/m}v(0) + \int_0^t \mathrm{d}\tau e^{-\zeta(t-\tau)/m}\frac{\delta F(\tau)}{m}. \tag{11.15}$$

The first term gives an exponential decay of the initial velocity due to friction, and the second term increases the velocity due to the random noise. A more straightforward indicator is the mean squared velocity:

$$\langle v(t)^2\rangle = ① + ② + ③, \tag{11.16}$$

where

$$① = e^{-2\zeta t/m}\langle v(0)^2\rangle \tag{11.17}$$

comes from the friction and goes to zero at long time;

$$\begin{aligned} ② &= \left\langle 2v(0)e^{-\zeta t/m}\int_0^t \mathrm{d}\tau e^{-\zeta(t-\tau)/m}\frac{\delta F(\tau)}{m}\right\rangle \\ &= 2\langle v(0)\rangle e^{-\zeta t/m}\int_0^t \mathrm{d}\tau e^{-\zeta(t-\tau)/m}\frac{\langle\delta F(\tau)\rangle}{m} \end{aligned} \tag{11.18}$$

is the cross term and is equal to zero since the average of the noise is zero $\langle \delta F(t)\rangle = 0$ (we also used the fact that $v(0)$ and $\delta F(t)$ are not correlated);

$$\begin{aligned} ③ &= \left\langle\left(\int_0^t \mathrm{d}\tau_1 e^{-\zeta(t-\tau_1)/m}\frac{\delta F(\tau_1)}{m}\right)\left(\int_0^t \mathrm{d}\tau_2 e^{-\zeta(t-\tau_2)/m}\frac{\delta F(\tau_2)}{m}\right)\right\rangle \\ &= \int_0^t \mathrm{d}\tau_1 \int_0^t \mathrm{d}\tau_2 e^{-\frac{\zeta(2t-\tau_1-\tau_2)}{m}}\frac{\langle \delta F(\tau_1)\delta F(\tau_2)\rangle}{m^2} \\ &= \int_0^t \mathrm{d}\tau_1 \int_0^t \mathrm{d}\tau_2 e^{-\frac{\zeta(2t-\tau_1-\tau_2)}{m}}\frac{2B\delta(\tau_1-\tau_2)}{m^2} \\ &= \frac{B}{\zeta m}(1-e^{-2\zeta t/m}) \end{aligned} \tag{11.19}$$

is due to the noise.

Therefore, the mean squared velocity is

$$\langle v(t)^2\rangle = e^{-2\zeta t/m}\langle v(0)^2\rangle + \frac{B}{\zeta m}(1-e^{-2\zeta t/m}). \tag{11.20}$$

At long enough time, $\langle v(t)^2\rangle$ becomes

$$\lim_{t\to\infty}\langle v(t)^2\rangle = \frac{B}{\zeta m}. \tag{11.21}$$

On the other hand, at long time limit, the mean squared velocity should approach its equilibrium value k_BT/m, therefore

$$\boxed{B = \zeta k_B T}. \tag{11.22}$$

This is know as the *fluctuation-dissipation theorem*, which gives the quantitative relationship between the strength of the random noise B and the magnitude of the friction (or dissipation) ζ.

Appendix: Solving first-order linear differential equations

Homogeneous differential equations

The first order homogeneous differential equation has the form

$$\frac{\mathrm{d}y}{\mathrm{d}t} + w(t)y = 0, \tag{11.23}$$

which can be rewritten as

$$\frac{\mathrm{d}y}{y} = -w(t)\mathrm{d}t. \tag{11.24}$$

Integrating both sides, we get

$$\begin{gathered}\int_{y(0)}^{y}\frac{1}{y}\mathrm{d}y = \int_0^t -w(t)\mathrm{d}t,\\ \ln y - \ln y(0) = -W(t) + W(0),\end{gathered} \tag{11.25}$$

where $W(t)$ is the antiderivative of $w(t)$. Absorbing $y(0)$ and $W(0)$ into a factor A, we get

$$y = Ae^{-W(t)}. \tag{11.26}$$

Example When $\delta F(t)$ is zero, Eq. (11.13) becomes a homogeneous differential equation

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = -\zeta v, \tag{11.27}$$

where $w(t) = \zeta/m$, therefore $W(t) = \zeta t/m$. The solution is

$$v(t) = v(0)e^{-\zeta t/m}. \tag{11.28}$$

With only friction, $v(t)$ decays to zero exponentially.

Inhomogeneous differential equations

The inhomogeneous differential equation has the form

$$\frac{\mathrm{d}y}{\mathrm{d}t} + w(t)y = f(t). \tag{11.29}$$

Suppose $h(t)$ is a solution to the inhomogeneous DE Eq. (11.29), and $g(t)$ is a solution to the corresponding homogeneous DE Eq. (11.23), then it is obvious that $h(t) + g(t)$ is also a solution to Eq. (11.29). Therefore, the solution $y(t)$ can be a specific solution plus the homogeneous solution $g(t)$,

$$y(t) = g(t) + h(t) = Ae^{-W(t)} + h(t), \tag{11.30}$$

where $h(t)$ is a specific solution. Determining $h(t)$ requires guessing. We guess $h(t)$ has the form similar to $g(t)$, but replace the constant A with a function $a(t)$:

$$h(t) = a(t)e^{-W(t)}. \tag{11.31}$$

Substituting $h(t)$ into Eq. (11.29), we get

$$\frac{\mathrm{d}a}{\mathrm{d}t}e^{-W(t)} - a(t)e^{-W(t)}w(t) + w(t)a(t)e^{-W(t)} = f(t), \tag{11.32}$$

which can be simplified as

$$\frac{\mathrm{d}a}{\mathrm{d}t} = f(t)e^{W(t)} \tag{11.33}$$

therefore,

$$h(t) = e^{-W(t)} \int_0^t f(\tau)e^{W(\tau)}\mathrm{d}\tau = \int_0^t f(\tau)e^{W(\tau)-W(t)}\mathrm{d}\tau \tag{11.34}$$

where we assumed $a(0) = 0$ without lose of generality.

Therefore the general solution to Eq. (11.29) is

$$y(t) = Ae^{-W(t)} + \int_0^t f(\tau)e^{W(\tau)-W(t)}\mathrm{d}\tau. \tag{11.35}$$

Exercise Derive Eq. (11.15).

Lecture 12: Langevin Equation II

In the second part of the Langevin equation lecture, we will see some applications of the Langevin equation, and discuss more general and complicated extensions to the original form of the Langevin equation.

12.1 Characterizing the Brownian motion

We evaluate the *velocity autocorrelation function* $\langle v(t)v(t')\rangle$ and the *mean square displacement* $\langle \Delta x(t)^2\rangle$ from the solution of the Langevin equation Eq. (11.15).

12.1.1 Velocity autocorrelation function

The velocity autocorrelation function $C_v(t,t') = \langle v(t)v(t')\rangle$ is computed from the Langevin equation as[1]

$$\begin{aligned} C_v(t,t') &= \left\langle \left(e^{-\frac{\zeta t}{m}} v(0) + \int_0^t \mathrm{d}\tau_1 e^{-\frac{\zeta(t-\tau_1)}{m}} \frac{\delta F(\tau_1)}{m} \right) \left(e^{-\frac{\zeta t'}{m}} v(0) + \int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t'-\tau_2)}{m}} \frac{\delta F(\tau_2)}{m} \right) \right\rangle \\ &= e^{-\frac{\zeta(t+t')}{m}} \langle v(0)^2 \rangle + \frac{B}{m\zeta} \left(e^{-\frac{\zeta|t'-t|}{m}} - e^{-\frac{\zeta(t+t')}{m}} \right). \end{aligned} \tag{12.1}$$

From last lecture, we learned that the mean square velocity is $\langle v(t)^2\rangle = B/\zeta m$, therefore,

$$C_v(t,t') = \frac{B}{m\zeta} e^{-\frac{\zeta|t'-t|}{m}}. \tag{12.2}$$

According to the *fluctuation-dissipation theorem*, $B = \zeta k_B T$, we get

$$\boxed{C_v(t,t') = \frac{k_B T}{m} e^{-\frac{\zeta|t'-t|}{m}}} \tag{12.3}$$

which indicates that the velocity correlation decays exponentially with respect to the time difference $|t-t'|$.

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[1] One can find the computational details at the end of the lecture

12.1.2 Mean squared displacement

We first introduce the Einstein's formula for the mean squared displacement of a diffusing particle

$$\langle \Delta x(t)^2 \rangle = 2Dt \tag{12.4}$$

where D is called the *self-diffusion coefficient*. Now we can figure out the value of D by evaluating $\langle \Delta x(t)^2 \rangle$.

The displacement from time 0 to time t is defined as

$$\Delta x(t) = \int_0^t \mathrm{d}\tau \; v(\tau). \tag{12.5}$$

Therefore[2]

$$\begin{aligned} \langle \Delta x(t)^2 \rangle &= \left\langle \int_0^t \mathrm{d}\tau_1 \; v(\tau_1) \int_0^t \mathrm{d}\tau_2 \; v(\tau_2) \right\rangle \\ &= \int_0^t \mathrm{d}\tau_1 \int_0^t \mathrm{d}\tau_2 \; \langle v(\tau_1) v(\tau_2) \rangle \\ &= \int_0^t \mathrm{d}\tau_1 \int_0^t \mathrm{d}\tau_2 \; \frac{B}{m\zeta} e^{-\frac{\zeta |\tau_1 - \tau_2|}{m}} \\ &= \frac{2B}{\zeta^2} \left(t - \frac{m}{\zeta} + \frac{m}{\zeta} e^{-\frac{\zeta}{m} t} \right). \end{aligned} \tag{12.6}$$

Again, using the conclusion from the fluctuation-dissipation theorem, we have

$$\boxed{\langle \Delta x(t)^2 \rangle = \frac{2k_B T}{\zeta} \left(t - \frac{m}{\zeta} + \frac{m}{\zeta} e^{-\frac{\zeta}{m} t} \right)} \tag{12.7}$$

A qualitative plot[3] of the mean squared displacement is shown in Fig. 12.1.

We examine Eq. (12.7) at two limits: $t << 1$ and $t \to \infty$.

- $t \to 0$. We have $\frac{\zeta t}{m} << 1$ assuming that ζ/m is bounded, thus we can Taylor expand $e^{-\frac{\zeta}{m} t}$,

$$\begin{aligned} \lim_{t \to 0} \langle \Delta x(t)^2 \rangle &= \frac{2k_B T}{\zeta} \left[t - \frac{m}{\zeta} + \frac{m}{\zeta} \left(1 - \frac{\zeta}{m} t + \frac{1}{2} \left(\frac{\zeta}{m} \right)^2 t^2 + \cdots \right) \right] \\ &\approx \frac{k_B T}{m} t^2 \\ &= \langle v(t)^2 \rangle t^2. \end{aligned} \tag{12.8}$$

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[2] Find the full derivation at the end of the lecture.

[3] Chandler book Fig. 8.10.

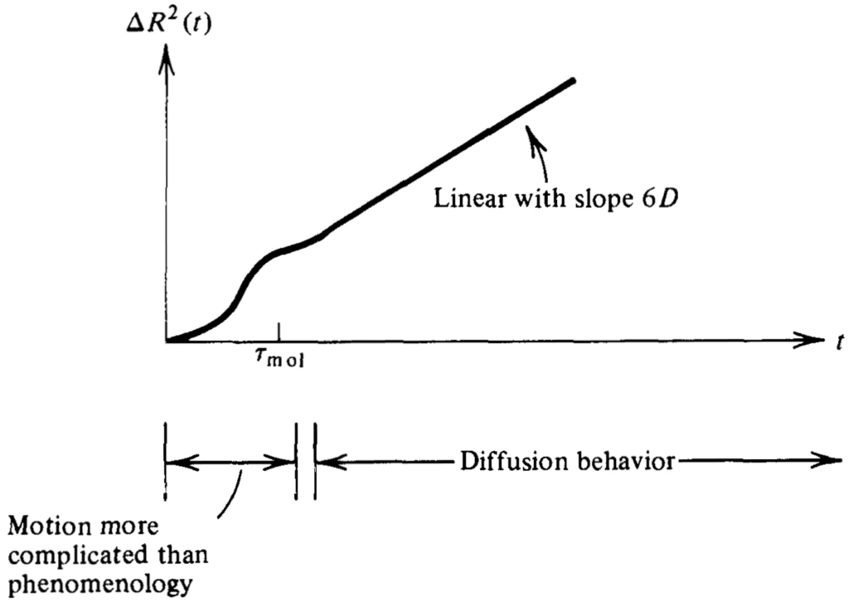

Figure 12.1: Mean squared displacement of a diffusing particle.

Therefore, at small t, $\langle \Delta x(t)^2 \rangle$ increases *quadratically* with time, due to the inertial behavior from the initial velocity. This trend is referred to as *ballistic motion*.

- $t \to \infty$. At very long time t, we have

$$\lim_{t\to\infty} \langle \Delta x(t)^2 \rangle = \frac{2k_B T}{\zeta} t. \tag{12.9}$$

At long times, the effects of the noise are dominant, and $\langle \Delta x(t)^2 \rangle$ increases only *linearly* with time. This trend is indicative of a *random walk*, diffusive motion.

Compare the long time limit Eq. (12.9) with Einstein's formula Eq. (12.4), we derive

$$\boxed{D = \frac{k_B T}{\zeta}.} \tag{12.10}$$

12.2 Application: chemical reactions

To illustrate how we can use Langevin equation to study the kinetics of chemical reactions, we use the following reaction as an example:

$$A \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} B$$

where A and B are two chemical species in the system at very low concentration, k_{AB} and k_{BA} are the forward and back reaction rate constants respectively.

For simplicity, we use $A(t)$ and $B(t)$ as the concentrates of the two chemicals, and the total concentrate $A(t)+B(t)=A_{\mathrm{eq}}+B_{\mathrm{eq}}$ is a constant. The basic rate equations are

$$\begin{aligned}\frac{\mathrm{d}A}{\mathrm{d}t} &= -k_{AB}A + k_{BA}B,\\ \frac{\mathrm{d}B}{\mathrm{d}t} &= -k_{BA}B + k_{AB}A.\end{aligned} \tag{12.11}$$

Suppose the deviation of A from the equilibrium value A_{eq} is C, then

$$A = A_{\mathrm{eq}} + C, \qquad B = B_{\mathrm{eq}} - C. \tag{12.12}$$

At equilibrium, A_{eq} and B_{eq} obey the *detailed balance condition*,

$$k_{BA}A_{\mathrm{eq}} = k_{AB}B_{\mathrm{eq}}. \tag{12.13}$$

Now we can reduce Eq. (12.11) to one equation

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -(k_{AB}+k_{BA})C, \tag{12.14}$$

and the solution is

$$C(t) = C(0)e^{-(k_{AB}+k_{BA})t}. \tag{12.15}$$

It seems that $C(t)$ becomes zero exponentially with time. However, if we think about fluctuations at equilibrium, the mean squared value $\langle C(t)^2\rangle$ should be constant, since there are always thermal fluctuations! To avoid $C(t)$ decaying to zero, we add a *fluctuation* term as in the Langevin equation

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -(k_{AB}+k_{BA})C + \delta F(t). \tag{12.16}$$

The *fluctuation-dissipation theorem* requires

$$\langle \delta F(t)\delta F(t')\rangle = 2(k_{AB}+k_{BA})\langle C^2\rangle_{\mathrm{eq}}\delta(t-t'). \tag{12.17}$$

By observing the particle number fluctuations over a long time, one can find the reaction rate constants.

12.3 Generalized Langevin equations

Given a Hamiltonian

$$H = \frac{p^2}{2m} + U(x), \tag{12.18}$$

the Hamilton's equation of motion gives

$$\begin{aligned}\frac{\mathrm{d}x}{\mathrm{d}t} &= \frac{\partial H}{\partial p} = \frac{p}{m}, \\ \frac{\mathrm{d}p}{\mathrm{d}t} &= -\frac{\partial H}{\partial x} = -\frac{\mathrm{d}U}{\mathrm{d}x}.\end{aligned} \tag{12.19}$$

The Langevin equation modifies $\mathrm{d}p/\mathrm{d}t$ by adding the friction and fluctuation parts,

$$\begin{aligned}\frac{\mathrm{d}x}{\mathrm{d}t} &= \frac{p}{m}, \\ \frac{\mathrm{d}p}{\mathrm{d}t} &= -\frac{\mathrm{d}U}{\mathrm{d}x} - \zeta\frac{p}{m} + \delta F(t).\end{aligned} \tag{12.20}$$

One can then get the trajectory of $x(t)$ and $p(t)$ by integrating the above equations with, e.g., velocity-Verlet algorithm. Note that even though the form of $\mathrm{d}x/\mathrm{d}t$ remains the same as in the Hamiltons EOMs, since $p(t)$ experiences friction and fluctuation forces, $x(t)$ will experience them as well through $p(t)/m$.

Now we make our model a little more realistic (and more complicated) by adding a "memory" to the friction. This means that the friction ratio is no longer a constant ζ, but a memory function $\zeta \to K(t)$, and the frictional force becomes

$$-\zeta v(t) \to -\int_{-\infty}^{t} \mathrm{d}s\, K(t-s)v(s). \tag{12.21}$$

Since the friction force has a memory now, the fluctuation force can no longer be white noise. Otherwise the system will not approach equilibrium at long times. This type of problem is called *non-Markovian*.

We illustrate how non-Markovian behavior can arise by showing an example of the Brownian motion of a harmonic oscillator. In fact, we are going to examine the time evolution of $x(t)$ by eliminating the momentum $p(t)$.

Starting from the Markovian Langevin equation Eq. (12.20) and assuming that $p(-\infty) = 0$, we can get the solution of $p(t)$

$$p(t) = \int_{-\infty}^{t} e^{-\frac{\zeta}{m}(t-s)}\Big(-m\omega^2 x(s) + \delta F(s)\Big). \tag{12.22}$$

Substituting Eq. (12.22) back into $\mathrm{d}x/\mathrm{d}t$, we get

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = -\int_{-\infty}^{t} K(t-s)x(s)\mathrm{d}s + F_x(t), \tag{12.23}$$

where $K(t-s)$ is the memory function for the friction force, and $F_x(t)$ is the fluctuating

”force” for the position[4]

$$\begin{aligned} K(t-s) &= \omega^2 e^{-\frac{\zeta}{m}|t-s|}, \\ F_x(t) &= \frac{1}{m}\int_{-\infty}^{t} \mathrm{d}s\, e^{-\frac{\zeta}{m}(t-s)}\delta F(s). \end{aligned} \tag{12.24}$$

At equilibrium, the mean squared position is

$$\langle x^2\rangle_{\text{eq}} = \frac{k_B T}{m\omega^2}, \tag{12.25}$$

which leads to

$$\langle F_x(t)F_x(t')\rangle = \frac{k_B T}{m\omega^2}K(|t-t'|). \tag{12.26}$$

The above equation is the non-Markovian version of the fluctuation-dissipation theorem, where the correlation function of the new noise is proportional to the memory function of the new friction.

12.4 Brownian motion in a harmonic oscillator bath

In this section, we study a prototype for many statistical mechanical models - the Brownian motion in a harmonic oscillator bath. We first define the Hamiltonian

$$H = H_S + H_B, \tag{12.27}$$

where H_S is the system Hamiltonian, and H_B is the heat bath Hamiltonian which also includes the coupling between the system and the bath. We use x and p as the coordinate and conjugate momentum for the Brownian particle with mass m, and use $\{q_j\}$ and $\{p_j\}$ as the coordinates and conjugate momenta for the heat bath oscillators with masses 1. H_S and H_B are then

$$\begin{aligned} H_S &= \frac{p^2}{2m} + U(x), \\ H_B &= \sum_j \frac{p_j^2}{2} + \frac{1}{2}\omega_j^2\left(q_j - \frac{\gamma_j}{\omega_j^2}x\right)^2, \end{aligned} \tag{12.28}$$

where ω_j is the frequency of the jth oscillator and γ_j measures the strength of coupling of the Brownian particle with the jth oscillator.

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[4] Note that $F_x(t)$ does not have the unit of force, but the unit of velocity.

Now we can write down the Hamilton's equation of motion of the Brownian particle and the oscillators

$$\begin{aligned} \frac{\mathrm{d}x}{\mathrm{d}t} &= \frac{p}{m}, & \frac{\mathrm{d}p}{\mathrm{d}t} &= -\frac{\mathrm{d}U(x)}{\mathrm{d}x} + \sum_j \gamma_j (q_j - \gamma_j x/\omega_j^2); \\ \frac{\mathrm{d}q_j}{\mathrm{d}t} &= p_j, & \frac{\mathrm{d}p_j}{\mathrm{d}t} &= -\omega_j^2 q_j + \gamma_j x. \end{aligned} \tag{12.29}$$

Since $\{q_j\}$ and $\{p_j\}$ only depends on x, we can solve their equations of motion assuming $x(t)$ is known[5]. Then we can put the solutions of $\{q_j(t)\}$ and $\{p_j(t)\}$ back to $\mathrm{d}p/\mathrm{d}t$, and obtain

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{\mathrm{d}U(x)}{\mathrm{d}x} - \int_{-\infty}^{t} \mathrm{d}s\, K(t-s)\frac{p(s)}{m} + F_p(t). \tag{12.30}$$

With the above setting, we get a solution to the *non-Markovian* Langevin equation! The memory function and the "noise" are

$$\begin{aligned} K(t) &= \sum_j \frac{\gamma_j}{\omega_j^2} \cos \omega_j t, \\ F_p(t) &= \sum_j \gamma_j p_j(0) \frac{\sin \omega_j t}{\omega_j} + \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right) \cos \omega_j t. \end{aligned} \tag{12.31}$$

This prototype is powerful in the sense that one can adjust the frequencies $\{\omega_j\}$ and the coupling strength $\{\gamma_j\}$ to produce many different forms of memory functions, and thus this model can be used to study a variety of practical problems.

12.5 More on Onsager's regression hypothesis*

In the last lecture, we gave the *Onsager's regression hypothesis* without proof. Here we give an analysis based on a simplified version of the *linear response theory*.

Consider a thermal observable $A(t)$, and we relate the macroscopic displacement $\Delta\langle A(t)\rangle$ with the correlation function of the microscopic fluctuation $\langle \delta A(0)\delta A(t)\rangle$.

Given a Hamiltonian, the equilibrium average of A is

$$\langle A \rangle = \frac{\mathrm{Tr}[e^{-\beta H} A]}{\mathrm{Tr}[e^{-\beta H}]}. \tag{12.32}$$

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[5] See *Zwanzig Ch1 Eq. (1.89) and Eq. (1.90)* for the solutions.

At time $t = 0$, we turn on a small perturbation of a field f coupled to A, the Hamiltonian becomes

$$\tilde{H} = H + \Delta H = H - fA. \tag{12.33}$$

The initial value of A is

$$\langle A(0)\rangle = \frac{\mathrm{Tr}[e^{-\beta(H+\Delta H)}A(0,x)]}{\mathrm{Tr}[e^{-\beta(H+\Delta H)}]}. \tag{12.34}$$

and $A(t)$ becomes

$$\langle A(t)\rangle = \frac{\mathrm{Tr}[e^{-\beta(H+\Delta H)}A(t,x)]}{\mathrm{Tr}[e^{-\beta(H+\Delta H)}]}, \tag{12.35}$$

where x is a microstate depending on the initial condition.

Since ΔH is very small, we can Taylor expand Eq. (12.35), and get

$$\langle A(t)\rangle \approx \langle A\rangle - \beta[\langle \Delta H A(t,x)\rangle - \langle A\rangle\langle \Delta H\rangle] + \mathcal{O}[(\beta\Delta H)^2]. \tag{12.36}$$

The macroscopic displacement is

$$\begin{aligned}\Delta\langle A(t)\rangle &= \langle A(t)\rangle - \langle A\rangle \\ &= \beta[\langle \Delta H A(t,x)\rangle - \langle A\rangle\langle \Delta H\rangle] + \mathcal{O}[(\beta\Delta H)^2]\end{aligned} \tag{12.37}$$

Inserting $\Delta H = -fA$, we get

$$\boxed{\Delta\langle A(t)\rangle = \beta f\langle \delta A(0)\delta A(t)\rangle + \mathcal{O}(f^2)} \tag{12.38}$$

which agrees with the Onsager's regression hypothesis.

Appendix 1: Derivation of Eq. (12.1)

The velocity autocorrelation function is evaluated by

$$\begin{aligned}C_v(t,t') = &\left\langle\left(e^{-\frac{\zeta t}{m}}v(0) + \int_0^t \mathrm{d}\tau_1 e^{-\frac{\zeta(t-\tau_1)}{m}}\frac{\delta F(\tau_1)}{m}\right)\left(e^{-\frac{\zeta t'}{m}}v(0) + \int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t'-\tau_2)}{m}}\frac{\delta F(\tau_2)}{m}\right)\right\rangle \\ = &\, e^{-\frac{\zeta(t+t')}{m}}\langle v(0)^2\rangle \\ &+ e^{-\frac{\zeta t}{m}}\int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t'-\tau_2)}{m}}\frac{\langle v(0)\delta F(\tau_2)\rangle}{m} + e^{-\frac{\zeta t'}{m}}\int_0^{t} \mathrm{d}\tau_1 e^{-\frac{\zeta(t-\tau_1)}{m}}\frac{\langle v(0)\delta F(\tau_1)\rangle}{m} \\ &+ \int_0^t \mathrm{d}\tau_1\int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t+t'-\tau_1-\tau_2)}{m}}\frac{\langle \delta F(\tau_1)\delta F(\tau_2)\rangle}{m^2} \\ = &\, e^{-\frac{\zeta(t+t')}{m}}\langle v(0)^2\rangle + \int_0^t \mathrm{d}\tau_1\int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t+t'-\tau_1-\tau_2)}{m}}\frac{2B\delta(\tau_1-\tau_2)}{m^2}\end{aligned} \tag{12.39}$$

We evaluate the following integral:

$$\int_0^t \mathrm{d}\tau_1 \int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t+t'-\tau_1-\tau_2)}{m}} \frac{2B\delta(\tau_1-\tau_2)}{m^2}. \tag{12.40}$$

Suppose $t' > t$, then $(0,t] \in (0,t']$, and for $\forall \tau_1$, we can find a τ_2 s.t. $\tau_2 = \tau_1$. Therefore, we need to integrate over τ_2 first to remove the Delta function,

$$\begin{aligned} &\int_0^t \mathrm{d}\tau_1 \int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t+t'-\tau_1-\tau_2)}{m}} \frac{2B\delta(\tau_1-\tau_2)}{m^2} \\ =&\int_0^t \mathrm{d}\tau_1 \left(\int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t+t'-\tau_1-\tau_2)}{m}} \frac{2B\delta(\tau_1-\tau_2)}{m^2} \right) \\ =&\int_0^t \mathrm{d}\tau_1 e^{-\frac{\zeta(t+t'-2\tau_1)}{m}} \frac{2B}{m^2} \\ =&\frac{B}{m\zeta}\left(e^{-\frac{\zeta(t'-t)}{m}} - e^{-\frac{\zeta(t+t')}{m}} \right). \end{aligned} \tag{12.41}$$

Similarly, if $t > t'$, we have

$$\int_0^t \mathrm{d}\tau_1 \int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t+t'-\tau_1-\tau_2)}{m}} \frac{2B\delta(\tau_1-\tau_2)}{m^2} = \frac{B}{m\zeta}\left(e^{-\frac{\zeta(t-t')}{m}} - e^{-\frac{\zeta(t+t')}{m}} \right). \tag{12.42}$$

Therefore, for the general case,

$$\int_0^t \mathrm{d}\tau_1 \int_0^{t'} \mathrm{d}\tau_2 e^{-\frac{\zeta(t+t'-\tau_1-\tau_2)}{m}} \frac{2B\delta(\tau_1-\tau_2)}{m^2} = \frac{B}{m\zeta}\left(e^{-\frac{\zeta|t-t'|}{m}} - e^{-\frac{\zeta(t+t')}{m}} \right). \tag{12.43}$$

We then get the final form of $C_v(t,t')$,

$$C_v(t,t') = e^{-\frac{\zeta(t+t')}{m}} \langle v(0)^2 \rangle + \frac{B}{m\zeta}\left(e^{-\frac{\zeta|t'-t|}{m}} - e^{-\frac{\zeta(t+t')}{m}} \right). \tag{12.44}$$

Appendix 2: Derivation of Eq. (12.6)

We evaluate the integral of $\langle \Delta x(t)^2 \rangle$. The tricky part is how to treat an integrand with absolute values. We have already worked with an example in Homework 3, where we divide the integration domains according to the absolute value. Here we use the same strategy.

$$\begin{aligned}
&\int_0^t \mathrm{d}\tau_1 \int_0^t \mathrm{d}\tau_2 \, \frac{B}{m\zeta} e^{-\frac{\zeta|\tau_1-\tau_2|}{m}} \\
=&\frac{B}{m\zeta} \int_0^t \mathrm{d}\tau_1 \left(\int_0^{\tau_1} \mathrm{d}\tau_2 \, e^{-\frac{\zeta(\tau_1-\tau_2)}{m}} + \int_{\tau_1}^t \mathrm{d}\tau_2 \, e^{-\frac{\zeta(\tau_2-\tau_1)}{m}} \right) \\
=&\frac{B}{\zeta^2} \int_0^t \mathrm{d}\tau_1 \left(e^{-\frac{\zeta(\tau_1-\tau_2)}{m}} \Big|_0^{\tau_1} - e^{-\frac{\zeta(\tau_2-\tau_1)}{m}} \Big|_{\tau_1}^t \right) \\
=&\frac{B}{\zeta^2} \int_0^t \mathrm{d}\tau_1 \left(2 - e^{-\frac{\zeta}{m}\tau_1} - e^{-\frac{\zeta}{m}(t-\tau_1)} \right) \\
=&\frac{2B}{\zeta^2} \left(t - \frac{m}{\zeta} + \frac{m}{\zeta} e^{-\frac{\zeta}{m}t} \right).
\end{aligned} \tag{12.45}$$