

Thermodynamics and Statistical Physics

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Chapter 1

Thermodynamics

Chapter 2

Classical statistical mechanics

Chapter 3

Canonical ensemble and grand canonical ensemble

Chapter 4

Quantum statistical mechanics

4.1 Quantum mechanics

4.1.1 Fundamental principles

A Hilbert space:

a space spanned by a complete orthonormal set of stationary function, e.g., $\{e^{ixp}\}$, in general, $\{\phi_n\}$.

A state of the microscopic system corresponds to a point in the Hilbert space, expressed as a linear superposition of $\{\phi_n\}$,

$$\psi = \sum_n C_n(t) \phi_n,$$

i.e., a state including the dynamic evolution is given by a set of $\{C_n(t)\}$.

A physical observable is associated with a Hermitian operator in the Hilbert space.

The value of an observable in a state is calculated by

$$\langle O(t) \rangle = \int dx \psi^*(x, t) O(x) \psi(x, t)$$

Therefore, $\psi^*(x, t)\psi(x, t)dx$ is the probability of finding the particle at the x position, and at the time t .

Note that at a certain time t , the particle can be found at any x with certain probability, it is not that the particle can move from here to there. This is just the uncertainty principle.

Fundamental problems:

- How to construct the operator $O(x)$?
- How to find the state $\psi(x, t)$?

We adopt the expression $O(x, p)$ from classical mechanics.

Quantization:

$$\begin{aligned}x &\rightarrow x \\ p &\rightarrow -i\frac{\partial}{\partial x}\end{aligned}$$

Now, x and p is non-commutable

$$[x, p] = [x, -i\frac{\partial}{\partial x}] = x(-i\frac{\partial}{\partial x}) - (-i\frac{\partial}{\partial x})x = i$$

but the ordering of x and p is a little subtle.

Schroedinger equation

$$\begin{aligned}i\frac{\partial}{\partial t}\psi(x, t) &= H\psi(x, t) \\ + \quad &\text{initial conditions} \\ &\text{boundary conditons}\end{aligned}$$

The principle of the linear superposition is resulted from the Schroedinger equation.

Assuming H is independent of t , i.e., isolated system.
let

$$\psi(x, t) = C_n(t)\phi_n(x)$$

we have

$$\begin{aligned} i\frac{\partial}{\partial t}C_n(t)\phi_n(x) &= H\phi_n(x)C_n(t) \\ \Leftrightarrow H\phi_n &= E_n\phi_n \\ i\frac{\partial}{\partial t}C_n(t) &= E_nC_n(t) \end{aligned}$$

In general, $\{\phi_n\}$ form a complete set of the Hilbert space.

Let us denote

$$\begin{aligned} \langle O \rangle &\equiv \int \psi^*(x)O\psi(x)dx = (\psi, O\psi) \\ &= \left(\sum_n C_n(t)\phi_n, O \sum_m C_m\phi_m \right) \\ &= \sum_{n,m} C_n^*(t)C_m(t)(\phi_n, O\phi_m) \end{aligned}$$

$\{C_n(t)\}$ in quantum mechanics is similar to $\{p(t), q(t)\}$ in classical mechanics.

Statistical mechanics does not intend to solve $\{C_n(t)\}$ from the Schrodinger equation, but give a probability distribution to $\{C_n(t)\}$ in equilibrium state.

4.1.2 Theory of representations

Representations in quantum mechanics

A state is described by

$$\psi(x, t)$$

An inner product must be defined

$$(\psi, \phi) \equiv \int dx \psi^*(x, t) \phi(x, t)$$

An observable

$$\langle \hat{O}(x) \rangle \equiv (\psi, \hat{O}\psi) \equiv \int dx \psi^*(x, t) \hat{O}(x) \psi(x, t)$$

If $\{\phi_n(x)\}$ is a complete orthonormal set of wave functions, i.e.,

$$(\phi_n, \phi_m) = \delta_{mn}$$

then, in general

$$\begin{aligned} \psi(x, t) &= \sum_n C_n(t) \phi_n(x) \\ \phi &= \sum_n b_n(t) \phi_n(x) \end{aligned}$$

The inner product

$$\begin{aligned} (\psi, \phi) &= \left(\sum_n C_n(t) \phi_n, \sum_m b_m(t) \phi_m \right) \\ &= \sum_n C_n^*(t) b_n(t) \end{aligned}$$

The observable

$$\begin{aligned} (\psi, \hat{O}\psi) &= \left(\sum_n C_n(t) \phi_n, \sum_m C_m(t) \hat{O}\phi_m \right) \\ &= \sum_{n,m} C_n^*(t) C_m(t) O_{nm} \\ O_{nm} &= (\phi_n, \hat{O}\phi_m) \end{aligned}$$

$\{O_{nm}\}$ defines a matrix

$$\{O_{nm}\} = \begin{pmatrix} O_{11} & O_{12} & \cdots \\ O_{21} & O_{22} & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix} \equiv O$$

$\{C_n\}$ defines also a matrix

$$\{C_n(t)\} = \begin{pmatrix} C_1(t) \\ C_2(t) \\ \vdots \end{pmatrix} \equiv C$$

$$B \equiv \begin{pmatrix} b_1(t) \\ b_2(t) \\ \vdots \end{pmatrix}$$

$$C^+ = (C_1^*(t) C_2^*(t) \cdots)$$

C and O are the representations of the state ψ and operator \hat{O} with the complete set $\{\phi_n\}$, and

$$(\psi, \phi) = C^+ B$$

$$(\psi, \hat{O}\psi) = C^+ O C$$

e.g.,

$$(1) \quad \phi_n(x) = e^{ipx} \quad (p \leftrightarrow n)$$

$$\hat{p} = -i \frac{\partial}{\partial x}$$

$$\hat{p}e^{ipx} = pe^{ipx}$$

$$(2) \quad \phi_n(x) = \delta(x - x') \quad (x' \leftrightarrow n)$$

$$\hat{x}\delta(x - x') = x\delta(x - x')$$

$$= (x - x')\delta(x - x') + x'\delta(x - x')$$

$$= x'\delta(x - x')$$

$$\psi(x, t) = \int dx' \psi(x', t) \delta(x - x')$$

$$\psi \rightarrow \begin{pmatrix} \psi(x'_1, t) dx'_1 \\ \psi(x'_2, t) dx'_2 \\ \vdots \end{pmatrix}$$

Question: what is the representation of an operator in this case?

Transformation between representations

If $\{\psi_n\}$ is another complete set

$$\psi = \sum_n C'_n(t) \psi_n \rightarrow C'$$

$$O_{nm} = (\psi_n, \hat{O} \psi_m) \rightarrow O'$$

we may find out transformation between the two representations.

Suppose

$$\psi_n = \sum_m \phi_m t_{mn}$$

$$\psi = \sum_n C'_n \psi_n = \sum_{n,m} C'_n \phi_m t_{mn}$$

$$= \sum_m \left(\sum_n t_{mn} C'_n \right) \phi_m$$

hence

$$C_m(t) = \sum_n t_{mn} C'_n(t)$$

i.e.,

$$\begin{aligned}C &= TC' & T &\equiv \{t_{mn}\} \\C^+ &= C'^+T^+\end{aligned}$$

It can be proved

$$T^+T = TT^+ = 1, O = TO'T^+. \quad (\text{exercise})$$

then, both

$$\begin{aligned}(\psi, \phi) &= C^+B \\&= C'^+T^+TB' \\&= C'^+B'\end{aligned}$$

and

$$\begin{aligned}(\psi, \hat{O}\psi) &= C^+OC \\&= C'^+T^+TO'T^+TC' \\&= C'^+O'C'\end{aligned}$$

are independent of the representations.

Dirac notations

Introduce	$ \psi\rangle$	to describe	ψ
e.g.,	$ \psi\rangle$	$= \sum_n C_n(t)$	$ \psi_n\rangle$
similarly	$\langle\psi $	to describe	ψ^*
	$\langle\psi $	$= \sum_n \langle\psi_n $	$C_n^*(t)$
	$(\psi\rangle)^+$	$=$	$\langle\psi $

An inner product

$$(\psi, \phi) \equiv \langle\psi|\phi\rangle$$

the observable

$$(\psi, \hat{O}\psi) \equiv \langle \psi | \hat{O} | \psi \rangle$$

both are independent of representation, but computations of their values must be carried out in a specified representation, e.g.,

$$\begin{aligned} \langle \psi | \phi \rangle &= \sum_n \langle \phi_n | C_n^*(t) \cdot \sum_m b_m(t) | \phi_m \rangle \\ &= \sum_n C_n^*(t) b_n(t) \\ \langle \psi | \hat{O} | \psi \rangle &= \sum_n \langle \phi_n | C_n^*(t) \hat{O} \sum_m C_m^*(t) | \phi_m \rangle \\ &= \sum_{n,m} C_n^*(t) C_m(t) \langle \phi_n | \hat{O} | \phi_m \rangle \\ &= \sum_{n,m} C_n^*(t) C_m(t) O_{nm} \\ \langle \phi_n | \psi \rangle &= \langle \phi_n | \sum_m C_m(t) | \phi_m \rangle = C_n(t) \end{aligned}$$

Formally, a unit operator

$$\hat{1} = \sum_n |\phi_n \rangle \langle \phi_n| \quad (\neq \sum_n \langle \phi_n | \phi_n \rangle),$$

e.g.,

$$\begin{aligned} \langle \phi_n | \hat{1} | \phi_m \rangle &= \langle \phi_n | \sum_{n'} |\phi_{n'} \rangle \langle \phi_{n'}| | \phi_m \rangle \\ &= \sum_{n'} \langle \phi_n | \phi_{n'} \rangle \langle \phi_{n'} | \phi_m \rangle \\ &= \sum_{n'} \delta_{nn'} \delta_{n'm} \\ &= \delta_{nm} \end{aligned}$$

Then

$$\begin{aligned}
\langle \psi | \phi \rangle &= \langle \psi | \hat{1} | \phi \rangle = \langle \psi | \sum_n |\phi_n\rangle \langle \phi_n| | \phi \rangle \\
&= \sum_n \langle \psi | \phi_n \rangle \langle \phi_n | \phi \rangle \\
&= \sum_n C_n^*(t) b_n(t) \\
\langle \psi | \hat{O} | \psi \rangle &= \langle \psi | \sum_n |\phi_n\rangle \langle \phi_n| \hat{O} \sum_m |\phi_m\rangle \langle \phi_m| | \psi \rangle \\
&= \sum_{n,m} \langle \psi | \phi_n \rangle \langle \phi_n | \hat{O} | \phi_m \rangle \langle \phi_m | \psi \rangle \\
&= \sum_{n,m} C_n^*(t) C_m(t) O_{nm}
\end{aligned}$$

4.2 Postulates of quantum statistical mechanics

4.2.1 Postulates

- Isolated systems
- In thermodynamic equilibrium
- Any macroscopic time interval is long enough in microscopic sense.

then, statistical average of an observable is

$$\overline{\langle O(x) \rangle} = \sum_{n,m} \overline{C_n^*(t) C_m(t)} (\phi_n, O \phi_m)$$

Postulates: Assuming $\{\phi_n\}$ are eigen-functions of energy,

- $\overline{C_n^*(t)C_m(t)} = 0 \quad n \neq m$
- $\overline{C_n^*(t)C_n(t)} = \begin{cases} \text{const.} & E < E_n < E + \Delta \\ 0 & \text{otherwise} \end{cases}$

This is the so-called microcanonical ensemble.

Therefore, *effectively* we may write

$$|b_n|^2 = \begin{cases} \text{const.} & E < E_n < E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

then

$$\langle O \rangle = \sum_n |b_n|^2 (\phi_n, O\phi_n) / \sum_n |b_n|^2.$$

Here $\langle O \rangle$ denotes both statistical average and average in quantum mechanics.

In classical statistical mechanics, the equal a priori probability assumption is based on the so-called "ergodicity".

In quantum mechanics, it seems not possible for ergodicity. The equal a priori probability postulates are assumed, based on possible interactions with the external environment. In other words, $C_n(t)$ include the coordinates of the environment and the time evolution (see, page 171 in the textbook). In the fundamental sense, therefore, the statistical average $\overline{C_n^*(t)C_m(t)}$ should effectively describe the average over microscopic times and the interactions with the environment.

4.2.2 Density matrix

The purpose of introducing the density matrix

- Describe statistical mechanics without the phases of the states
- Generalize the theory to any representation.

Let us define the density matrix ρ_{nm} by

$$\rho_{nm} \equiv (\phi_n, \rho \phi_m) \equiv \delta_{mn} |b_n|^2$$

where $\{\phi_n\}$ are the eigen-functions of H .

In Dirac notations

$$\rho = \sum_{n'} |\phi_{n'} \rangle |b_{n'}|^2 \langle \phi_{n'}|.$$

Here the sum is over all possible states, and different macroscopic conditions correspond to different $|b_{n'}|^2$.

Then

$$\langle O \rangle = \frac{\sum_n \langle \phi_n | O \rho | \phi_n \rangle}{\sum_n \langle \phi_n | \rho | \phi_n \rangle} = \frac{T_r(O\rho)}{T_r\rho}$$

where T_r is independent of representations, and we have generalized the calculation of $\langle O \rangle$ to any representation.

Exercise: Prove it.

4.3 Ensembles

4.3.1 Microcanonical ensemble

Since $\rho_{mn} = \delta_{mn}|b_n|^2$ is defined only up to a constant, let us take

$$\rho = \sum_{E < E_n < E + \Delta} |\phi_n\rangle\langle\phi_n|$$

where $H|\phi_n\rangle = E_n|\phi_n\rangle$, and the sum is over the states, not the energy levels. We now define

$$\Gamma(E) = T_r \rho$$

Obviously, $\Gamma(E)$ is the number of states with energy between E and $E + \Delta$, since

$$\begin{aligned} T_r \rho &= \sum_n \langle\phi_n|\rho|\phi_n\rangle \\ &= \sum_n \langle\phi_n| \sum_{E < E_m < E + \Delta} |\phi_m\rangle\langle\phi_m|\phi_n\rangle \\ &= \sum_{E < E_n < E + \Delta} 1 \end{aligned}$$

To derive thermodynamics, we simply identify the entropy

$$\begin{aligned} S(E, V) &= k \log \Gamma(E) \\ \langle O \rangle &= \frac{T_r(O\rho)}{T_r \rho} \end{aligned}$$

4.3.2 Canonical ensemble

In the derivation of the canonical ensemble in classical statistical mechanics, we replace

$$\frac{1}{N!} \int dp dq \rightarrow \sum_n$$

then

$$\rho_{mn} = \delta_{mn} e^{-\beta E_n} \quad \beta = \frac{1}{kT}$$

In Dirac notations,

$$\begin{aligned} \rho &= \sum_n |\phi_n \rangle e^{-\beta E_n} \langle \phi_n| = e^{-\beta H} \sum_n |\phi_n \rangle \langle \phi_n| \\ &= e^{-\beta H} \end{aligned}$$

The partition function

$$\begin{aligned} Q_N(V, T) &= \text{Tr} \rho \\ &= \text{Tr} e^{-\beta H} = \sum_n \langle \phi_n | e^{-\beta H} | \phi_n \rangle \\ &= \sum_n e^{-\beta E_n} \end{aligned}$$

Here \sum_n is over all eigenstates of all energy, not the eigenvalues of energy. For a macroscopic system, this is very different.

For an observable

$$\langle O \rangle = \frac{\text{Tr}(O\rho)}{\text{Tr}\rho} = \frac{1}{Q_N} \text{Tr}(Oe^{-\beta H})$$

In the energy representation,

$$\langle O \rangle = \frac{1}{Q_N} \sum_n O_{nn} e^{-\beta E_n}$$

very similar to the formulism in classical statistical mechanics.

4.3.3 Grand canonical ensemble

$$Z(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta\mu N} \cdot Q_N(V, T)$$
$$\langle O \rangle = \frac{1}{Z} \sum_{N=0}^{\infty} e^{\beta\mu N} \langle O \rangle_N$$

where $\langle O \rangle_N$ is the canonical ensemble average.

More generally

$$Z(\mu, V, T) = T_r e^{-\beta(H-\mu N)}$$
$$\langle O \rangle = \frac{1}{Z} T_r \left[O e^{-\beta(H-\mu N)} \right]$$

i.e., the density matrix is

$$\rho = e^{-\beta(H-\mu N)}$$

4.4 Ideal gases: microscopic ensemble

4.4.1 Quantum states

The system: N identical particles in quantum mechanics

$$H = \sum_{i=1}^N \frac{p_i^2}{2m}.$$

The particles are non-distinguishable. Therefore, in nature there are two types of identical particles

- **Bosons**

Wave functions are symmetric under an interchange of any pair of particle coordinates.

- **Fermions**

Wave functions are anti-symmetric under an interchange of any pair of particle coordinates

e.g., $N = 2$
a single-particle wave function

$$\psi_1(x_1), \psi_2(x_2)$$

Then, in general, the wave function for two particles can not be written as

$$\psi(x_1, x_2) = \psi_1(x_1)\psi_2(x_2)$$

Assume $\psi_1(x)$ and $\psi_2(x)$ are orthonormal,
Bosons

$$\psi(x_1, x_2) = \frac{1}{2!}(\psi_1(x_1)\psi_2(x_2) + \psi_1(x_2)\psi_2(x_1))$$

Fermions

$$\psi(x_1, x_2) = \frac{1}{2!}(\psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1))$$

If $\psi_1(x) = \psi_2(x)$, then $\psi(x_1, x_2) = 0$

\implies the Pauli principle.

Thermodynamics: we must compute the number of states $\Gamma(E)$ of the system with the energy between E and $E + \Delta$.

Assume the particles are spinless, then a single particle energy is

$$\epsilon_p = \frac{p^2}{2m}$$

Where $p \equiv |\vec{p}|$, \vec{p} is the momentum of the particle.

$$\vec{p} = \frac{2\pi\hbar}{L}\vec{m} \Leftrightarrow \begin{cases} p_x = \frac{2\pi\hbar}{L}m_x \\ p_y = \frac{2\pi\hbar}{L}m_y \\ p_z = \frac{2\pi\hbar}{L}m_z \end{cases}$$

$$m_x, m_y, m_z = 0, \pm 1, \pm 2, \dots$$

L is the size of the cubic box.

The plane wave function in 1 dimension

$$e^{\frac{i}{\hbar}p_x x}$$

The periodic boundary condition

$$\begin{aligned} e^{\frac{i}{\hbar}p_x x} &= e^{\frac{i}{\hbar}p_x(x+L)} \\ \therefore e^{\frac{i}{\hbar}p_x L} &= e^{im_x 2\pi} \quad m_x = 0, \pm 1, \pm 2 \dots \\ \therefore p_x &= \frac{2\pi\hbar}{L}m_x \end{aligned}$$

In the limit $L \rightarrow \infty$

$$\sum_{\vec{p}} = \sum_{\vec{m}} \rightarrow \frac{V}{h^3} \int d^3p \quad h = 2\pi\hbar$$

A state of an ideal gas can be uniquely specified by a set of occupation number $\{n_{\vec{p}}\}$, with $n_{\vec{p}}$ being the number of the particles having the momentum \vec{p} . - This is different from a classical ideal gas, or the ideal Boltzmann gas discussed below.

Obviously, the total energy and number of particles

$$\begin{aligned}
 E &= \sum_{\vec{p}} \epsilon_{\vec{p}} n_{\vec{p}} \\
 N &= \sum_{\vec{p}} n_{\vec{p}} \\
 n_{\vec{p}} &= \begin{cases} 0, 1, 2, \dots & \text{bosons} \\ 0, 1 & \text{fermions} \end{cases}
 \end{aligned}$$

4.4.2 Distribution of particles

Let us divide the spectrum

$$\epsilon_p = \frac{p^2}{2m}$$

into groups of levels containing respectively g_1, g_2, \dots levels, as shown in Fig. 4.1. Each g_i is assumed to be very large.

Each group is called a cell, the i -th cell has an average energy ϵ_i and the occupation number n_i

$$\Gamma(E) = \sum_{\{n_i\}} W\{n_i\}$$

$W\{n_i\} \equiv$ number of the states corresponding to $\{n_i\}$.
 $\sum_{\{n_i\}}$ satisfies the conditions

$$\begin{aligned}
 E &= \sum_i \epsilon_i n_i \\
 N &= \sum_i n_i
 \end{aligned}$$

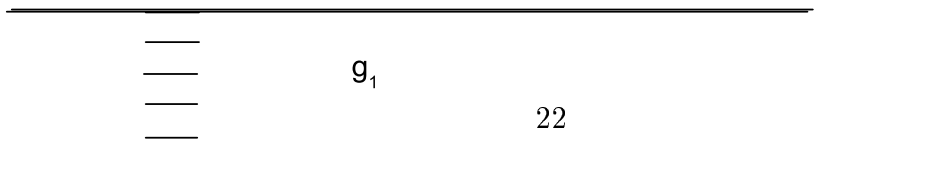
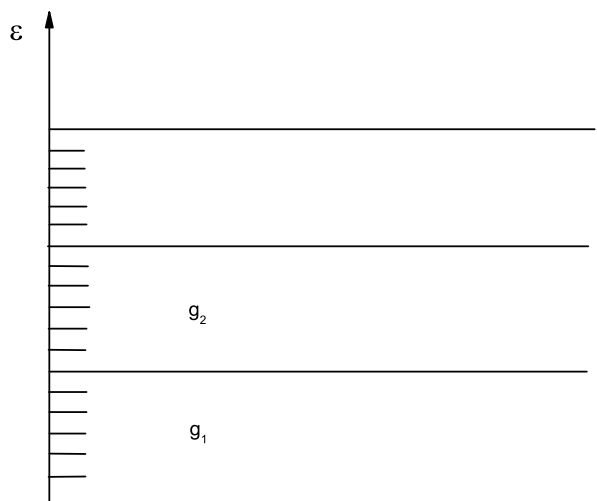


Figure 4.1:

In other words, we may consider ϵ_i labels the energy level with g_i degeneracy, i.e., there are g_i different states at the energy level ϵ_i .

Question: why do we assume each g_i to be very large?

How to compute $W\{n_i\}$?

The key is to find out ω_i : the number of ways in which n_i particles can be assigned to the i -th cell (which contains g_i levels), i.e., the number of ways to distribute n_i particles to g_i levels inside the i -th cell.

It is important that in quantum mechanics interchanging particles does not lead to new states of the system.

- keep in mind this in computing ω_i
- for a fixed set of $\{n_i\}$, we simply have

$$W\{n_i\} = \prod_j \omega_j$$

Bosons

The first position on the left can only be state

If particles are distinguishable and the order of the states are relevant, then there are $g_i(n_i + g_i - 1)!$ ways to assign n_i particles into g_i states.

However, particles are not distinguishable. There are $n_i!$ ways for permuting the n_i particles which do not lead to new states. Taking into account the order the states

are also irrelevant

$$\omega_i = \frac{g_i(n_i + g_i - 1)!}{n_i!g_i!} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

$$W\{n_i\} = \prod_i \omega_i = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

Fermions

The number of particles assigned to a state can be only 0 or 1. If $n_i \leq g_i$,

$$\omega_i = \frac{g_i!}{n_i!(g_i - n_i)!} \quad W\{n_i\} = \prod_i \omega_i$$

If $n_i > g_i$, it is not allowed.

4.4.3 The most probable distribution

The entropy

$$S = k \log \Gamma(E)$$

$$= k \log \sum_{\{n_i\}} W\{n_i\}$$

In equilibrium and in thermodynamic limit, the most probable distribution $\{\bar{n}_i\}$ dominates

$$S = k \log W\{\bar{n}_i\}$$

Note: we request \bar{n}_i is a large number, while $n_{\bar{p}}$ is not.

How to maximize $W\{n_i\}$?

Fermions

$$\begin{aligned}\log W\{n_i\} &= \sum_i \log g_i! - \log n_i! - \log(g_i - n_i)! \\ \therefore \log n_i! &\simeq n_i(\log n_i - 1) \\ \therefore \log W\{n_i\} &= \sum_i g_i(\log g_i - 1) - n_i(\log n_i - 1) \\ &\quad - (g_i - n_i)(\log(g_i - n_i) - 1) \\ &= \sum_i g_i \log g_i - n_i \log n_i - (g_i - n_i) \log(g_i - n_i)\end{aligned}$$

The method of Lagrange multipliers

$$\delta[\log W\{n_i\}] - \delta(\alpha \sum n_i + \beta \sum_i \epsilon_i n_i) = 0$$

$$\begin{aligned}\delta[\log W\{n_i\}] &= \sum_i [-(\log n_i + 1) + (\log(g_i - n_i) + 1)] \delta n_i \\ &= \sum_i \log \frac{g_i - n_i}{n_i} \delta n_i\end{aligned}$$

$$\begin{aligned}\therefore \log \frac{g_i - \bar{n}_i}{\bar{n}_i} &= \alpha + \beta \epsilon_i \\ \implies \bar{n}_i &= \frac{g_i}{e^{\alpha + \beta \epsilon_i} + 1}\end{aligned}$$

hence

$$\bar{n}_{\vec{p}} = \frac{1}{e^{\alpha + \beta \epsilon_{\vec{p}}} + 1} \quad \alpha = -\beta \mu$$

Exercise: Show for bosons

$$\bar{n}_{\vec{p}} = \frac{1}{e^{\alpha + \beta \epsilon_{\vec{p}}} - 1}$$

The parameters β and α are determined by

$$\sum_{\vec{p}} \epsilon_{\vec{p}} \bar{n}_{\vec{p}} = E$$
$$\sum_{\vec{p}} n_{\vec{p}} = N$$

With $\bar{n}_{\vec{p}}$ at hand, we are able to calculate all observable.

Question: how do the particle distributions for bosons and fermions go back to the classical Boltzmann distribution?

Hint: at high temperatures, the average number of particles at a state is very small.

4.5 The ideal Boltzmann gas

It is essentially a “classical” system

4.5.1 Quantum states

Assume the particles are distinguishable and do not follow the Pauli principle, a set of $\{n_{\vec{p}}\}$ specifies $N! / (\prod_{\vec{p}} n_{\vec{p}}!)$ states. This is different from the bosons and fermions.

4.5.2 Distribution of particles

First place the particles into cells, there are $\frac{N!}{\prod_{i=1}^K n_i!}$ ways

In the i th cell, there are $g_i^{n_i}$ ways to put n_i particles onto g_i states.

In total, the number of states for $\{n_i\}$

$$N! \prod_i \frac{g_i^{n_i}}{n_i!}$$

here $g_i^{n_i}$ represents that every particle has g_i possible states. Taking into account correct Boltzmann factor

$$W\{n_i\} = \prod_i \frac{g_i^{n_i}}{n_i!}$$

Question: why $\frac{N!}{\prod_{i=1}^k n_i!}$

- ① if all $n_i = 1$,
- ② if $n_i = 1, i \leq K - 1, n_K \neq 1$
- ③ $n_i = 1, i \leq K - 2, n_{k-1} \neq 1, n_k \neq 1$
- ④ in general

$$\frac{N!}{\prod_{i=1}^K n_i!}$$

For quasi-independent particles, we consider that particles in a cell contribute the same to physical observables.

4.5.3 Exercise:

Prove $\bar{n}_{\vec{p}} = e^{-\alpha - \beta \epsilon_{\vec{p}}}$

4.5.4 Thermodynamics

$$N = \sum_i g_i e^{-\alpha - \beta \epsilon_i} = e^{-\alpha} \sum_{\vec{p}} e^{-\beta \epsilon_{\vec{p}}}$$

$$\begin{aligned}
&= e^{-\alpha} \frac{V}{h^3} \int_{-\infty}^{+\infty} d^3p e^{-\beta \vec{p}^2/2m} \\
&= e^{-\alpha} \int d\Omega \int_{-\infty}^{+\infty} dp \cdot p^2 e^{-\beta p^2/2m}
\end{aligned}$$

Here $\int d\Omega = 4\pi$.

Exercise: Calculate the integrals

$$\begin{aligned}
&\int_0^{\infty} dp \cdot p^2 \cdot e^{-cp^2} \\
&\int_0^{\infty} dp \cdot p^4 \cdot e^{-cp^2}
\end{aligned}$$

hint: suppose $\int_0^{\infty} dp \cdot e^{-cp^2}$ can be picked up from the hand book.

$$N = e^{-\alpha} \frac{V}{\lambda^3} \quad \lambda = \sqrt{\frac{2\pi\hbar^2}{mkT}}$$

$$\begin{aligned}
E &= e^{-\alpha} \sum_i g_i \epsilon_i e^{\beta \epsilon_i} = e^{-\alpha} \sum_{\vec{p}} \epsilon_i e^{\beta \epsilon_{\vec{p}}} \\
&= \frac{e^{-\alpha}}{h^3} \int_0^{\infty} dp 4\pi p^2 \frac{p^2}{2m} e^{-\beta p^2/2m} \\
&= \frac{3}{2} N k T
\end{aligned}$$

$$\begin{aligned}
\frac{S}{k} &= \log W\{\bar{n}_i\} = \log \prod_i \frac{g_i^{\bar{n}_i}}{\bar{n}_i!} \\
&= \sum_i \log g_i^{\bar{n}_i} - \log \bar{n}_i! \\
&\simeq \sum_i \bar{n}_i \log \frac{g_i}{\bar{n}_i}
\end{aligned}$$

$$\begin{aligned}
&= \sum_i g_i e^{-\alpha - \beta \epsilon_i} (\alpha + \beta \epsilon_i) \\
&= \sum_{\vec{p}} e^{-\alpha - \beta \epsilon_{\vec{p}}} (\alpha + \beta \epsilon_{\vec{p}}) \\
&= \beta E + \alpha N \\
&= \frac{32}{N} - N \log \left[\frac{N}{V} \left(\frac{2\pi \hbar^2}{mkT} \right)^{3/2} \right]
\end{aligned}$$

4.6 Ideal gases: grand canonical ensemble

4.6.1 Partition function

$$\begin{aligned}
Z(\mu, V, T) &= \sum_{N=0}^{\infty} e^{\beta \mu N} Q_N(V, T) \\
&= \sum_{N=0}^{\infty} \sum_{\substack{\{n_{\vec{p}}\} \\ \sum_{\vec{p}} n_{\vec{p}} = N}} e^{\beta \mu N} e^{-\beta \sum_{\vec{p}} \epsilon_{\vec{p}} n_{\vec{p}}} \\
&= \dots \prod_{\vec{p}} (e^{\beta \mu - \beta \epsilon_{\vec{p}}})^{n_{\vec{p}}}
\end{aligned}$$

- in quantum mechanics, a set of $\{n_{\vec{p}}\}$ correspond to just one state

•

$$\sum_{N=0}^{\infty} \sum_{\substack{\{n_{\vec{p}}\} \\ \sum_{\vec{p}} n_{\vec{p}} = N}} = \sum_{n_0} \sum_{n_1} \dots$$

e.g. \vec{p} takes 3 states

$$\begin{array}{rcc}
 N = 0 & 0 & 0 & 0 \\
 N = 1 & 1 & 0 & 0 \\
 & 0 & 1 & 0 \\
 & 0 & 0 & 1
 \end{array}$$

$$\begin{aligned}
 Z(\mu, V, T) &= \sum_{n_0} \sum_{n_1} \dots \left(e^{\beta(\mu - \epsilon_0)} \right)^{n_0} \left(e^{\beta(\mu_1 - \epsilon_1)} \right)^{n_1} \dots \\
 &= \left[\sum_{n_0} \left(e^{\beta(\mu - \epsilon)} \right)^{n_0} \right] \left[\sum_{n_1} \left(e^{\beta(\mu - \epsilon_1)} \right)^{n_1} \right] \dots \\
 &= \prod_{\vec{p}} \left[\sum_n \left(e^{\beta\mu - \beta\epsilon_{\vec{p}}} \right)^n \right]
 \end{aligned}$$

$$\begin{array}{ll}
 n = 0, 1, 2 \dots & \text{for bosons} \\
 = 0, 1 & \text{fermions}
 \end{array}$$

$$\therefore Z(\mu, V, T) = \begin{cases} \prod_{\vec{p}} \frac{1}{1 - e^{\beta\mu - \beta\epsilon_{\vec{p}}}} & \text{bosons} \\ \prod_{\vec{p}} 1 + e^{\beta\mu - \beta\epsilon_{\vec{p}}} & \text{fermions} \end{cases}$$

then

$$\frac{PV}{kT} = \log Z(\mu, V, T)$$

$$\begin{aligned}
 \bar{N} &= \frac{1}{Z} \sum_{N=0}^{\infty} \sum_{\substack{\{n_{\vec{p}}\} \\ \sum n_{\vec{p}} = N}} N e^{\beta\mu N} e^{-\beta \sum \epsilon_{\vec{p}} n_{\vec{p}}} \\
 &= \frac{\partial}{\partial \beta\mu} \log Z(\mu, V, T)
 \end{aligned}$$

$$\begin{aligned}
\bar{n}_{\vec{p}} &= \frac{1}{Z} \sum_{N=0} e^{\beta\mu N} \sum_{\substack{\{n_{\vec{p}}\} \\ \sum n_{\vec{p}}=N}} n_{\vec{p}} e^{-\beta \sum \epsilon_{\vec{p}} n_{\vec{p}}} \\
&= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_{\vec{p}}} \log Z(\mu, V, T) \\
&= \frac{e^{\beta\mu - \beta\epsilon_{\vec{p}}}}{1 \mp e^{\beta\mu - \beta\epsilon_{\vec{p}}}}
\end{aligned}$$

\mp : **bosons**
 fermions

all results are equivalent to those in the microcanonical ensemble.

Note: $\because \bar{n}_{\vec{p}} \geq 0, \therefore$ it must be $e^{\beta\mu} \geq 0$ for both bosons and fermions, i.e., μ is real.

4.6.2 Equations of state

If the summand is finite for all \vec{p} , it is possible to replace

$$\sum_{\vec{p}} \rightarrow \frac{V}{h^3} \int d^3p$$

in the limit $V \rightarrow \infty$ (in microscopic unit)

Fermi gas

$$\begin{aligned}
\frac{PV}{kT} &= \sum_{\vec{p}} \log(1 + e^{\beta\mu - \beta\epsilon_{\vec{p}}}) \\
&= \frac{V}{h^3} \int d\Omega \int dp p^2 \log(1 + e^{\beta\mu - \beta p^2/2m}) \\
\therefore \begin{cases} \frac{P}{kT} = \frac{4\pi}{h^3} \int_0^\infty dp p^2 \log(1 + e^{\beta\mu - \beta p^2/2m}) \\ \frac{N}{V} = \frac{4\pi}{h^3} \int_0^\infty dp p^2 1/(e^{-\beta\mu + \beta p^2/2m} + 1) \end{cases}
\end{aligned}$$

Eliminating μ , we obtain the equation of state.

Bose gas

$$\frac{PV}{kT} = - \sum_{\vec{p}} \log(1 - e^{\beta\mu - \beta\epsilon_{\vec{p}}})$$

at $\vec{p} = 0$, $\log(1 - e^{\beta\mu})$ diverges when $\mu \rightarrow 0$. Therefore, we separate the mode $\vec{p} = 0$

$$\frac{P}{kT} = -\frac{4\pi}{h^3} \int_0^\infty dp p^2 \log(1 - e^{\beta\mu - \beta p^2/2m}) - \frac{1}{V} \log(1 - e^{\beta\mu})$$

Similarly

$$\frac{\bar{N}}{V} = \frac{4\pi}{h^3} \int_0^\infty dp p^2 \frac{1}{e^{-\beta\mu + \beta p^2/2m} - 1} + \frac{1}{V} \frac{e^{\beta\mu}}{1 - e^{\beta\mu}}$$

Actually,

$$\langle n_0 \rangle = \frac{e^{\beta\mu}}{1 - e^{\beta\mu}}$$

If $\langle n_0 \rangle / N$ is a finite number, it gives rise to the Bose-Einstein condensation.

4.6.3 The internal energy

It can be calculated from

$$\begin{aligned} U(\mu, V, T) &= \frac{1}{Z} \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\substack{\{n_{\vec{p}}\} \\ \sum n_{\vec{p}} = N}} e^{-\beta \sum \epsilon_{\vec{p}} n_{\vec{p}}} \sum_{\vec{p}} \epsilon_{\vec{p}} n_{\vec{p}} \\ &= -\frac{\partial}{\partial \beta} [\log Z(\mu, V, T)] \end{aligned}$$

However, to express $u = U/V$ in terms of \bar{N} , V , and T , we must eliminate μ . That is complicated.

Exercises

Assuming $\psi_n = \sum_m \phi_m t_{mn}$, prove

$$T^+T = TT^+ = 1, \quad O = TO'T^+.$$

Prove that $T_r(O)$ is independent of representations.
Show that for bosons

$$\bar{n}_{\vec{p}} = \frac{1}{e^{\alpha + \beta \epsilon_{\vec{p}}} - 1}.$$

Prove that for the ideal Boltzmann gas

$$\bar{n}_{\vec{p}} = e^{-\alpha - \beta \epsilon_{\vec{p}}}.$$

Calculate the integrals

$$\int_0^\infty dp \cdot p^2 \cdot e^{-cp^2}$$

$$\int_0^\infty dp \cdot p^4 \cdot e^{-cp^2}$$

hint: suppose $\int_0^\infty dp \cdot e^{-cp^2}$ can be picked up from the hand book.

Problems 8.2 and 8.5 in the textbook.

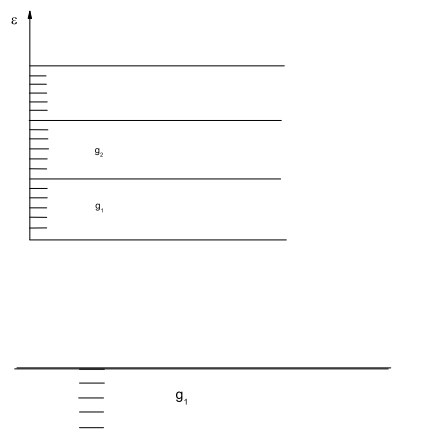


Figure 4.2: