

热力学与统计物理学笔记

Thermodynamics and Statistical Physics Notes

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Chapter 1 Basic Theorems and Equations of Thermodynamics

Discipline	Model	Parameters	Laws
Mechanics	Particle, Rigid Body, Ideal Elastic Body, Ideal Fluid	Position \mathbf{r} , Velocity \mathbf{v} , Force \mathbf{F} Acceleration \mathbf{a} , Momentum \mathbf{p} Kinetic Energy K , Potential Energy U Hamiltonian H Pressure p	$\mathbf{r} = \mathbf{v}t$ $\mathbf{F} = m\mathbf{a} = \dot{\mathbf{p}}$ $E = K + U = C$ $\dot{\mathbf{p}} = -\partial_{\mathbf{r}}H$ $\dot{r} = \partial_{\mathbf{p}}H$
Electromagnetism	Point Charge, Magnetic Dipole Moment, Electromagnetic Medium	Electric Charge Q , Current I , Magnetic Moment \mathbf{M} Electromagnetic Field Strength, Electric Displacement Vector Electromagnetic Field Energy, Momentum Hamiltonian H	Coulomb's Law Maxwell's Equations $E = \frac{\mathbf{E} \cdot \mathbf{D}}{2} + \frac{\mathbf{B} \cdot \mathbf{H}}{2}$ $\dot{\mathbf{p}} = -\partial_{\mathbf{r}}H$
Chemistry	Chemical Components N_2, H_2	Amount of Substance, Moles n_{N_2}, n_{H_2}	Chemical Reaction Equation $N_2 + 3H_2 = 2NH_3$
Thermodynamics	Thermodynamic Equilibrium State, Quasi-static Process	Temperature T , Internal Energy U , Entropy S Free Energy F , Gibbs Free Energy G Chemical Potential μ	Equation of State Three Laws of Thermodynamics

For different disciplines of physics, there are different parameter expressions. In thermodynamics, we focus on selecting **state variables**, such as (p, V, n) , which can form a set of parameters describing the state of an open system. They can be represented by phase diagrams in thermodynamics. They can also be further divided into extensive and intensive quantities, as seen in [注 3.1](#). Below, we introduce some basic theorems and mathematical methods of thermodynamics.

1.1 Four Laws

Theorem 1.1 (Zeroth Law of Thermodynamics). *Carathéodory and H. Fowler pointed out that if two systems are in thermal equilibrium (no energy exchange occurs after long-term thermal contact), then there must exist an equal thermal parameter, defined as **temperature**.*

Thus, we can extend this to the thermal equilibrium of three or more objects.

1.1.1 Thermodynamic Temperature Scale

The three elements of empirical temperature scales: the thermometric substance and its properties, calibration points (often phase transition points such as the triple point of water), and the functional relationship of the thermometric property (often linear).

For example, if a substance has volumes V_1 and V_2 at temperatures t_1 and t_2 , respectively, the temperature scale can be defined as

$$t = \frac{V - V_1}{V_2 - V_1}(t_2 - t_1) + t_1 \quad (1.1)$$

Rewriting this formula in terms of V as a function of temperature, we get

$$V = V_1 + \frac{V_2 - V_1}{t_2 - t_1}(t - t_1) \quad (1.2)$$

Experiments show that for ideal gases (generally, gases at very low pressures can be approximated as ideal gases because the molecular distances are large and interaction energy is small), the

relationship is

$$V = \left(\frac{V_0}{273.15} \right) t + V_0 \quad (1.3)$$

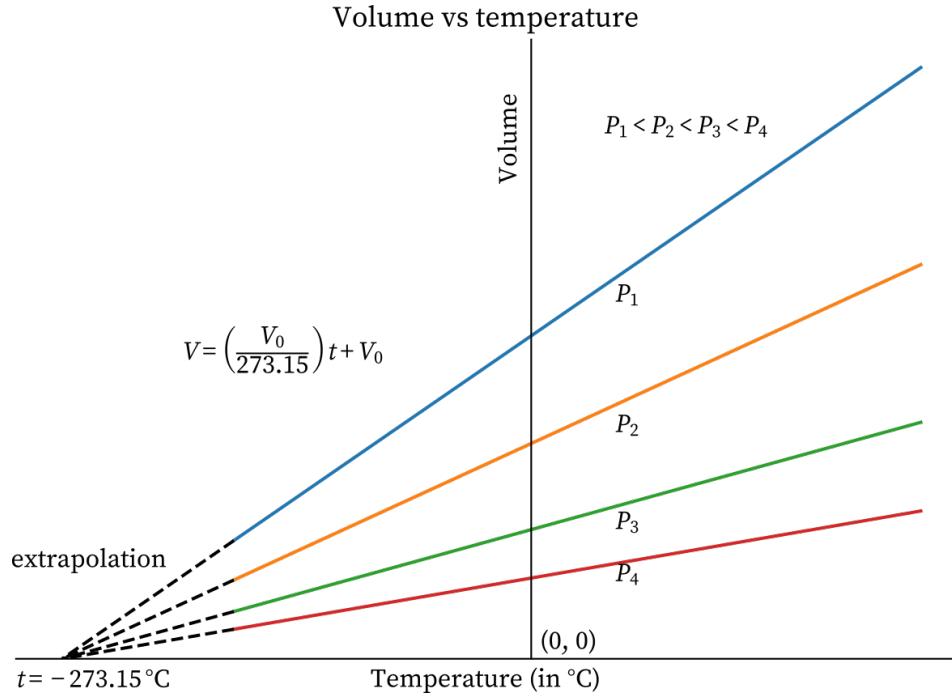


Fig. 1: Ideal Gas Temperature Scale

It can be seen that at different pressures, the volume approaches zero, and the temperature approaches a constant value (-273.15°C), which is absolute zero. By shifting the temperature zero point here, the ideal gas satisfies

$$\frac{pV}{T} = \text{const.} \quad (1.4)$$

Thus, the thermodynamic temperature scale T is defined as

$$T = t + 273.15 \quad (\text{K}) \quad (1.5)$$

It can also be calibrated using the triple point of water, with the temperature and volume at the triple point, the temperature is recorded as

$$T = \frac{V}{V_{tr}} T_{tr} \quad (1.6)$$

1.1.2 Equation of State

The equation of state describes a functional relationship between the variables of a system under thermodynamic equilibrium conditions, which can be formally written as $f(\text{geometric, mechanical, electromagnetic, chemical, temperature variables}) = 0$. The specific form will be

introduced in Chapter 2. Below is a mathematical description, which can be written as

$$f(x_1, x_2, \dots, x_n, T) = 0 \quad (1.7)$$

Abstracting three parameters (assuming other parameters remain unchanged during the process), these three parameters are interdependent

$$f(x, y, z) = 0 \quad (1.8)$$

Performing a differential expansion

$$\begin{aligned} x &= x(y, z), \quad dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz \\ y &= y(x, z), \quad dy = \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz \end{aligned} \quad (1.9)$$

From this, we obtain

$$dx = \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z dx + \left[\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x + \left(\frac{\partial x}{\partial z} \right)_y \right] dz \quad (1.10)$$

Thus, by comparing the coefficients of the differentials, we obtain two very important differential relationships in thermodynamics

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z = 1 \quad (1.11a)$$

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 \quad (1.11b)$$

Where Eq. 1.11a can be applied to reciprocal calculations of differential relationships, and Eq. 1.11b is used for the exchange of three differentials. Written in the specific (p, V, T) system

$$\left(\frac{\partial p}{\partial V} \right)_T = \frac{1}{\left(\frac{\partial V}{\partial p} \right)_T} \quad (1.12a)$$

$$\left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial T}{\partial p} \right)_V = -1 \quad (1.12b)$$

Starting from Eq. 1.12b, three commonly used physical quantities related to the measurement of the equation of state are defined

(1) Coefficient of volumetric expansion α_p :

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (1.13)$$

α_p gives the proportion of volume change per unit temperature increase or decrease during an isobaric process.

(2) Coefficient of pressure β_V :

$$\beta_V = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V \quad (1.14)$$

β_V gives the proportion of pressure change per unit temperature increase or decrease during an isochoric process.

(3) Isothermal compressibility coefficient κ_T :

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (1.15)$$

κ_T gives the proportion of volume change per unit pressure increase or decrease during an isothermal process.

Similarly, from Eq. 1.12b, the three coefficients satisfy

$$\alpha_p = \kappa_T \beta_V p \quad (1.16)$$

Measuring these three physical quantities can be used to solve the equation of state.

Theorem 1.2 (First Law of Thermodynamics). *The effect of heat and work on internal energy: The increase in internal energy U can be obtained by absorbing heat from the outside and doing work on the outside. Thus, the first law of thermodynamics is an extension of the law of conservation of energy to non-isolated systems.*

Due to the definition of the sign of work (imagine an expanding cylinder), the work done by the outside on the system is $-\Delta W$, the heat absorbed is ΔQ , and the change in internal energy is

$$\Delta U = \Delta Q - \Delta W \text{ or } \Delta Q = \Delta U + \Delta W \quad (1.17)$$

For an infinitesimal process, the first law of thermodynamics can be written as

$$dQ = dU + dW \quad (1.18)$$

where Q, W are related to the specific process, denoted by d , while U is only related to the state, denoted by d for changes.

1.1.3 Work

When discussing thermodynamic processes, since strictly reversible processes do not exist, we hope to provide a thermodynamic change function on the phase diagram. Therefore, we approximate the intermediate process as an equilibrium state (where all parameters of the system are stable and uniform), called a quasi-static process, which also conforms to the properties of a reversible process. However, the intermediate state of an irreversible process is not a thermal equilibrium state and cannot be expressed with a solid line on the phase diagram. There are several forms of work:

(1) Work done by gas expansion:

$$W = pdV, \quad \Delta W = \int_{V_1}^{V_2} pdV \quad (1.19)$$

(2) Work done by elastic rods or strings under tension:

$$W = -\mathbf{F} \cdot d\mathbf{l}, \quad \Delta W = - \int_{l_1}^{l_2} \mathbf{F} \cdot d\mathbf{l} \quad (1.20)$$

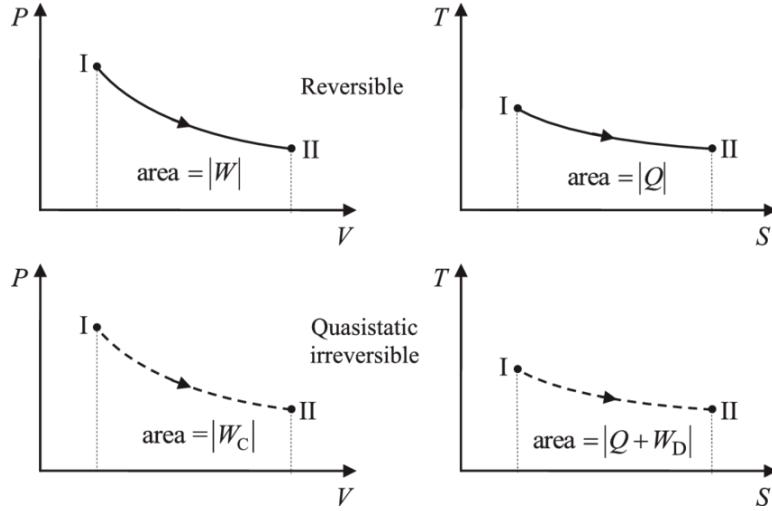


Fig. 2: Illustration of a Quasi-static Process

(3) Work done by liquid surface film:

$$W = -\mathbf{F} \cdot d\mathbf{l} = -\boldsymbol{\sigma} \cdot dA, \quad \Delta W = - \int_{A_1}^{A_2} \boldsymbol{\sigma} \cdot dA, \quad (1.21)$$

where A is twice the area of the liquid surface film because there is surface tension on both sides.

(4) Work done by dielectric:

$$W = -\mathbf{F} \cdot d\mathbf{l} = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \sum_{i=1}^n q_i \mathbf{E} \cdot d\mathbf{l} = - \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \sum_{i=1}^n \mathbf{E} \cdot d\mathbf{p}_i = -\mathbf{E} \cdot d\mathbf{P}, \quad \Delta W = - \int \mathbf{E} \cdot d\mathbf{P} \quad (1.22)$$

where the electric dipole moment is $\mathbf{p} = ql$, thus the polarization intensity

$$\mathbf{P} = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \sum_{i=1}^n \mathbf{p}_i \quad (1.23)$$

(5) Work done by magnetic medium, first consider the induced electromotive force,

$$V = -\mathbf{B} \cdot \frac{dS}{dt} \quad (1.24)$$

Since the magnetic moment is $\mu_i = IS_i$, the magnetization intensity (macroscopic magnetic moment) is

$$\mathbf{M} = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \sum_{i=1}^n \boldsymbol{\mu}_i \quad (1.25)$$

Thus, $d\mathbf{M} = IdS = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \sum_{i=1}^n d\boldsymbol{\mu}_i$, so the work done is

$$W = -VI \cdot dt = - \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \sum_{i=1}^n \mathbf{B} \cdot d\boldsymbol{\mu}_i = -\mathbf{B} \cdot d\mathbf{M}, \quad \Delta W = - \int \mathbf{B} \cdot d\mathbf{M} \quad (1.26)$$

(6) Battery (V is the electromotive force, q is the charge)

$$W = -Vdq = -VIdt, \quad \Delta W = - \int -VIdt \quad (1.27)$$

(7) Open system with particle exchange (μ is the chemical potential)

$$W = -\mu dN, \quad \Delta W = - \int \mu dN \quad (1.28)$$

In general, work done by the external generalized force Y multiplied by the generalized displacement y on the system is

$$W_{\text{ext}} = Ydy, \quad W = -Ydy, \quad \Delta W = - \int Ydy \quad (1.29)$$

Table 1: Common Generalized Forces and Displacements for External Work

System	Y	y	W
Gas	$-p$	V	$p dV$
Elastic rod	\mathbf{F}	\mathbf{l}	$-\mathbf{F} \cdot d\mathbf{l}$
Liquid film	$\boldsymbol{\sigma}$	\mathbf{A}	$-\boldsymbol{\sigma} \cdot d\mathbf{A}$
Dielectric	\mathbf{E}	\mathbf{P}	$-\mathbf{E} \cdot d\mathbf{P}$
Magnetic medium	\mathbf{B}	\mathbf{M}	$-\mathbf{B} \cdot d\mathbf{M}$
Open system	μ	N	$-\mu dN$

1.1.4 Heat Capacity

To describe the change of internal energy with temperature, heat capacity is introduced. For a specific process x , heat capacity is defined as the change in heat per unit temperature change

$$C_x = \frac{Q}{dT} = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T}, \quad \Delta Q = \int C_x dT \quad (1.30)$$

In the most common constant volume heat capacity,

$$C_V = \left(\frac{Q}{dT} \right)_V = \left(\frac{dU}{dT} \right)_V \quad (1.31)$$

and the constant pressure heat capacity is

$$C_p = \left(\frac{Q}{dT} \right)_p = \left(\frac{d(U + pV)}{dT} \right)_p = \left(\frac{dH}{dT} \right)_p \quad (1.32)$$

Introducing a state function—enthalpy $H = U + pV$

$$dH = dU + p dV + V dp \quad (1.33)$$

1.1.5 Energy Changes of Ideal Gases

According to Joule's law, from the free expansion experiment of gases, it is found that the internal energy of a gas is only related to temperature and not to its volume, i.e., **the internal energy of an ideal gas is only a function of temperature**

$$U = U(T) \quad (1.34)$$

Below, we discuss several processes of ideal gases, unified in the form $pV^n = \text{const.}$

1. Isobaric process: $n = 0, p = \text{const.}$

$$\Delta W = \int_1^2 p \, dV = p(V_2 - V_1) \quad (1.35)$$

The work done by the system is taken from the external heat source and the decrease in the system's internal energy.

2. Isochoric process: $n = \infty, Vp^{1/n} = V = \text{const.}$

$\Delta W = 0$, so $\Delta U = \Delta Q$, the increase in the system's internal energy is equal to the heat absorbed from the outside.

3. Isothermal process: $n = 1, pV \propto T, U(T) = \text{const.}$ According to the ideal gas equation of state $pV = nRT$

$$\Delta W = \int_1^2 p \, dV = \int_{V_1}^{V_2} \frac{nRT}{V} \, dV = nRT \ln \frac{V_2}{V_1} \quad (1.36)$$

In an isothermal process, the internal energy of an ideal gas does not change, and the work done by the system is taken from the external heat source.

4. Adiabatic process: $n = \gamma, pV^\gamma = \text{const.}$ This equation holds for the following reasons: define the adiabatic index (related to the degrees of freedom of the gas)

$$\gamma = \frac{C_p}{C_V} \quad (1.37)$$

and using the relationship

$$C_p - C_V = \frac{\partial(pV)}{\partial T} = nR \quad (1.38)$$

So the constant volume heat capacity and constant pressure heat capacity expressed in terms of the adiabatic index

$$C_V = \frac{nR}{\gamma - 1}, \quad C_p = \frac{\gamma nR}{\gamma - 1} \quad (1.39)$$

In an adiabatic process, $Q = 0$, there is no heat exchange with the outside,

$$dU = C_V dT = -pdV \quad (1.40)$$

Since $T = \frac{pV}{nR} = \frac{pV}{C_p - C_V}$, expand it into (p, V) differentials

$$dT = \frac{1}{C_V} \frac{1}{\gamma - 1} (pdV + Vdp) \quad (1.41)$$

Substitute back into Eq. 1.40, we get

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0 \quad (1.42)$$

Thus, the adiabatic equation of state for an ideal gas is given

$$pV^\gamma = \text{const.} \quad (1.43)$$

The adiabatic process also satisfies

$$TV^{\gamma-1} = \text{const.}, \quad T^\gamma p^{1-\gamma} = \text{const.} \quad (1.44)$$

Using the functional relationship Eq. 1.40 and heat capacity Eq. 1.39, the work done in an adiabatic process for an ideal gas is obtained

$$\begin{aligned} \Delta W &= -\Delta U = -C_V \Delta T = -C_V (T_2 - T_1) \\ &= \frac{nR}{1-\gamma} (T_2 - T_1) = \frac{p_2 V_2 - p_1 V_1}{1-\gamma} \end{aligned} \quad (1.45)$$

The adiabatic index γ of an ideal gas and the degrees of freedom f of the molecules have the following approximate relationship:

$$\gamma = \frac{f+2}{f}, \quad f = \frac{2}{\gamma-1} \quad (1.46)$$

5. Polytropic process: $pV^n = \text{const.}$

According to $pV^n = X$, the infinitesimal work is

$$W = pdV = \frac{X}{V^n} dV \quad (1.47)$$

$$\begin{aligned} \Delta W &= \int_1^2 \frac{X}{V^n} dV = \frac{1}{1-n} \left(\frac{X}{V_2^{n-1}} - \frac{X}{V_1^{n-1}} \right) = \frac{1}{1-n} \left(\frac{XV_2}{V_2^n} - \frac{XV_1}{V_1^n} \right) \\ &= \frac{1}{1-n} (p_2 V_2 - p_1 V_1) = \frac{nRT_2 - nRT_1}{1-n} \end{aligned} \quad (1.48)$$

The internal energy calculation refers to the adiabatic process Eq. 1.45, obtaining

$$\begin{aligned} \Delta U &= U_2 - U_1 = \int_1^2 dU = \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T} \right)_V dT \\ &= C_V (T_2 - T_1) = \frac{nR(T_2 - T_1)}{\gamma - 1} \end{aligned} \quad (1.49)$$

Thus, the heat change in a polytropic process is

$$\Delta Q = \Delta U + \Delta W = \left(\frac{1}{\gamma - 1} - \frac{1}{n - 1} \right) nR (T_2 - T_1) \quad (1.50)$$

When $n = \gamma$, it returns to the adiabatic process case, with no heat change.

1.1.6 Carnot Cycle

This is an ideal thermodynamic cycle proposed by the French physicist Sadi Carnot in 1824, consisting of two isothermal and two adiabatic processes. All four processes are reversible, and the Carnot cycle can drive a heat engine to transfer heat between a high-temperature heat source $T_1(T_H)$ and a low-temperature heat source $T_2(T_C)$.

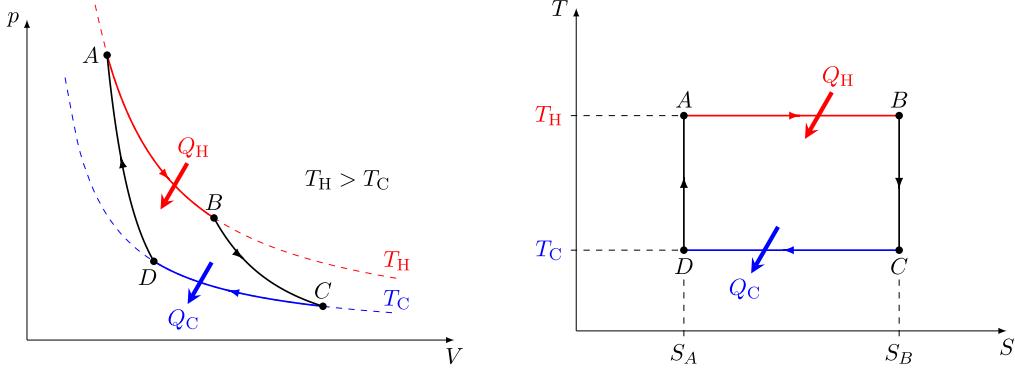


Fig. 3: Phase Diagram of the Carnot Cycle

The steps of the Carnot cycle are broken down as follows (assuming an ideal gas):

1. Isothermal expansion ($A \rightarrow B$): State $1(p_1, T_1, V_1)$ to state $2(p_2, T_1, V_2)$, satisfying the isothermal Boyle's law

$$\frac{V_2}{V_1} = \frac{p_2}{p_1} \quad (1.51)$$

Moreover, the internal energy $\Delta U_{12} = 0$, so the heat absorbed equals the work done

$$\Delta W_{12} = nRT_1 \ln \frac{V_2}{V_1}, \quad \Delta Q_{12} = \Delta W_{12} = nRT_1 \ln \frac{V_2}{V_1} \quad (1.52)$$

2. Adiabatic expansion ($B \rightarrow C$): State $2(p_2, T_1, V_2)$ to state $3(p_3, T_2, V_3)$, satisfying the adiabatic equation of state $pV^\gamma = \text{const}$. In this process, the heat remains unchanged $\Delta Q_{23} = 0$, so the work done and internal energy are

$$\Delta W_{23} = \frac{nR(T_2 - T_1)}{1 - \gamma}, \quad \Delta U_{23} = -\Delta W_{23} = \frac{nR(T_2 - T_1)}{\gamma - 1} \quad (1.53)$$

3. Isothermal compression ($C \rightarrow D$): State $3(p_3, T_2, V_3)$ to state $4(p_4, T_2, V_4)$, also satisfying the isothermal Boyle's law $\frac{V_3}{V_4} = \frac{p_3}{p_4}$, and the internal energy $\Delta U_{34} = 0$

$$\Delta W_{34} = nRT_2 \ln \frac{V_4}{V_3}, \quad \Delta Q_{34} = \Delta W_{34} = nRT_2 \ln \frac{V_4}{V_3} \quad (1.54)$$

4. Adiabatic compression ($D \rightarrow A$): State $4(p_4, T_2, V_4)$ to state $1(p_1, T_1, V_1)$, also satisfying the adiabatic equation of state $pV^\gamma = \text{const}$. In this process, the heat remains unchanged $\Delta Q_{41} = 0$, so the work done and internal energy are

$$\Delta W_{41} = \frac{nR(T_1 - T_2)}{1 - \gamma}, \quad \Delta U_{34} = -\Delta W_{34} = \frac{nR(T_1 - T_2)}{\gamma - 1} \quad (1.55)$$

Thus, the total work done by the system in one complete Carnot cycle is

$$\begin{aligned}\Delta W &= \Delta W_{12} + \Delta W_{23} + \Delta W_{34} + \Delta W_{41} = \Delta W_{12} + \Delta W_{34} \\ &= nRT_1 \ln \frac{V_2}{V_1} + nRT_2 \ln \frac{V_4}{V_3}\end{aligned}\quad (1.56)$$

The definition of thermal efficiency is given by

$$\eta = \frac{W}{Q_{\text{abs}}} = \frac{Q_{\text{abs}} - Q_{\text{rel}}}{Q_{\text{abs}}}\quad (1.57)$$

According to the adiabatic process satisfying Eq. 1.44,

$$\frac{V_4}{V_1} = \frac{V_3}{V_2} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}}, \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}\quad (1.58)$$

Thus, the thermal efficiency of the Carnot cycle can be calculated

$$\eta = \frac{W_{12} + W_{34}}{Q_{12}} = 1 + \frac{T_2 \ln(V_2/V_1)}{T_1 \ln(V_4/V_3)} = 1 - \frac{T_2}{T_1}\quad (1.59)$$

The thermal efficiency of the Carnot cycle depends only on temperature.

If considering extracting heat from a low-temperature source, there is also a coefficient of performance η' , defined as the heat extracted from the low-temperature source divided by the work done by the outside

$$\eta' = \frac{Q_{\text{rel}}}{W} = \frac{T_2}{T_1 - T_2}\quad (1.60)$$

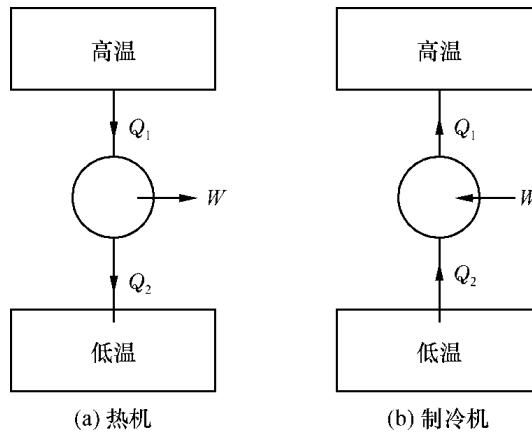


Fig. 4: Heat Engine and Refrigerator

It is worth noting that the volume ratio relationship Eq. 1.58 implies an invariant, because

$$\frac{\Delta Q_{12}}{T_1} + \frac{\Delta Q_{34}}{T_2} = nR \ln \frac{V_2 V_4}{V_1 V_3} = 0\quad (1.61)$$

Thus, for a complete Carnot cycle

$$\oint \frac{Q}{T} = 0\quad (1.62)$$

An important conclusion is: **Any reversible cycle can be decomposed into an infinite number of Carnot micro-cycles**, and thus their $\oint \frac{Q}{T} = 0$ holds, which is an invariant of reversible cycles, defined as the state function entropy.

Theorem 1.3 (Second Law of Thermodynamics).

Clausius Statement: *It is impossible to transfer heat from a colder body to a hotter body without causing other changes;*

Kelvin Statement: *It is impossible to convert all absorbed heat from a single heat source into work without causing other changes.*

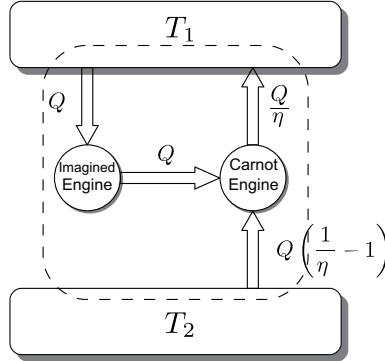


Fig. 5: Proof of the Equivalence of Clausius and Kelvin Statements

The second law of thermodynamics directly denies the possibility of a perpetual motion machine of the second kind.

Next, we need to discuss the issue of efficiency. What is the highest efficiency of a heat engine? Here we introduce Carnot's theorem.

Theorem 1.4 (Carnot's Theorem). *The efficiency of all reversible cycles operating between the same temperature heat source and sink is the maximum, and the efficiency of reversible cycles operating between the same temperature heat source and sink is the same.*

$$\eta_R = \frac{W}{Q_1} \geq \eta \quad (1.63)$$

To this end, we provide a proof in the heat engine diagram below. Assume an irreversible heat engine with heat sources T_1 and T_2 , with an efficiency of η . This heat engine and a reverse Carnot heat engine with efficiency $\eta_R = \eta'$ form a thermodynamic cycle, where the work produced by the irreversible heat engine is the source of work for the reverse Carnot heat engine. If $\eta = \eta'$, this thermodynamic cycle has no effect on the system, contradicting irreversibility, so it is not valid. If $\eta > \eta'$, this thermodynamic cycle can extract energy from the low-temperature heat source T_2

$$\Delta Q = \eta Q \left(\frac{1}{\eta'} - 1 \right) - (1 - \eta)Q = Q \left(\frac{\eta}{\eta'} - 1 \right) > 0 \quad (1.64)$$

and release this energy to the high-temperature heat source T_1 without causing other changes, violating the second law of thermodynamics, so it is not valid. Therefore, the conclusion is $\eta < \eta'$,

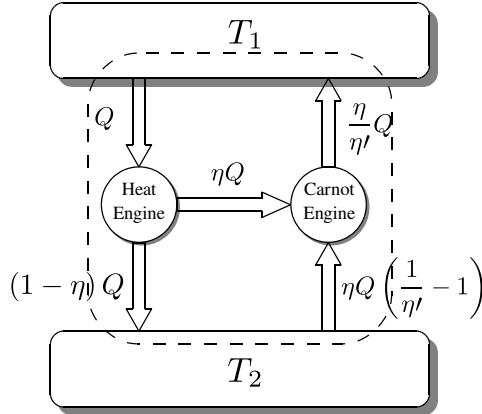


Fig. 6: Proof of Carnot's Theorem by Contradiction

the efficiency η of an irreversible heat engine is lower than the efficiency η' of a Carnot heat engine.

1.1.7 Calculation of Entropy

The efficiency of a reversible Carnot cycle is

$$\eta_R = \frac{W}{Q_1} = 1 - \frac{T_2}{T_1} \quad (1.65)$$

For any cycle, the efficiency is

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad (1.66)$$

Thus, the work done

$$\frac{T_2}{T_1} \leq \frac{Q_2}{Q_1} \Rightarrow \frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0 \quad (1.67)$$

Adding up an infinite number of micro-cycles, we get

$$\oint \frac{Q}{T} \leq 0 \quad (1.68)$$

The equality represents a reversible cycle.

For an irreversible process I from A to B , and a reversible process R from B back to A , for this cycle we have

$$\oint_{H+I} \frac{Q}{T} = \int_{A(I)}^B \frac{Q}{T} + \int_{B(R)}^A \frac{Q}{T} < 0 \quad (1.69)$$

The reversible process can be reversed, giving

$$\Delta S = S_B - S_A = \int_{A(-R)}^B \frac{Q}{T} > \int_{A(I)}^B \frac{Q}{T} \quad (1.70)$$

Combining the two cases above, we get (equality for reversible, greater than for irreversible)

$$S_B - S_A \geq \int_A^B \frac{Q}{T} \quad (1.71)$$

For an isolated adiabatic system, the right-hand term is 0, so

$$S_f - S_i \geq 0, \quad d_i S \geq 0 \quad (1.72)$$

Theorem 1.5 (Principle of Entropy Increase). *In the process of a thermodynamic system transitioning from one equilibrium state to another, its entropy never decreases: if the process is reversible, the entropy remains unchanged; if irreversible, the entropy increases.*

Entropy Flow and Entropy Production

For a reversible process, we have

$$dS = \frac{Q}{T} \quad (1.73)$$

Thus, we define entropy flow $d_e S$ (entropy exchanged between the system and the environment)

$$d_e S = \frac{Q}{T} \quad (1.74)$$

For an irreversible process, we have

$$dS > \frac{Q}{T} \quad (1.75)$$

Thus, the excess part is defined as entropy production (entropy increase caused by irreversible processes within the system), according to the principle of entropy increase Theorem 1.5, Entropy production is always greater than zero (irreversible process) or equal to zero (reversible process).

For any irreversible process, there is both entropy flow and entropy production

$$dS = d_e S + d_i S \quad (1.76)$$

The following expression often omits the latter term because for a reversible process $d_i S = 0$

$$Q = T d_e S = T dS - T d_i S = dU + W \quad (1.77)$$

Calculation Considering Entropy Flow

(1) The system is in contact with a large heat source, and the work W done by the environment on the system is converted into heat Q transferred to the large heat source, becoming the internal energy of the large heat source. At the end of the process, the state of the system does not change, so the entropy of the system remains unchanged

$$\Delta S(\text{ System }) = 0 \quad (1.78)$$

The entropy of the large heat source increases

$$\Delta S(\text{ Environment }) = \frac{+Q}{T} = \frac{W}{T} \quad (1.79)$$

We call the sum of the entropy change of the system and the environment the entropy change of the universe, so

$$\Delta S(\text{ Universe }) = \Delta S(\text{ System }) + \Delta S(\text{ Environment }) = \frac{W}{T} \quad (1.80)$$

(2) The system is not in contact with a large heat source and is adiabatic with the environment. In this process, there is energy loss, which is an irreversible process. The work W done by the environment on the system is converted into heat, becoming the internal energy of the system, raising the system's temperature from T_i to T_f . Assuming constant pressure. To calculate the entropy production of this irreversible process, a reversible isobaric process can be chosen, with the initial state as (T_i, p) and the final state as (T_f, p) . The entropy change of this process is (assuming C_p is constant)

$$\Delta S(\text{ System }) = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \ln \frac{T_f}{T_i} \quad (1.81a)$$

$$\Delta S(\text{ Environment }) = 0, \quad \Delta S(\text{ Universe }) = C_p \ln \frac{T_f}{T_i} \quad (1.81b)$$

(3) Free Expansion of Gas: In this process, the volume changes from V_i to V_f . Since the temperature remains constant during the free expansion of an ideal gas, $T_i = T_f = T$. The entropy change can be calculated using a reversible isothermal process:

$$\Delta S(\text{ System }) = \int_{V_i}^{V_f} \frac{dQ}{T} = \int_{V_i}^{V_f} \frac{dU + dW}{T} = \int_{V_i}^{V_f} \frac{dW}{T} = nR \int_{V_i}^{V_f} \frac{dV}{V} = nR \ln \frac{V_f}{V_i} \quad (1.82)$$

Here, the internal energy of an ideal gas is only a function of temperature. Free expansion is adiabatic, so

$$\begin{aligned} \Delta S(\text{ Environment }) &= 0 \\ \Delta S(\text{ Universe }) &= nR \ln \frac{V_f}{V_i} \end{aligned} \quad (1.83)$$

(4) Heat Conduction Process: Heat Q is transferred from a heat source (temperature T_1) to a cold source (temperature T_2) through a system, which remains unchanged. In this irreversible

process, we have

$$\begin{aligned}\Delta S(\text{ System }) &= 0 \\ \Delta S(\text{ Heat Source }) &= -\frac{Q}{T_1} \\ \Delta S(\text{ Cold Source }) &= +\frac{Q}{T_2} \\ \Delta S(\text{ Environment }) &= \frac{Q}{T_2} - \frac{Q}{T_1}\end{aligned}\tag{1.84}$$

(5) Diffusion of Two Different Gases: A container with a volume of $2V$ is divided by a partition separating two different gases, both at temperature T and volume V . After removing the partition, the gases mix completely. This irreversible process can be seen as two ideal gases undergoing free expansion. Assuming each gas has a mass of 1 mol, the entropy change for each gas is

$$\Delta S_1 = \Delta S_2 = nR \ln \frac{V_f}{V_i} = R \ln 2\tag{1.85}$$

The total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2 = 2R \ln 2\tag{1.86}$$

However, if the gases are the same, the total entropy change is 0 due to the presence of information entropy.

(6) Entropy Change of a Heat Conduction Rod: A case where the initial state is non-equilibrium and the final state is equilibrium. A uniform metal rod of length L and cross-sectional area A is in contact with a heat reservoir (T_1) and a cold reservoir (T_2) until thermal equilibrium is reached. After disconnecting from the reservoirs, the rod is thermally insulated from the environment. Over time, due to internal heat conduction, the rod reaches equilibrium with a final temperature T_f . We calculate the entropy change for this process.

Using the local equilibrium assumption, although the rod is initially in a non-equilibrium state, a small volume element $A dx$ at position x can be considered in equilibrium. Thus, both the initial and final states of the small volume element are equilibrium states. First, calculate the entropy change of the small volume element, then integrate over the entire rod to obtain the entropy change of the heat conduction rod. Assume the density of the metal rod is ρ , the mass of the small volume element is $\rho A dx$, and the specific heat capacity C_p is temperature-independent. The heat capacity of the small volume element is: $C_p \rho A dx$. When the temperature of the small volume element changes by dT , it absorbs (or releases) heat $dQ = C_p \rho A dx dT$. The entropy change of the small volume element from temperature T_i to T_f is $dS = \int_{T_i}^{T_f} \frac{dQ}{T}$, where

$$T_f = \frac{T_1 + T_2}{2}, \quad T_i = T_1 - \frac{T_1 - T_2}{L}x\tag{1.87a}$$

$$dS = C_p \rho A dx \int_{T_i}^{T_f} \frac{dT}{T} = C_p \rho A dx \ln \frac{T_f}{T_i} = -C_p \rho dx \ln \left(\frac{T_1}{T_f} - \frac{T_1 - T_2}{LT_f} x \right)\tag{1.87b}$$

Integrating over the rod gives the total entropy change

$$\begin{aligned}\Delta S &= -C_p \rho A \int_0^L \ln \left(\frac{T_1}{T_f} - \frac{T_1 - T_2}{LT_f} x \right) dx \\ &= C_p \rho A L \left(1 + \ln T_f + \frac{T_2}{T_1 - T_2} \ln T_2 - \frac{T_1}{T_1 - T_2} \ln T_1 \right)\end{aligned}\quad (1.88)$$

1.2 Characteristic Functions

According to the first and second laws of thermodynamics, and the discussion in Eq. 1.77, $d_i S = 0$,

$$TdS = dU + W \quad (1.89)$$

Since $W = Y dy$, for a reversible infinitesimal process in a gas system $Y = p$, $y = V$, the differential expression of internal energy is

$$dU = TdS - pdV \quad (1.90)$$

Here, temperature T and entropy S , pressure p and volume V are two pairs of conjugate variables. (There is also chemical potential μ and particle number N . How should the function form be changed to keep the information contained in the function unchanged?)

1.2.1 Legendre Transform

For a function $f(x_1, x_2, \dots, x_n)$

$$df(x_1, x_2, \dots, x_n) = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \dots + \frac{\partial f}{\partial x_n} dx_n. \quad (1.91)$$

It can be simplified as: $df = y_1 dx_1 + y_2 dx_2 + \dots + y_n dx_n$. Using

$$d(xy) = x dy + y dx \Rightarrow y dx = -x dy + d(xy) \quad (1.92)$$

we have

$$d(x_1 y_1 + x_2 y_2 + \dots + x_n y_n - f) = x_1 dy_1 + x_2 dy_2 + \dots + x_n dy_n \quad (1.93)$$

Thus, a type of Legendre transform is defined (it can also be applied to only one conjugate term)

$$\tilde{f}(y_1, y_2, \dots, y_n) = \sum x_i y_i - f \quad (1.94)$$

The differential expressions of \tilde{f} and f contain the same information.

1.2.2 Thermodynamic Functions

The internal energy, enthalpy, Helmholtz free energy, and Gibbs free energy can be expressed through Legendre transforms.

$$\text{Internal Energy: } U = U(S, V) \quad dU = TdS - pdV \quad (1.95\text{a})$$

$$\text{Enthalpy: } H = H(S, p) = U + pV \quad dH = TdS + Vdp \quad (1.95\text{b})$$

$$\text{Helmholtz Free Energy: } F = F(T, V) = U - TS \quad dF = -SdT - pdV \quad (1.95\text{c})$$

$$\text{Gibbs Free Energy: } G = G(T, p) = U - TS + pV \quad dG = -SdT + Vdp \quad (1.95\text{d})$$

$$= F + pV = H - TS \quad (1.95\text{e})$$

In solving practical problems, the appropriate thermodynamic function is often chosen based on the characteristics of the independent variables. For example, with (T, V) as parameters, several thermodynamic function expressions are given. Based on the expression of Helmholtz free energy, we can obtain

$$F = F(T, V) = U - TS, \quad dF = -SdT - pdV \quad (1.96)$$

According to the relationship of partial derivatives, the state equation is obtained

$$p = p(T, V) = -\left(\frac{\partial F}{\partial V}\right)_T, \quad S = S(T, V) = -\left(\frac{\partial F}{\partial T}\right)_V \quad (1.97)$$

Here we introduce the **common heat capacity calculation formula**

$$C_x = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} \Big|_x = \lim_{\Delta T \rightarrow 0} \frac{T \Delta S}{\Delta T} \Big|_x = T \left(\frac{\partial S}{\partial T}\right)_x \quad (1.98)$$

Thus, the constant volume heat capacity under this parameter is

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V = -T \left(\frac{\partial^2 F}{\partial T^2}\right)_V \quad (1.99)$$

The other three thermodynamic functions are expressed as

$$U = U(T, V) = F + TS = F - T \left(\frac{\partial F}{\partial T}\right)_V \quad (1.100\text{a})$$

$$G = G(T, V) = F + pV = F - V \left(\frac{\partial F}{\partial V}\right)_T \quad (1.100\text{b})$$

$$H = H(T, V) = U + pV = F + TS + pV = F - T \left(\frac{\partial F}{\partial T}\right)_V - V \left(\frac{\partial F}{\partial V}\right)_T \quad (1.100\text{c})$$

1.2.3 Jacobian Determinant

When thermodynamic quantities involve variable transformations, the relationship transformation between partial derivatives is calculated using the Jacobian determinant. For

$$\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} u(x, y) \\ v(x, y) \end{pmatrix} \quad (1.101)$$

Calculating partial derivatives gives

$$\begin{pmatrix} du \\ dv \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y dx + \left(\frac{\partial u}{\partial y}\right)_x dy \\ \left(\frac{\partial v}{\partial x}\right)_y dx + \left(\frac{\partial v}{\partial y}\right)_x dy \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix} \begin{pmatrix} dx \\ dy \end{pmatrix} = J \begin{pmatrix} u, v \\ x, y \end{pmatrix} \begin{pmatrix} dx \\ dy \end{pmatrix} \quad (1.102)$$

The Jacobian determinant is defined as:

$$\begin{aligned} \frac{\partial(u, v)}{\partial(x, y)} &= \left| J \begin{pmatrix} u, v \\ x, y \end{pmatrix} \right| = \left| \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix} \right| \\ &= \left(\frac{\partial u}{\partial x} \right)_y \left(\frac{\partial v}{\partial y} \right)_x - \left(\frac{\partial u}{\partial y} \right)_x \left(\frac{\partial v}{\partial x} \right)_y \end{aligned} \quad (1.103)$$

There are some commonly used simplification formulas:

(1) Partial derivatives expressed using the Jacobian determinant

$$\left(\frac{\partial u}{\partial x} \right)_y = \frac{\partial(u, y)}{\partial(x, y)} = \left| \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial y}{\partial x}\right)_y & \left(\frac{\partial y}{\partial y}\right)_x \end{pmatrix} \right| = \left| \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ 0 & 1 \end{pmatrix} \right| \quad (1.104)$$

(2) Switching odd rows/columns changes the sign of the determinant (equivalent to changing the position of two parameters)

$$\begin{aligned} \frac{\partial(u, v)}{\partial(x, y)} &= - \frac{\partial(v, u)}{\partial(x, y)} = - \frac{\partial(u, v)}{\partial(y, x)} = \frac{\partial(v, u)}{\partial(y, x)} \\ \left| \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix} \right| &= - \left| \begin{pmatrix} \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \\ \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \end{pmatrix} \right| = - \left| \begin{pmatrix} \left(\frac{\partial u}{\partial y}\right)_x & \left(\frac{\partial u}{\partial x}\right)_y \\ \left(\frac{\partial v}{\partial y}\right)_x & \left(\frac{\partial v}{\partial x}\right)_y \end{pmatrix} \right| \end{aligned} \quad (1.105)$$

(3) The determinant of a matrix product equals the product of the determinants,

$$\frac{\partial(s, t)}{\partial(x, y)} = \frac{\partial(s, t)}{\partial(u, v)} \frac{\partial(u, v)}{\partial(x, y)} \quad (1.106)$$

It can be proven

$$\begin{aligned} \begin{pmatrix} ds \\ dt \end{pmatrix} &= \begin{pmatrix} \left(\frac{\partial s}{\partial u}\right)_v & \left(\frac{\partial s}{\partial v}\right)_u \\ \left(\frac{\partial t}{\partial u}\right)_v & \left(\frac{\partial t}{\partial v}\right)_u \end{pmatrix} \begin{pmatrix} du \\ dv \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial s}{\partial u}\right)_v & \left(\frac{\partial s}{\partial v}\right)_u u \\ \left(\frac{\partial t}{\partial u}\right)_v & \left(\frac{\partial t}{\partial v}\right)_u u \end{pmatrix} \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix} \begin{pmatrix} dx \\ dy \end{pmatrix} \\ &= \begin{pmatrix} \left(\frac{\partial s}{\partial x}\right)_y & \left(\frac{\partial s}{\partial y}\right)_x \\ \left(\frac{\partial t}{\partial x}\right)_y & \left(\frac{\partial t}{\partial y}\right)_x \end{pmatrix} \begin{pmatrix} dx \\ dy \end{pmatrix} \end{aligned} \quad (1.107)$$

(4) The determinant of an inverse matrix equals the inverse of the determinant, because

$$\begin{pmatrix} dx \\ dy \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{pmatrix}^{-1} \begin{pmatrix} du \\ dv \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial x}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{pmatrix} \begin{pmatrix} du \\ dv \end{pmatrix} \quad (1.108)$$

The inverse transformation is obtained

$$\frac{\partial(x, y)}{\partial(u, v)} = 1 / \frac{\partial(u, v)}{\partial(x, y)} \quad (1.109)$$

It is worth noting that for multiple parameters, there are also corresponding properties of the Jacobian matrix.

1.2.4 Maxwell Relations

In thermodynamics, Maxwell relations are a set of equations that relate the partial derivatives of thermodynamic variables. They are derived from the symmetry of second derivatives and the definition of thermodynamic potentials. Maxwell relations are particularly useful for understanding the relationships between different thermodynamic properties and for simplifying thermodynamic calculations.

The most common form of Maxwell relations is:

$$1. \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad 2. \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad 3. \left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial p}{\partial S}\right)_V \quad 4. \left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_p$$

These relations can be derived from the fundamental thermodynamic relationships and the definition of thermodynamic potentials.

1.2.5 Absolute Entropy

Theorem 1.6 (Thermodynamic Third Law).

Nernst's statement: When the temperature approaches 0 K, the entropy change of any condensed system undergoing a reversible isothermal process approaches zero.

Planck's statement: At absolute zero, the entropy of all systems in internal equilibrium is the same, and it can be taken as zero.

Thus, there is a very famous statement: No matter what an ideal process is, it is impossible to lower the temperature of a thermodynamic system to absolute zero through a finite number of operations within a finite time, in other words, **absolute zero cannot be reached**. There are several implications:

- At temperatures close to absolute zero, the heat capacity tends to zero (does not satisfy the equipartition theorem), and the coefficient of volume expansion tends to zero;
- There is no ideal gas model, as the interaction between molecules dominates;

- The paramagnetic medium model fails, as the Curie law no longer holds, and the interaction between magnetic moments dominates.

Statistical mechanics gives the definition of entropy:

$$S - S_0 = k_B \ln \Omega \quad (1.110)$$

k_B is the Boltzmann constant, Ω is the number of microscopic states consistent with the macroscopic configuration. S_0 represents the entropy at absolute zero, which can be taken as zero.

1.2.6 Adiabatic Process

The adiabatic equation of an ideal gas has been discussed in Subsubsec. 1.1.5, and below is the cooling coefficient of adiabatic decompression

$$\begin{aligned} \mu_S &= \left(\frac{\partial T}{\partial p} \right)_S = \frac{\partial(T, S)}{\partial(p, S)} = \frac{\partial(T, S)}{\partial(T, p)} \frac{\partial(T, p)}{\partial(p, S)} \\ &= \left(\frac{\partial S}{\partial p} \right)_T / \left(-\frac{\partial S}{\partial T} \right)_p, \quad dG = -SdT + Vdp \\ &= \frac{T \left(\frac{\partial V}{\partial T} \right)_p}{C_p} \end{aligned} \quad (1.111)$$

Another description of the rate of temperature change is

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial T}{\partial S} \right)_V = - \frac{T}{C_V} \left(\frac{\partial p}{\partial T} \right)_V \quad (1.112)$$

The adiabatic process with the highest cooling efficiency is reversible: $\Delta U = \Delta Q - \Delta W = -\Delta W$, because only the system does work, and no energy is input from the outside. Adiabatic expansion cooling can be combined with isothermal compression to reduce the entropy of the system. The pressure can also be changed to a magnetic field for adiabatic demagnetization cooling.

1.2.7 Throttling Process

Throttling is an isenthalpic, irreversible process. The pressure difference ensures that the gas can only flow in one direction.

In a thermally insulated tube, there is a thermally insulated partition in the middle, with a small hole on both ends. At the initial state, the left piston A is in contact with the partition, and the volume between A and the partition is V_1 , the pressure of the gas is P_1 , and the right piston B is in contact with the partition.

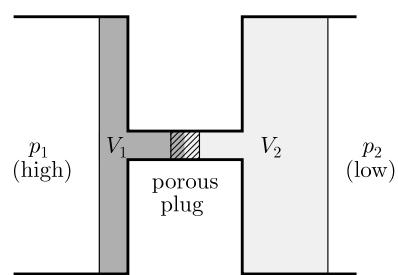


Fig. 7: Throttling Process

The piston A moves slowly to the right at a constant pressure P_1 , allowing the gas to flow through the small hole, and the piston B moves to the right at a constant pressure $P_2 < P_1$. At the

end of the process, the piston A reaches the partition, and the gas volume at the end of the process when the piston B stops moving is V_2 . Applying the first law of thermodynamics $\Delta Q = \Delta U + \Delta W$ to this process, since $\Delta Q = 0$, we have $\Delta U = -\Delta W \Rightarrow U_2 - U_1 = p_1 V_1 - p_2 V_2$

$$H_2 = U_2 + p_2 V_2 = U_1 + p_1 V_1 = H_1 \quad (1.113)$$

To express the cooling efficiency of the throttling process, the Joule-Thomson coefficient (μ_{JT}) is introduced

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H \quad (1.114)$$

Another form of the J-T coefficient is given

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H = \frac{\partial(T, H)}{\partial(p, H)} = \frac{\partial(T, H)}{\partial(T, p)} \frac{\partial(T, p)}{\partial(p, H)} = - \left(\frac{\partial H}{\partial p} \right)_T / \left(\frac{\partial H}{\partial T} \right)_p \quad (1.115)$$

Using the total differential of enthalpy $dH = T dS + V dp$, we get

$$\left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p = C_p, \quad \left(\frac{\partial H}{\partial p} \right)_T = T \left(\frac{\partial S}{\partial p} \right)_T + V = -T \left(\frac{\partial V}{\partial T} \right)_p + V \quad (1.116)$$

Thus, an equivalent form of the J-T coefficient is

$$\mu_{JT} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] \quad (1.117)$$

In other cases with complex state equations, the J-T coefficient can be given using the product of three differentials equal to -1 Eq. 1.11b,

$$\mu = - \frac{V \left(\frac{\partial p}{\partial V} \right)_T + T \left(\frac{\partial p}{\partial T} \right)_V}{C_p \left(\frac{\partial p}{\partial V} \right)_T} \quad (1.118)$$

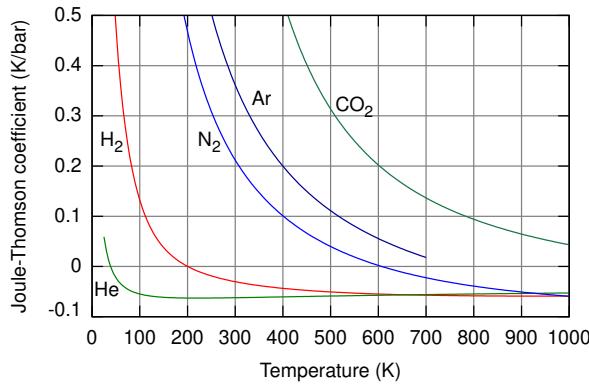


Fig. 8: Joule-Thomson Coefficient for Various Gases Under Atmospheric Pressure

Using Van der Waals equation Eq. 2.14 to discuss the J-T coefficient, according to the state equation:

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \quad (1.119)$$

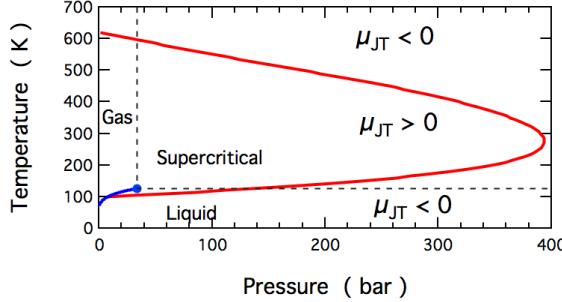


Fig. 9: Symbol of Ideal Gas μ_{JT} . The region inside the red line indicates cooling ($\mu_{JT} > 0$); outside the region, expansion produces heat. The coexistence curve of gas and liquid is represented by a blue line, terminating at the critical point. The region between the blue line and the dashed line is the supercritical fluid (property between liquid and gas)

we get

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{\frac{2a}{v^3} - \frac{v-b}{(v-b)^2}} \quad (1.120)$$

Let $\mu_{JT} = 0$, then:

$$RT = \frac{2a}{v^2} \frac{(v-b)^2}{b} = \frac{2a}{b} \left(1 - \frac{b}{v}\right)^2 \quad (1.121)$$

$$\frac{1}{v} = \frac{1 - C(T)}{b},$$

where $C(T) = \sqrt{\frac{RTb}{2a}}$. So the inversion curve equation is:

$$p = \frac{a}{b^2} [1 - C(T)] [3C(T) - 1] \quad (1.122)$$

We can also analyze the J-T coefficient using Onne's equation/Virial expansion, rewriting μ_{JT} as:

$$\mu_{JT} = \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] = \frac{T^2}{c_p p} \left[\frac{\partial}{\partial T} \left(\frac{pv}{T} \right) \right]_p \quad (1.123)$$

where c_p is the specific heat capacity at constant pressure per mole. Using Onnes' equation

$$\frac{pv}{T} = R + \frac{B(T)}{T} p + \frac{C(T)}{T} p^2 + \dots \quad (1.124)$$

we get:

$$\mu_{JT} \simeq \frac{T^2}{c_p} \frac{d}{dT} \left(\frac{B(T)}{T} \right) \quad (1.125)$$

Chapter 2 Different Systems

Classify systems according to different boundaries/interfaces: three typical types of systems

1. Isolated System: Fixed boundary, non-deformable, no transfer of energy and matter No contact between the system and the environment in all properties All internal and external balances can be different
2. Closed System: Boundary can deform, can transfer energy, but cannot transfer matter Can have force (including electromagnetic force), thermal contact, but no chemical contact Internal and external can achieve mechanical and thermal equilibrium, but can be chemically unbalanced
3. Open System (virtual boundary): Boundary can deform, can transfer energy and matter Has all possible force, thermal, and chemical contact Internal and external achieve all balances: mechanical, thermal, and chemical equilibrium
4. Systems in between: Between isolated/closed systems: boundary can be rigid and heat-conducting, or elastic and adiabatic Between closed/open systems: semi-permeable membrane, only partial matter can achieve chemical contact

2.1 Ideal Gas

Following the properties of ideal gas introduced in Subsubsec. 1.1.5, the ideal gas equation of state (amount of substance $n_m = N/N_A$ mole, number of particles N)

$$pV = n_m RT = Nk_B T \quad (2.1)$$

It is based on Boyle's law, Charles's law, Avogadro's law, and Gay-Lussac's experimental laws, derived by Clapeyron, and can also be statistically interpreted as proven later. A diagram can clearly reflect the relationships between various state equations of ideal gas.

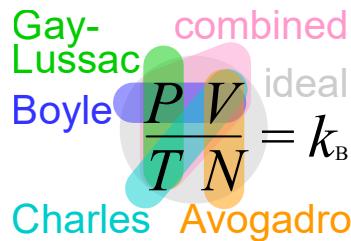


Fig. 10: Relationships between ideal gas state equations

Among them, the relationship between Boltzmann constant k_B , universal gas constant R , and Avogadro constant N_A is

$$k_B = \frac{R}{N_A} = \frac{n_m R}{N} \quad (2.2)$$

The characteristic function of ideal gas (taking monoatomic molecules as an example), the heat capacity is

$$C_V = \frac{3}{2}Nk_B, \quad C_p = \frac{5}{2}Nk_B \quad (2.3)$$

The expression for the entropy S of an ideal gas can be given:

$$\begin{aligned} S(T, V) &= \int_{(T_0, V_0)}^{(T, V)} \frac{dU + p dV}{T} = \int_{T_0}^T C_V \frac{dT}{T} + Nk_B \int_{V_0}^V \frac{dV}{V} \\ &= Nk_B \left[\frac{3}{2} \ln \left(\frac{T}{T_0} \right) + \ln \left(\frac{V}{V_0} \right) \right] + S_0(T_0, V_0) \\ &= Nk_B \left(\frac{3}{2} \ln T + \ln V \right) + S_0(T_0, V_0) - \frac{3}{2} \ln T_0 - \ln V_0, \end{aligned} \quad (2.4)$$

After introducing the number of particles, the entropy becomes

$$S(T, V, N) = Nk_B \left(\frac{3}{2} \ln T + \ln V - \ln N + s_0 \right) \quad (2.5)$$

According to the Legendre transformation, the Helmholtz free energy $F(T, V, N)$ is obtained

$$F(T, V, N) = U - TS = -Nk_B T \left[\frac{3}{2} \ln T + \ln \left(\frac{V}{N} \right) + \left(s_0 - \frac{3}{2} \right) \right] \quad (2.6)$$

From the differential of free energy $dF = -S dT - p dV + \mu dN$, various thermodynamic quantities are obtained

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N} = Nk_B \left[\frac{3}{2} \ln T + \ln \left(\frac{V}{N} \right) + s_0 \right], \quad (2.7a)$$

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T, N} = \frac{Nk_B T}{V}, \quad (2.7b)$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V} = -k_B T \left[\frac{3}{2} \ln T + \ln \left(\frac{V}{N} \right) + \left(s_0 - \frac{5}{2} \right) \right] \quad (2.7c)$$

By solving equation Eq. 6.58, the temperature and entropy-dependent function is obtained

$$T(S, V, N) = \left(\frac{N}{V} \right)^{2/3} \exp \left[\frac{2}{3} \left(\frac{S}{Nk_B} - s_0 \right) \right] \quad (2.8)$$

Substituting the above equation into the expression for internal energy $U(T) = 3Nk_B T / 2$, we get:

$$U(S, V, N) = \frac{3}{2} k_B \frac{N^{5/3}}{V^{2/3}} \exp \left[\frac{2}{3} \left(\frac{S}{Nk_B} - s_0 \right) \right] \quad (2.9)$$

And other thermodynamic quantities

$$H(S, p, N) = \frac{5}{2} N k_B^{3/5} p^{2/5} \exp \left[\frac{2}{5} \left(\frac{S}{Nk_B} - s_0 \right) \right] \quad (2.10a)$$

$$G(T, p, N) = -Nk_B T \left[\frac{3}{2} \ln T + \ln \left(\frac{k_B T}{p} \right) + \left(s_0 - \frac{5}{2} \right) \right] \quad (2.10b)$$

$$J(T, V, \mu) = -p(T, \mu)V = -V k_B T^{5/2} \exp \left[\frac{\mu}{k_B T} + \left(s_0 - \frac{5}{2} \right) \right] \quad (2.10c)$$

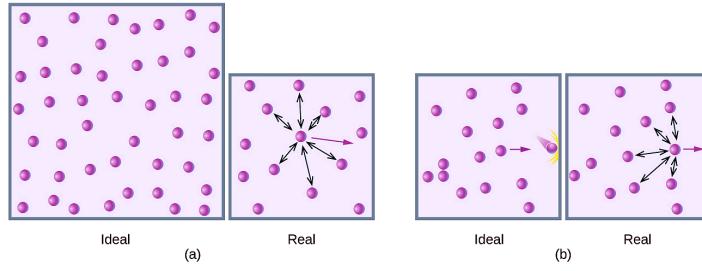


Fig. 11: Microscopic diagram of ideal gas and real gas

2.2 Van der Waals Gas

We will derive another form of the Van der Waals gas equation of state from the ideal gas equation of state Eq. 2.1, where $v = \frac{V}{N}$ is the average space occupied by each molecule

$$pv = k_B T \quad (2.11)$$

First consider the correction of volume, the actual system volume needs to subtract the volume of gas molecules (assuming b' is the volume contained by a single molecule itself), then $v' = v - b'$. Next, consider the correction of pressure, the attraction between atoms will reduce the average Helmholtz free energy of molecules, the reduction is proportional to the density of the fluid $\rho \propto \frac{1}{v}$, so since the pressure satisfies

$$p = - \left(\frac{\partial \bar{f}}{\partial v} \right)_T \quad (2.12)$$

The increase in pressure $\Delta p \propto \frac{1}{v^2}$, introducing a phenomenological parameter a' to measure the intermolecular attraction, $p = p' + \frac{a'}{v^2}$. According to $p'v' = k_B T$, the Van der Waals gas equation of state is obtained

$$\left(p + \frac{a'}{v^2} \right) (v - b') = k_B T \quad (2.13)$$

The more commonly used form is:

$$\left(p + a \frac{n^2}{V^2} \right) (V - nb) = nRT \quad (2.14)$$

Where a is the parameter measuring intermolecular attraction $a = N_A^2 a'$, and b is the sum of the volumes contained by 1 mole of molecules $b = N_A b'$.

Below, the characteristic function is calculated based on the differential expansion of internal energy, because:

$$dU(T, V) = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_V dT + \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] dV \quad (2.15)$$

Where, the Van der Waals gas satisfies

$$T \left(\frac{\partial p}{\partial T} \right)_V - p = \frac{N^2 a}{V^2} \quad (2.16)$$

According to Eq. 2.16, it is easy to judge that the constant volume heat capacity C_V of the gas is only a function of temperature:

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \left[\frac{\partial}{\partial T} \left(\frac{N^2 a}{V^2} \right) \right]_V = 0 \quad (2.17)$$

When the temperature change is very small, C_V is approximately constant, so

$$U(T, V) = C_V (T - T_0) - N^2 a \left(\frac{1}{V} - \frac{1}{V_0} \right) + U_0 (T_0, V_0) \quad (2.18)$$

When $V \rightarrow \infty$, the above equation returns to the result of an ideal gas.

Next, calculate the entropy $S(T, V)$. Using:

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \\ &= \frac{C_V(T)}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV \\ &= \frac{C_V(T)}{T} dT + \frac{Nk_B}{V - Nb} dV \end{aligned} \quad (2.19)$$

Integrating gives:

$$\begin{aligned} S(T, V) &= \int_{T_0}^T \frac{C_V(T)}{T} dT + Nk_B \ln \left(\frac{V - Nb}{V_0 - Nb} \right) + S_0 (T_0, V_0) \\ &\simeq C_V \ln \left(\frac{T}{T_0} \right) + Nk_B \ln \left(\frac{V - Nb}{V_0 - Nb} \right) + S_0 (T_0, V_0) \end{aligned} \quad (2.20)$$

Then the free energy is:

$$\begin{aligned} F(T, V) &= \int_{T_0}^T C_V(T) dT - T \int_{T_0}^T \frac{C_V(T)}{T} dT - N^2 a \left(\frac{1}{V} - \frac{1}{V_0} \right) \\ &\quad - Nk_B T \ln \left(\frac{V - Nb}{V_0 - Nb} \right) + U_0 (T_0, V_0) - TS_0 (T_0, V_0) \\ &\simeq C_V (T - T_0) - C_V T \ln \left(\frac{T}{T_0} \right) - N^2 a \left(\frac{1}{V} - \frac{1}{V_0} \right) \\ &\quad - Nk_B T \ln \left(\frac{V - Nb}{V_0 - Nb} \right) + U_0 (T_0, V_0) - TS_0 (T_0, V_0). \end{aligned} \quad (2.21)$$

Other characteristic functions can be obtained through the Legendre transformation. Below is the work done by gas expansion from V_i to V_f

$$\begin{aligned} W &= \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \left[\frac{Nk_B T}{V - Nb} - \frac{N^2 a}{V^2} \right] dV \\ &= Nk_B T \ln \left(\frac{V_f - Nb}{V_i - Nb} \right) + N^2 a \left(\frac{1}{V_f} - \frac{1}{V_i} \right) \end{aligned} \quad (2.22)$$

And the heat change at constant temperature T

$$\begin{aligned} \Delta Q &= T \Delta S = T \int_{V_i}^{V_f} \left(\frac{\partial S}{\partial V} \right)_T dV = T \int_{V_i}^{V_f} \left(\frac{\partial p}{\partial T} \right)_V dV \\ &= T \int_{V_i}^{V_f} \frac{NR}{V - b} dV = NRT \ln \frac{V_f - b}{V_i - b} \end{aligned} \quad (2.23)$$

More detailed discussion on the phase transition of Van der Waals gas can be found in Subsubsec. 3.4.1. The partition function of Van der Waals gas can also be given

$$Z_N = \frac{1}{N!} \left(\frac{V - nb}{\lambda_T^3} \right)^N e^{\beta an^2/V} \quad (2.24)$$

2.3 Magnetic Medium System

The work done by the external magnetic field on the magnetic medium system is

$$W = \mu_0 H dM, \quad (2.25)$$

Considering mechanical work, the total work done by the external world (including the magnetic field) on the system is:

$$W = \mu_0 H dM - p dV \quad (2.26)$$

The total differential expression of the internal energy $U(S, V, M)$ of the system is:

$$dU = T dS - p dV + \mu_0 H dM \quad (2.27)$$

The total differential of the Gibbs free energy $G(T, p, H) = U - TS + pV - \mu_0 HM$ of the system is:

$$dG = -S dT + V dp - \mu_0 M dH \quad (2.28)$$

The above equation gives the following three Maxwell relations:

$$\left(\frac{\partial S}{\partial H} \right)_{T,p} = \mu_0 \left(\frac{\partial M}{\partial T} \right)_{p,H}, \quad (2.29a)$$

$$\left(\frac{\partial V}{\partial H} \right)_{T,p} = -\mu_0 \left(\frac{\partial M}{\partial p} \right)_{T,H}, \quad (2.29b)$$

$$\left(\frac{\partial S}{\partial p} \right)_{T,H} = - \left(\frac{\partial V}{\partial T} \right)_{p,H} \quad (2.29c)$$

First consider the magnetocaloric effect, considering the temperature change of the magnetic medium under adiabatic and constant pressure conditions

$$\left(\frac{\partial T}{\partial H} \right)_{S,p} = - \left(\frac{\partial S}{\partial H} \right)_{T,p} \left(\frac{\partial T}{\partial S} \right)_{H,p} = -\frac{\mu_0 T}{C_H} \left(\frac{\partial M}{\partial T} \right)_{H,p}, \quad (2.30)$$

Where $C_H = T \left(\frac{\partial S}{\partial T} \right)_{H,p}$ is the constant magnetic (pressure) heat capacity, the equation of state of paramagnetic medium (Curie's law) is

$$M = \frac{C\mu_0}{T} H, \quad (M = \chi H, \quad \chi = \frac{C}{T}) \quad (2.31)$$

Substituting into Eq. 2.30, we get:

$$\left(\frac{\partial T}{\partial H} \right)_{S,p} = \frac{C}{C_H T} \mu_0 H > 0 \quad (2.32)$$

The heat capacities of the magnetic medium also satisfy

$$C_H - C_M = T \left(\frac{\partial M}{\partial T} \right)_H^2 / \left(\frac{\partial M}{\partial H} \right)_T \quad (2.33)$$

2.4 Photon Gas

In 1901, the Lebedev experiment gave the relationship between the radiation pressure of the radiation field and its internal energy density:

$$p = \frac{1}{3}u \quad (2.34)$$

According to the definition of internal energy density $U(T, V) = u(T)V$. Using the thermodynamic formula:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad (2.35)$$

The differential equation of internal energy density can be obtained

$$u(T) = \frac{T}{3} \frac{du}{dT} - \frac{u}{3} \quad (2.36)$$

Integrating gives

$$u(T) = aT^4 \quad (2.37)$$

Where a is the integration constant, which can be calculated later as $a = \frac{4\sigma}{c}$.

Next, further calculate the expression for entropy: $S(T, V)$. According to the basic thermodynamic equation:

$$dS = \frac{dU + p dV}{T} \quad (2.38)$$

We get:

$$\begin{aligned} dS &= \frac{1}{T} d(aT^4V) + \frac{1}{3}aT^3 dV \\ &= 4aT^2V dT + \frac{4}{3}aT^3 dV \\ &= \frac{4}{3}ad(T^3V) \end{aligned} \quad (2.39)$$

Integrating the above equation, the total entropy $S(T, V)$ of the radiation field can be obtained:

$$S = \frac{4}{3}aT^3V \quad (2.40)$$

That is, the entropy density of the radiation field is: $s(T) = \frac{4}{3}aT^3$.

According to the Legendre transformation, we finally obtain the free energy of the photon gas:

$$F(T, V) = U - TS = -\frac{1}{3}aT^4V \quad (2.41)$$

Thus, the thermodynamic parameter is obtained

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{U}{3V} = \frac{1}{3}u = \frac{1}{3}aT^4 \quad (2.42)$$

We can also obtain the entropy of the system:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{4}{3}aT^3V \quad (2.43)$$

Another commonly used physical quantity is the constant volume heat capacity of the system:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 4aT^3V \quad (2.44)$$

And the Gibbs free energy G of the system is:

$$G = U - TS + pV = aT^4V - T \frac{4}{3}aT^3V + \frac{1}{3}aT^4V = 0 \quad (2.45)$$

The photon gas will be extended to the black body radiation problem, for the energy density u of electromagnetic waves ω, \mathbf{k} :

$$\begin{aligned} u &= \frac{1}{2} \langle \mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H} \rangle = \frac{\varepsilon_0 \mathbf{E}^2(\omega, \mathbf{k})}{2} + \frac{\mathbf{B}^2(\omega, \mathbf{k})}{2\mu_0} \\ &= \frac{\varepsilon_0}{2} \left[\mathbf{E}^2 + \frac{\mathbf{B}^2}{\varepsilon_0 \mu_0} \right] = \frac{\varepsilon_0}{2} (\mathbf{E}^2 + c^2 \mathbf{B}^2) = \varepsilon_0 \mathbf{E}^2 \end{aligned} \quad (2.46)$$

The Poynting vector as the energy flow density is \mathbf{S} (energy emitted per unit area)

$$\begin{aligned} \mathbf{S} &= \langle \mathbf{E} \times \mathbf{H} \rangle = \frac{1}{\mu_0} \mathbf{E} \times \mathbf{B} = \frac{1}{\mu_0 c} \mathbf{E} \times (\hat{\mathbf{k}} \times \mathbf{E}) \\ &= \frac{\varepsilon_0}{\varepsilon_0 \mu_0 c} \left[\mathbf{E}^2 \hat{\mathbf{k}} - (\hat{\mathbf{k}} \cdot \mathbf{E}) \mathbf{E} \right] = cu \hat{\mathbf{k}} \end{aligned} \quad (2.47)$$

According to the isotropy of the radiation field, the energy flow density per unit solid angle is

$$|S_0| = \frac{cu}{4\pi} \quad (2.48)$$

The energy of photons passing through area A in time dt is

$$dE = S_0 (A \cos \theta) d\Omega dt \quad (2.49)$$

Photon radiation flux $J(\omega)$

$$J = \frac{1}{A} \frac{dE}{dt} = \int S \cos \theta d\Omega = \frac{1}{4} cu = \frac{1}{4} caT^4 \equiv \sigma T^4 \quad (2.50)$$

Where the Stefan-Boltzmann constant $\sigma = \frac{ca}{4}$ is

$$\sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.669 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4} \quad (2.51)$$

And the energy-momentum tensor of the electromagnetic wave

$$T(\omega, \mathbf{k}) = -\mathbf{DE} - \mathbf{HB} + Iu(\omega, \mathbf{k}) = (\mathbf{D} \cdot \mathbf{E} + \mathbf{H} \cdot \mathbf{B})/2 \quad (2.52)$$

Thus, the relationship between pressure and internal energy is obtained,

$$\begin{aligned} p(\omega) &= \langle T_{ii} \rangle = -\langle D_i E_i + H_i B_i \rangle = -(\mathbf{D} \cdot \mathbf{E} + \mathbf{H} \cdot \mathbf{B})/3 + u(\omega) \\ &= -(2/3)u(\omega) + u(\omega) = u(\omega)/3 \end{aligned} \quad (2.53)$$

This proves Eq. 2.34

2.4.1 Heat Transfer

Before discussing heat flow balance, it is necessary to understand the **three modes of heat transfer**:

- Heat Conduction: Experimentally, the amount of heat transferred by conduction per unit time is

$$\dot{Q} = \frac{\kappa A (T_2 - T_1)}{l} \quad (2.54)$$

- Heat Convection: Natural convection and forced convection
- Heat Radiation: Stefan-Boltzmann law gives

$$\dot{Q} = \varepsilon A \sigma T^4 \quad (2.55)$$

Where A is the surface area of the object, σ is the Stefan-Boltzmann constant, its value is $\sigma = 5.67 \times 10^{-8} \text{ J} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$, ε is called the emissivity or emissivity, the ideal black body has $\varepsilon = 1$, the ideal bright body has $\varepsilon = 0$, and general objects are between $0 \sim 1$

Assuming the radiation in a vacuum is $J(\omega) = \frac{cu(\omega)}{4}$, incident on an object at temperature T , part is reflected $R(T, \omega)J(\omega)$, R is the reflection coefficient; part is absorbed $\varepsilon(T, \omega)J(\omega)$, $\varepsilon = 1 - R$ is the absorption coefficient;

$$J = RJ + (1 - R)J = RJ + \varepsilon J \quad (2.56)$$

The object itself has radiation $J_e(T, \omega)$, reaching equilibrium

$$J(\omega) = R(T, \omega)J(\omega) + J_e(T, \omega) \quad (2.57)$$

After reaching thermodynamic equilibrium, the thermal radiation in the vacuum is the same as that of an ideal black body, often represented by the thermal radiation in a cavity, where the internal energy density $u(T, \omega)$ in the cavity is a universal function, independent of the properties of the cavity walls (such as composition, shape, etc.).

The first example is the radiation heat transfer of a plane

$$\dot{Q} = AJ_e = A\varepsilon\sigma T^4 \quad (2.58)$$

If it is the radiation heat transfer of two parallel planes: absorption coefficients $\varepsilon_1 = 1 - R_1, \varepsilon_2 = 1 - R_2$ According to the heat flow of the two sides

$$\begin{aligned} J_{1e} &= \varepsilon_1\sigma T_1^4, & J_1 &= J_{1e} + R_1 J_2 \\ J_{2e} &= \varepsilon_2\sigma T_2^4, & J_2 &= J_{2e} + R_2 J_1 \end{aligned} \quad (2.59)$$

Solving the matrix equation gives

$$\begin{aligned} \begin{pmatrix} 1 & -R_1 \\ -R_2 & 1 \end{pmatrix} \begin{pmatrix} J_1 \\ J_2 \end{pmatrix} &= \begin{pmatrix} J_{1e} \\ J_{2e} \end{pmatrix} \\ \begin{pmatrix} J_1 \\ J_2 \end{pmatrix} &= \frac{1}{1 - R_1 R_2} \begin{pmatrix} 1 & R_1 \\ R_2 & 1 \end{pmatrix} \begin{pmatrix} \varepsilon_1\sigma T_1^4 \\ \varepsilon_2\sigma T_2^4 \end{pmatrix} = \frac{1 \times \sigma}{\varepsilon_1 + \varepsilon_2 - \varepsilon_1\varepsilon_2} \begin{pmatrix} \varepsilon_1 T_1^4 + (1 - \varepsilon_1)\varepsilon_2 T_2^4 \\ \varepsilon_2 T_2^4 + (1 - \varepsilon_2)\varepsilon_1 T_1^4 \end{pmatrix} \end{aligned} \quad (2.60)$$

Thus, the heat flow from plane 1 is

$$\begin{aligned}\dot{Q}_1 &= A(J_1 - J_2) = A \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2 - \varepsilon_1 \varepsilon_2} \sigma (T_1^4 - T_2^4) \\ &= A \sigma (T_1^4 - T_2^4), \quad \varepsilon_1 = \varepsilon_2 = 1, \quad \text{Black body} \\ &\simeq \frac{\varepsilon}{2} A \sigma (T_1^4 - T_2^4), \quad \varepsilon_1 = \varepsilon_2 = \varepsilon \ll 1, \quad \text{Bright body}\end{aligned}\quad (2.61)$$

A second example similar to black body radiation is the surface energy model, since the elemental work is $W = -\sigma dA$, the differential of free energy is

$$dF = -SdT + \sigma dA \quad (2.62)$$

Thus, the internal energy density is

$$u = \frac{U}{A} = \left(\frac{\partial U}{\partial A} \right)_T = \left(\frac{\partial F}{\partial A} \right)_T + T \left(\frac{\partial S}{\partial A} \right)_T = \sigma + T \left(\frac{\partial \sigma}{\partial T} \right)_A = \sigma - T \frac{d\sigma}{dT} \quad (2.63)$$

A common surface energy equation is

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_C} \right)^n, \quad n = 1 \sim 2 \quad (2.64)$$

Substituting gives the internal energy density

$$u = \frac{(1-n)T - T_C}{T - T_C} \sigma \quad (2.65)$$

Further, the Carnot cycle of the photon gas can be discussed, according to

$$p = \frac{1}{3} u = \frac{4\sigma}{3c} T^4 \quad (2.66)$$

From this or the differential expansion of heat, the adiabatic process equation of state is obtained

$$p^{-\frac{1}{3}} V^{\frac{4}{3}} = \text{const.} \quad (2.67)$$

So the adiabatic index $\gamma = \frac{4}{3}$, the efficiency of the heat engine gas is

$$\eta = 1 - \left| \frac{Q_2}{Q_1} \right| = 1 - \frac{T_L}{T_H} \quad (2.68)$$

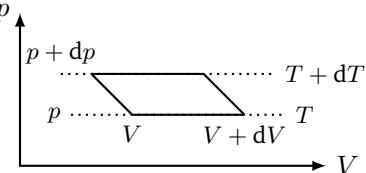


Fig. 12: Carnot cycle of photon

2.4.2 Black Hole Thermodynamics

The Schwarzschild radius of a black hole is

$$r_s = \frac{2GM}{c^2} \quad (2.69)$$

According to Hawking radiation, considering the simplest case, a non-rotating, uncharged Schwarzschild black hole with mass M , the Hawking radiation temperature can be derived as:

$$T_H = \frac{\hbar c^3}{8\pi GM k_B} \quad (2.70)$$

For a solar mass black hole, its Hawking temperature is 6.170×10^{-8} K, Wien's displacement law tells us, the maximum wavelength of black hole radiation

$$\lambda_{\max} = \frac{b}{T_H} = \frac{8\pi^2}{4.9651} r_s = 15.902 r_s \quad (2.71)$$

The horizon area of the black hole

$$A_s = 4\pi r_s^2 = 4\pi \left(\frac{2GM}{c^2} \right)^2 = \frac{16\pi G^2 M^2}{c^4} \quad (2.72)$$

According to the Stefan-Boltzmann law, the power of black body radiation is

$$P = A_s J = A_s \varepsilon \sigma T^4 \quad (2.73)$$

The black hole is an absolute black body, so $\varepsilon = 1$, the radiation power of the black hole is

$$P = A_s \varepsilon \sigma T_H^4 = \left(\frac{16\pi G^2 M^2}{c^4} \right) \left(\frac{\pi^2 k_B^4}{60\hbar^3 c^2} \right) \left(\frac{\hbar c^3}{8\pi GM k_B} \right)^4 = \frac{\hbar c^6}{15360\pi G^2 M^2} \quad (2.74)$$

Assuming the energy possessed by the black hole

$$E = Mc^2 \quad (2.75)$$

Then the heat capacity of the black hole is

$$C = \frac{dE}{dT} = \frac{d}{dT} \frac{\hbar c^5}{8\pi GT k_B} = -\frac{\hbar c^5}{8\pi GT^2 k_B} \quad (2.76)$$

From the following relationship

$$\frac{1}{T} = \frac{3\pi GM k_B}{\hbar c^3} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial (Mc^2)} \quad (2.77)$$

The entropy of the black hole is obtained

$$S = \frac{4\pi GM^2 k_B}{\hbar c} = \frac{\hbar c^5}{16\pi G k_B T^2} \quad (2.78)$$

Which contains a Planck length

$$l_{Pl} = \sqrt{\frac{\hbar G}{c^3}} \quad (2.79)$$

The entropy can be written as

$$S = \frac{k_B}{4} \frac{A_s}{l_{Pl}^2} \quad (2.80)$$

This indicates that the entropy of the black hole is proportional to its surface area, which is the Bekenstein-Hawking entropy formula.

2.5 Plasma

Plasma is composed of equal amounts of positively charged ions and negatively charged electrons. An important parameter of plasma is the Debye radius λ_D (characteristic length), in regions larger than λ_D , the region is overall electrically neutral, in regions smaller than λ_D , there is an uneven distribution of charge. The expression for λ_D is

$$\lambda_D = \sqrt{\frac{k_B T V}{8\pi N e^2}} \quad (2.81)$$

The internal energy $U = C_V T$ of particles. Another part is the Coulomb potential of the interaction between charged particles. Assuming the total Coulomb potential of the system:

$$V = -\frac{N e^2}{\lambda_D} \quad (2.82)$$

$$U = C_V T - N e^2 \sqrt{\frac{8\pi N e^2}{k_B T V}} \quad (2.83)$$

Hope to solve the Helmholtz free energy, according to the internal energy

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right]_V \quad (2.84)$$

Integration gives the free energy:

$$F = -C_V T \ln T - \frac{2}{3} N e^2 \sqrt{\frac{8\pi N e^2}{k_B T V}} + T f(V) \quad (2.85)$$

Where $f(V)$ is the integration constant that appears when integrating with respect to T . When $V \rightarrow \infty$, the above equation returns to the result of an ideal gas. The above equation can be simplified to:

$$F = F_{ig} - \frac{2}{3} N e^2 \sqrt{\frac{8\pi N e^2}{k_B T V}} \quad (2.86)$$

According to the total differential relationship of $F(N, T, V)$, it is easy to obtain:

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{2\nu_c R T}{V} - \frac{2N e^2}{3V} \sqrt{\frac{8\pi N e^2}{k_B T V}}, \quad (2.87a)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = S_{ig} - \frac{1}{3} N e^2 \sqrt{\frac{8\pi N e^2}{k_B T^3 V}}, \quad (2.87b)$$

$$\mu = + \left(\frac{\partial F}{\partial N} \right)_{T,V} = \mu_{ig} - e^2 \sqrt{\frac{8\pi N e^2}{k_B T V}}, \quad (2.87c)$$

2.6 Liquid System

First, we start from determining the pressure difference inside and outside the curved liquid surface. The model gives a liquid surface system including the interior, exterior, and surface layer, denoted as i, o, γ , respectively. According to the criterion of free energy in equilibrium state (see later), the free energy of the system takes its minimum value when the liquid surface system is stable, denoting the free energy of the three parts as F_i, F_o, F_γ , respectively, we have

$$\delta F_i + \delta F_o + \delta F_\gamma = 0 \quad (2.88)$$

Since the free energy of each part

$$\begin{aligned} \delta F_i &= W_i = -p_i \delta V_i, \\ \delta F_o &= W_o = -p_o \delta V_o, \\ \delta F_\gamma &= W_\gamma = \sigma \delta A_s, \end{aligned} \quad (2.89)$$

So we get

$$p_i \delta V_i + p_o \delta V_o = \sigma \delta A_s \quad (2.90)$$

Since the total volume of the internal and external surface layers of the liquid remains unchanged

$$\delta V_i + \delta V_o = 0 \quad (2.91)$$

The pressure difference inside and outside the liquid surface depends on the ratio of the change in surface area to the change in internal volume

$$p_i - p_o = \sigma \frac{\delta A_s}{\delta V_i} \quad (2.92)$$

Thus, by analyzing the area-volume change relationship, the Young-Laplace equation is obtained

$$\Delta p = p_i - p_o = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.93)$$

Where R_1 and R_2 are two orthogonal principal curvatures.

For a spherical droplet, $R_1 = R_2 = R$, so

$$p_{i,s} - p_{o,s} = \frac{2\sigma}{R} \quad (2.94)$$

For a liquid column, the radius of the liquid column surface $R_1 = R$. Taking another plane parallel to the axis, its intersection with the liquid column surface is also a principal section, so $R_2 = \infty$. Therefore

$$p_{i,c} - p_{o,c} = \frac{\sigma}{R} \quad (2.95)$$

A commonly discussed soap bubble problem, because it is an air-soap film-air structure, the pressure difference inside and outside is

$$\Delta p = p - p_0 = (p - p_{inner}) + (p_{inner} - p_0) = \frac{4\sigma}{r} \quad (2.96)$$

If a liquid can uniformly adhere to the surface of another liquid or solid, it is called a wetting phenomenon, or infiltration phenomenon; otherwise, it is called a non-wetting phenomenon, or non-infiltration phenomenon. According to the degree of uniform adhesion, it is further divided into complete wetting, partial wetting, partial non-wetting, and complete non-wetting. A contact angle θ will be introduced to classify infiltration.

Illustration	Contact Angle	Wetting Degree	Interaction Strength	
			Solid-Liquid	Liquid-Liquid
S	$\theta = 0$	Complete Wetting	Strong	Weak
C	$0 < \theta < 90^\circ$	Partial Wetting	Strong Weak	Strong Weak
B	$90^\circ \leq \theta < 180^\circ$	Partial Non-Wetting	Weak	Strong
A	$\theta = 180^\circ$	Complete Non-Wetting	Weak	Strong

Table 2: Classification of Infiltration Phenomena

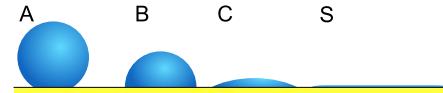


Fig. 13: Characteristics of Different Infiltration Phenomena

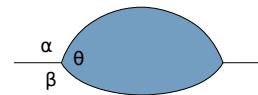


Fig. 14: Three-Phase Intersecting Liquid Interface

For a three-phase intersecting liquid interface, the surface tension along the interface is γ_{ij} , in equilibrium, the forces along the three-phase boundary line balance, so

$$\gamma_{\alpha\theta} + \gamma_{\theta\beta} \cos(\theta) + \gamma_{\alpha\beta} \cos(\alpha) = 0 \quad (2.97a)$$

$$\gamma_{\alpha\theta} \cos(\theta) + \gamma_{\theta\beta} + \gamma_{\alpha\beta} \cos(\beta) = 0 \quad (2.97b)$$

$$\gamma_{\alpha\theta} \cos(\alpha) + \gamma_{\theta\beta} \cos(\beta) + \gamma_{\alpha\beta} = 0 \quad (2.97c)$$

It can be translated into a Neumann triangle, for example If the β phase is replaced by a flat

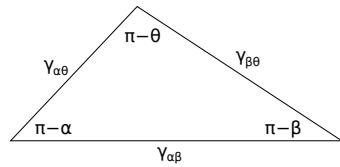


Fig. 15: Neumann Triangle Formed by Surface Tension

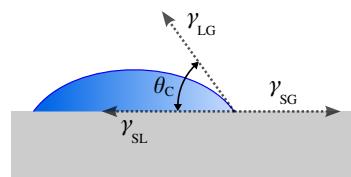


Fig. 16: Young's Relation of Surface Tension

surface, then $\beta = \pi$, the second net force equation simplifies to Young's relation

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos(\theta) \quad (2.98)$$

Young's relation can also be derived based on variation.

Chapter 3 Equilibrium and Phase Transition

3.1 Equilibrium Criteria and Stability Criteria

Mechanical equilibrium is divided into stable equilibrium, neutral equilibrium, and unstable equilibrium, corresponding to the second derivative of a certain potential energy with respect to the generalized coordinate being greater than, equal to, and less than 0, respectively. Stable equilibrium means that even with large disturbances, equilibrium can be restored; neutral equilibrium means small disturbances maintain equilibrium, while large disturbances disrupt it; and unstable equilibrium means any disturbance leads to imbalance.

Analogously, in the process of establishing equilibrium in thermodynamics, entropy continuously increases, leading to the **entropy criterion**: thermodynamic equilibrium corresponds to the maximum value of entropy, and stability corresponds to the second derivative of entropy being less than 0, using the language of functional variation:

$$\delta S = 0, \quad \delta^2 S < 0 \quad (3.1)$$

This is the equilibrium and stability criterion in thermodynamics. Next, calculate the variation of the total entropy δS of an isolated system due to virtual changes δU_1 and δV_1 :

$$\begin{aligned} \delta S &= \delta S_1 + \delta S_2 \\ &= \frac{\delta U_1}{T_1} + \frac{p_1}{T_1} \delta V_1 + \frac{\delta U_2}{T_2} + \frac{p_2}{T_2} \delta V_2 \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta U_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) \delta V_1. \end{aligned} \quad (3.2)$$

Since the variations δU_1 and δV_1 are independent, from $\delta S = 0$, the conditions for system equilibrium are obtained:

$$T_1 = T_2, \quad p_1 = p_2 \quad (3.3)$$

Next, discuss the conditions for stability, with the second derivative expanded as

$$\begin{aligned} \delta^2 S &= \frac{1}{2} \left[\frac{\partial^2 S}{\partial U^2} (\delta U)^2 + 2 \frac{\partial^2 S}{\partial U \partial V} (\delta U \delta V) + \frac{\partial^2 S}{\partial V^2} (\delta V)^2 \right] \\ &= \frac{1}{2} (\delta U, \delta V) \begin{pmatrix} \frac{\partial^2 S}{\partial U^2} & \frac{\partial^2 S}{\partial U \partial V} \\ \frac{\partial^2 S}{\partial V \partial U} & \frac{\partial^2 S}{\partial V^2} \end{pmatrix} \begin{pmatrix} \delta U \\ \delta V \end{pmatrix} \\ &= \frac{1}{2} (\delta U, \delta V) \begin{pmatrix} \frac{\partial}{\partial U} \left(\frac{1}{T} \right) & \frac{\partial}{\partial V} \left(\frac{1}{T} \right) \\ \frac{\partial}{\partial U} \left(\frac{p}{T} \right) & \frac{\partial}{\partial V} \left(\frac{p}{T} \right) \end{pmatrix} \begin{pmatrix} \delta U \\ \delta V \end{pmatrix} \end{aligned} \quad (3.4)$$

The stability condition $\delta^2 S < 0$ requires the following matrix to be positive definite:

$$\begin{pmatrix} -\frac{\partial}{\partial U} \left(\frac{1}{T} \right) & -\frac{\partial}{\partial V} \left(\frac{1}{T} \right) \\ -\frac{\partial}{\partial U} \left(\frac{p}{T} \right) & -\frac{\partial}{\partial V} \left(\frac{p}{T} \right) \end{pmatrix} \quad (3.5)$$

According to the positive definiteness of the matrix, each order determinant is greater than 0, we have

$$-\frac{\partial}{\partial U} \left(\frac{1}{T} \right)_V = \frac{1}{T^2 C_V} > 0, \quad -\frac{\partial}{\partial V} \left(\frac{p}{T} \right) > 0 \quad (3.6a)$$

$$\begin{aligned} & \left| \begin{array}{cc} -\frac{\partial}{\partial U} \left(\frac{1}{T} \right) & -\frac{\partial}{\partial V} \left(\frac{1}{T} \right) \\ -\frac{\partial}{\partial U} \left(\frac{p}{T} \right) & -\frac{\partial}{\partial V} \left(\frac{p}{T} \right) \end{array} \right| = -\frac{1}{T^3} \begin{vmatrix} \frac{\partial T}{\partial U} & \frac{\partial T}{\partial V} \\ \frac{\partial p}{\partial U} & \frac{\partial p}{\partial V} \end{vmatrix} = -\frac{1}{T^3} \frac{\partial(T, p)}{\partial(U, V)} \\ & = -\frac{1}{T^3} \frac{\partial(T, p)}{\partial(T, V)} \frac{\partial(T, V)}{\partial(U, V)} = -\frac{1}{T^3} \frac{\left(\frac{\partial p}{\partial V} \right)_T}{C_V} = \frac{1}{T^3 V C_V \kappa_T} > 0 \end{aligned} \quad (3.6b)$$

Therefore, the stability condition $\delta^2 S < 0$ actually requires

$$C_V > 0, \quad \kappa_T > 0 \quad (3.7)$$

Using different characteristic function extremum conditions, different system equilibrium criteria and uniform system stability criteria are obtained. For an adiabatic isochoric system with S, V as parameters, there is a minimum internal energy criterion:

$$\delta U = 0, \quad \delta^2 U > 0 \quad (3.8)$$

According to the positive definiteness of the matrix, each order determinant is greater than 0, we have

$$\left(\frac{\partial^2 U}{\partial S^2} \right) = \left(\frac{\partial T}{\partial S} \right) = \frac{T}{C_V} > 0, \quad \left(\frac{\partial^2 U}{\partial V^2} \right)_S = -\left(\frac{\partial P}{\partial V} \right)_S = \frac{1}{V \kappa_S} > 0 \quad (3.9a)$$

$$\left| \begin{array}{cc} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial V \partial S} \\ \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial V^2} \end{array} \right| = \left(\frac{\partial^2 U}{\partial S \partial V} \right)^2 - \frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} = \left(\frac{\partial T}{\partial V} \right)_S^2 - \frac{T}{C_V} \frac{1}{V \kappa_S} > 0 \quad (3.9b)$$

So we have

$$C_V > 0, \quad \kappa_S > 0, \quad C_V \kappa_S > \alpha_S^2 TV \quad (3.10)$$

There are also minimum criteria for Helmholtz free energy and Gibbs free energy, which can also derive different equilibrium and stability conditions.

3.2 Chemical/Phase Equilibrium

In systems where the number of particles N can change, the establishment of equilibrium is related to the number of particles, writing internal energy in the form $U(S, V, N)$, defining chemical potential as the partial derivative of internal energy with respect to the number of particles

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} \quad (3.11)$$

Thus giving the extended form of the differential of internal energy

$$dU = TdS - pdV + \mu dN \quad (3.12)$$

Thermodynamic quantities are

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N}, \quad p = - \left(\frac{\partial U}{\partial V} \right)_{S,N}, \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} \quad (3.13)$$

The differential form of Helmholtz free energy is

$$dF = -SdT - pdV + \mu dN \quad (3.14)$$

Thermodynamic quantities are

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N}, \quad p = - \left(\frac{\partial F}{\partial V} \right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} \quad (3.15)$$

The differential form of Gibbs free energy is

$$dG = -SdT + Vdp + \mu dN \quad (3.16)$$

Thermodynamic quantities are

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p,N}, \quad V = \left(\frac{\partial G}{\partial p} \right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{T,p} \quad (3.17)$$

Remark 3.1 (Extensive and Intensive Quantities). *Intensive quantities can be written as functions that depend only on intensive quantities, such as T, p, μ ;*

Extensive quantities can be written as functions of the number of particles (or volume) times intensive quantities, such as S, V, N, U, F, G .

Extensive quantities can be converted into molar quantities, such as molar heat capacity/volume/entropy/molar internal energy/free energy

$$c_x = \frac{C_x}{N}, \quad v = \frac{V}{N} = \frac{1}{\rho}, \quad s = \frac{S}{N}, \quad u = \frac{U}{N}, \quad f = \frac{U}{N}, \quad g = \frac{G}{N} \quad (3.18)$$

The Gibbs-Duhem equation can express extensive quantities in terms of molar components

$$\begin{aligned} dU &= d(Nu) = Ndu + udN \\ &= TdNs - pdNv + \mu dN \\ &= NTds + TsdN - Npdv - pvdN + \mu dN \\ &= N(Tds - pdv) + (Ts - pv + \mu)dN \end{aligned} \quad (3.19)$$

Thus the molar internal energy and its differential are

$$u = Ts - pv + \mu, \quad du = Tds - pdv \quad (3.20)$$

Thus giving the dependency relationship of chemical potential

$$\mu = u - Ts + pv \quad (3.21)$$

Observing

$$N\mu = Nu - TNs + pNv = U - TS + pV = G = Ng \quad (3.22)$$

So the chemical potential is essentially the molar Gibbs free energy

$$\mu = \frac{G}{N} = g = g(T, p) \quad (3.23)$$

Since

$$\begin{aligned} dG &= d(N\mu) = N d\mu + \mu dN \\ &= -SdT + Vdp + \mu dN = N(-sdT + vdp) + \mu dN \end{aligned} \quad (3.24)$$

The differential of chemical potential is

$$d\mu = -sdT + vdp \quad (3.25)$$

Exergy—Since In a simple isothermal system, the work done externally does not exceed the change in free energy

$$\begin{aligned} dF &= -SdT - pdV + \mu dN + Td_iS \\ dW &= -pdV = dF + SdT (\text{isothermal } = 0) - \mu dN (\text{simple system } = 0) - Td_iS (\geq 0) \quad (3.26) \\ &\leq dF \end{aligned}$$

Exergy/available energy is the maximum work done by the system in reaching equilibrium with the environment, where p_R, T_R, μ_{iR} are environmental parameters.

$$E = U + p_R V - T_R S - \sum_i \mu_{iR} N_i, \quad \Delta W \leq \Delta E \quad (3.27)$$

Phase Transition Mechanism: Internal energy and entropy compete with each other, leading to different phases at low and high temperatures,

- At low temperatures, the contribution of S is relatively small, U plays a leading role \Rightarrow ordered arrangement \Rightarrow crystal;
- At high temperatures, S plays a leading role \Rightarrow disorder, occupying all possible spaces \Rightarrow gas

Intermediate temperatures may see coexistence of two phases; more complex systems can have more complex phases.

According to the entropy criterion, the chemical phase equilibrium condition of the system is

$$T_1 = T_2, \quad p_1 = p_2, \quad \mu_1(T, p) = \mu_2(T, p) \quad (3.28)$$

- When the chemical potential is different, the system is in a single phase, and it is stable in the phase with a smaller chemical potential (Gibbs free energy minimum criterion);
- When $\mu_1 = \mu_2$, ΔN can be arbitrary: two phases coexist, and changes in the number of particles in the two phases do not affect the system's equilibrium and stability.

3.3 Phase Diagram and Phase Transition

For the chemical potential $\mu(T, p)$, the first and second derivatives with respect to temperature are given as:

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -s < 0, \quad \frac{\partial^2 \mu}{\partial T^2} = -\left(\frac{\partial s}{\partial T}\right)_p = -\frac{c_p}{T} < 0 \quad (3.29)$$

The first and second derivatives with respect to pressure are:

$$\left(\frac{\partial \mu}{\partial p}\right)_T = v > 0, \quad \frac{\partial^2 \mu}{\partial p^2} = \left(\frac{\partial v}{\partial p}\right)_T = (-v)\frac{-1}{v} \left(\frac{\partial v}{\partial p}\right)_T = -v\kappa_T < 0 \quad (3.30)$$

The different thermodynamic parameters of high and low temperature phases are given:

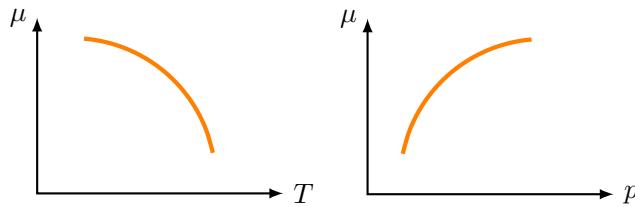


Fig. 17: Relationship of chemical potential μ with different parameters

- Low temperature phase (I): ordered (s small), low energy (u small), high density (v small)
- High temperature phase (II): disordered (s large), high energy (u large), low density (v large)

A $T - \mu$ phase diagram is drawn, showing that a system with a smaller chemical potential is stable, and there exists a transition temperature T^* where the chemical potentials of the two phases are equal.

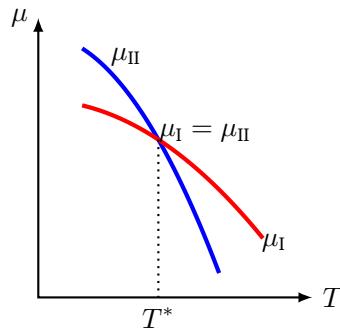


Fig. 18: Phase diagram of low temperature phase (I) and high temperature phase (II)

This transition temperature is called the phase transition temperature. At the phase transition temperature, the system absorbs heat but the temperature (pressure, free energy) does not change, and thermodynamic functions may exhibit singularities. The latent heat is defined as:

$$L = T(s_{II} - s_I) \quad (3.31)$$

General phase diagrams are considered in the $T - p$ phase diagram, such as the phase diagram of water, showing the triple point T_{tr} where three phases coexist, and the supercritical fluid region appearing in the upper right when a liquid-gas mixture reaches a certain state.

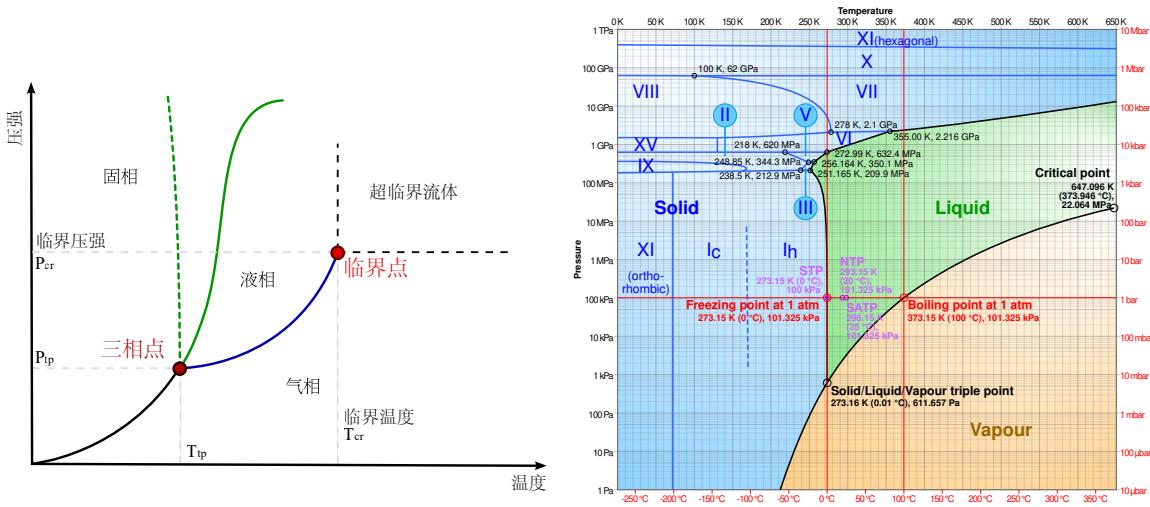


Fig. 19: Phase diagram of water, the green dashed line represents the anomalous phase transition of water

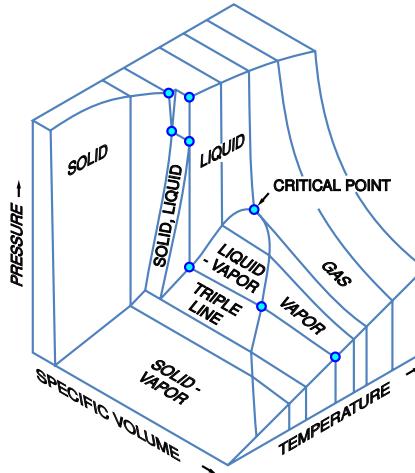


Fig. 20: A pVT phase diagram

Ehrenfest classified phase transitions into three categories based on the singularity of the chemical potential function:

- (1) First-order phase transition: the first derivative of the chemical potential is discontinuous, involving latent heat L . On both sides of the phase transition, both phases can stably exist. The chemical potentials of the two phases are different, with one phase being stable and the other metastable. After the phase transition, the stable and metastable phases exchange positions, typical examples include solid-liquid-gas phase transitions;

(2) Second-order phase transition/continuous phase transition: the first derivative of the chemical potential is continuous, but the second derivative is discontinuous. On one side of the phase transition point, only one phase is stable, and the other phase is unstable. Characteristics include divergent sensitivity, infinite correlation length, and power-law decay near the critical point, typical examples include ferromagnetic transitions and superconducting transitions;

(3) Higher-order phase transition: theoretically possible, but not observed experimentally. Bose-Einstein condensation was once thought to be a third-order phase transition, but is now generally considered a special first-order phase transition.

3.4 First-order Phase Transition

3.4.1 Gas-liquid Fluid Phase Transition

For gas-liquid low density fluid phase transition, from Eq. 2.14, 1 mol Van der Waals fluid equation can be used to describe

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad (3.32)$$

Rewritten as a form of pressure

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \quad (3.33)$$

Then make a pv diagram, observe the characteristics of isotherms. It can be seen that there is a

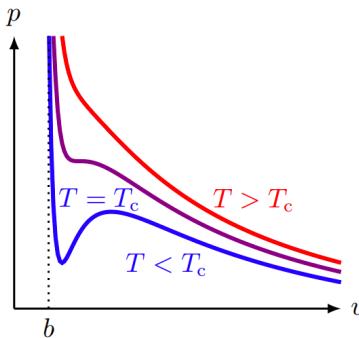


Fig. 21: Isotherms of pv diagram of Van der Waals gas

minimum molar volume $v = b$

- When $T > T_c$, the isotherm is monotonic.
- When $T < T_c$, the isotherm has two extremum points, one is a local maximum, and the other is a local minimum.
- When $T = T_c$, the two extremum points coincide, corresponding to the inflection point of the isotherm \Rightarrow critical point.

How to calculate the critical temperature? Using the state equation Eq. 3.33 first and second derivatives are zero, i.e.:

$$\left(\frac{\partial p}{\partial v}\right)_{T_c} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \Rightarrow \frac{RT_c}{(v-b)^2} = \frac{2a}{v^3} \quad (3.34a)$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_{T_c} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0 \Rightarrow \frac{RT_c}{(v-b)^3} = \frac{3a}{v^4} \quad (3.34b)$$

So the critical specific volume is $v_c = 3b$

$$v - b = \frac{2}{3}v \Rightarrow v_c = 3b, \quad b = \frac{v_c}{3} \quad (3.35)$$

Then substitute back into the state equation, get the critical temperature T_c as:

$$T_c = \frac{2a(v_c - b)^2}{Rv_c^3} = \frac{8a}{27bR} \quad (3.36)$$

and the critical pressure p_c

$$p_c = \frac{RT_c}{v_c - v_c/3} - \frac{a}{v_c^2} = \frac{4a}{3v_c^2} - \frac{a}{v_c^2} = \frac{a}{3v_c^2} = \frac{a}{27b^2} \quad (3.37)$$

Put the physical quantities in dimensionless form according to the critical parameters,

$$\tilde{p} = \frac{p}{p_c}, \quad \tilde{v} = \frac{v}{v_c}, \quad \tilde{T} = \frac{T}{T_c} \quad (3.38)$$

The Van der Waals equation becomes

$$\tilde{p} = \frac{8\tilde{T}}{3\tilde{v} - 1} - \frac{3}{\tilde{v}^2} \Leftrightarrow \left(\tilde{p} + \frac{3}{\tilde{v}^2}\right)\left(\tilde{v} - \frac{1}{3}\right) = \frac{8\tilde{T}}{3} \quad (3.39)$$

This equation is not dependent on any free parameters, which is called the corresponding state law, and thus an independent value is obtained:

$$\frac{p_c v_c}{RT_c} = \frac{3}{8} = 0.375 \quad (3.40)$$

Experimental results show that the above equation is generally consistent with the results obtained from different actual gases.

Re-arrange the Van der Waals state equation, write it as a cubic algebraic equation in v :

$$pv^3 - (pb + RT)v^2 + av - ab = 0 \quad (3.41)$$

When $T < T_c$, it has three real roots: L, U, G; when $T > T_c$, there is one real root and two complex conjugate roots. At $T = T_c$, $T = T_c$ must have three equal real roots. Can draw isotherms as follows: where, L point corresponds to liquid state, G point corresponds to gas state, and U

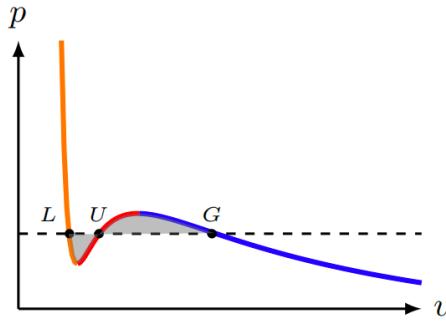


Fig. 22: Three real roots L, U, G when $T < T_c$, these three points have the same T, p but different v

point corresponds to unstable state, called metastable state. And we can also deduce from this that when $T > T_c$, the difference between liquid and gas disappears.

We hope to find the coexistence point of two phases. According to the relationship between chemical potential and area on the vp diagram

$$\mu(T, p) = \mu(T, p_0) + \int_{p_0}^p v dp \quad (3.42)$$

When two phases coexist, the shaded area is equal, or called Maxwell's equal area law

$$\int_G^L v dp = 0 \quad (3.43)$$

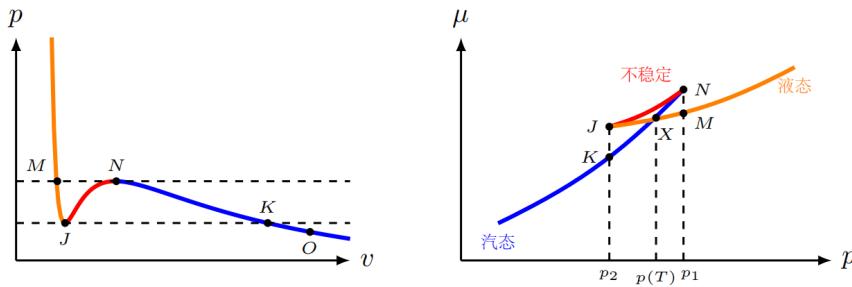


Fig. 23: Along the isotherm $T < T_c$, the chemical potential changes with pressure, JX is metastable superheated liquid

Similarly, when $T < T_c$, we discuss the difference between single phase and coexistence of two

phases. According to $df = -sdT - pdv$ and the Van der Waals equation without parameters, the free energy is

$$\begin{aligned} f(T, v) &= f(T, v_0) - \int_{v_0}^v pdv \\ &= f_0(T) - \frac{8T}{3} \ln\left(v - \frac{1}{3}\right) - \frac{3}{v} \end{aligned} \quad (3.44)$$

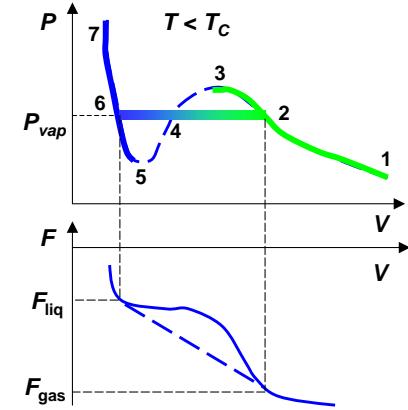
$v_l < v < v_g$ indicates a two-phase coexistence state. If the system is required to remain homogeneous, the relationship between free energy and volume in the range $v_l < v < v_g$ is represented by the green line, which is convex upwards. However, if spontaneous spatial inhomogeneity is allowed, i.e., two-phase coexistence, the $f(T, v)$ curve is a dashed line, lower than that of a homogeneous system. According to the proportion of the amount of substance

$$n_l v_l + n_g v_g = v, \quad n_l + n_g = 1 \quad (3.45)$$

The proportion of the amount of substance in the two phases is

$$\begin{aligned} n_l &= \frac{v_g - v}{v_g - v_l}, \\ n_g &= \frac{v - v_l}{v_g - v_l} \end{aligned}$$

Fig. 24: Two-phase coexistence
(3.46) phase diagram



$T = T_c$ indicates the critical temperature state, where the derivative of the curve is 0, i.e.,

$$\left(\frac{\partial p}{\partial v}\right)_{T_c} = 0 \quad (3.47)$$

The adiabatic compressibility coefficient diverges to infinity

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_{T_c} \rightarrow \infty \quad (3.48)$$

3.4.2 Critical Exponent

Consider the Van der Waals equation without parameters, give a small variation at the critical point

$$T = 1 + \tau, \quad p = 1 + \pi, \quad v = 1 + \omega \quad (3.49)$$

Then according to

$$p = \frac{8T}{3} \frac{1}{v - \frac{1}{3}} - \frac{3}{v^2} \Leftrightarrow 1 + \pi = \frac{8}{3} \frac{1 + \tau}{\frac{2}{3} + \omega} - \frac{3}{(1 + \omega)^2} = 4 \frac{1 + \tau}{1 + \frac{3}{2}\omega} - \frac{3}{(1 + \omega)^2} \quad (3.50)$$

Can get several state equations between variation parameters

$$\begin{aligned} \pi &= 4(1 + \tau) \left[1 - \frac{3\omega}{2} + \frac{9\omega^2}{4} - \frac{27\omega^3}{8} + \dots \right] - 3 [1 - 2\omega + 3\omega^2 - 4\omega^3 + \dots] - 1 \\ \Rightarrow \pi &= 4\tau - 6\tau\omega + 9\tau\omega^2 - \frac{3\omega^3}{2} + \dots \end{aligned} \quad (3.51)$$

When $T > T_c \Rightarrow \tau > 0$, the isothermal compressibility can be obtained

$$\begin{aligned}\frac{1}{\kappa_T} &= -(1 + \omega) \left(\frac{\partial \pi}{\partial \omega} \right)_\tau = 6\tau + O(\omega) \\ \kappa_T &= -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = \frac{1}{6\tau} = \frac{1}{6} \frac{1}{1 - T/T_c} \propto |1 - T/T_c|^{-1}\end{aligned}\quad (3.52)$$

When $T = T_C \Rightarrow \tau = 0$, the pressure variation is obtained

$$\pi = -\frac{3\omega^3}{2} \Rightarrow |p - p_c| \propto |v - v_c|^3 \quad (3.53)$$

The chemical potential at the critical point can be derived

$$\begin{aligned}\mu &= f(T, v) + pv = f_0(T) - \frac{8T}{3} \ln(v - 1/3) - \frac{3}{v} + \frac{8T}{3} \frac{v}{v - 1/3} - \frac{3}{v} \\ &= f_0(T) - \frac{8T}{3} \ln(2/3 + \omega) + \frac{8T}{3} \frac{1 + \omega}{2/3 + \omega} - \frac{6}{1 + \omega} \\ &= f_0(T) - \frac{8T}{3} \ln \frac{2}{3} + 4T - 6 - \frac{8T}{3} \ln \left(1 + \frac{3\omega}{2} \right) + 4T \left[\frac{1 + \omega}{1 + 3\omega/2} - 1 \right] + \frac{6\omega}{1 + \omega} \\ &= \mu_0(T) - \frac{8T}{3} \ln \left(1 + \frac{3\omega}{2} \right) - \frac{2T\omega}{1 + 3\omega/2} + \frac{6\omega}{1 + \omega} \\ &= \mu_0(\tau) - \frac{8(1 + \tau)}{3} \left[\frac{3\omega}{2} - \frac{1}{2} \frac{9\omega^2}{4} + \frac{1}{3} \frac{27\omega^3}{8} \right] \\ &\quad - 2(1 + \tau)\omega \left[1 - \frac{3\omega}{2} + \frac{9\omega^2}{4} + \dots \right] + 6\omega (1 - \omega + \omega^2 + \dots) \\ &= \mu_0(\tau) - 6\tau\omega + 6\tau\omega^2 - \frac{3\omega^3}{2}\end{aligned}\quad (3.54)$$

When $T < 1$ ($\tau < 0$), there are two phases. At phase equilibrium, the molar volumes of the liquid and gas phases are $v_l = 1 + \omega_l$ and $v_g = 1 + \omega_g$, respectively.

The pressure and volume must be equal

$$\begin{aligned}\pi_l &= 4\tau - 6\tau\omega_l + 9\tau\omega_l^2 - \frac{3\omega_l^3}{2} + \dots = \pi_g = 4\tau - 6\tau\omega_g + 9\tau\omega_g^2 - \frac{3\omega_g^3}{2} + \dots \\ \mu_l &= \mu_0 - 6\tau\omega_l + 6\tau\omega_l^2 - \frac{3\omega_l^3}{2} + \dots = \mu_g = \mu_0 - 6\tau\omega_g + 6\tau\omega_g^2 - \frac{3\omega_g^3}{2} + \dots\end{aligned}\quad (3.55)$$

For both sets of equations to hold simultaneously, it requires $\omega_l^2 = \omega_g^2 \Rightarrow -\omega_l = \omega_g = \omega$, and $0 = 6\tau\omega + 3\omega^3/2 \Rightarrow \omega = 2\sqrt{-\tau}$. This gives the relationship between volume change and temperature:

$$-\omega_l = \omega_g = 2\sqrt{-\tau} \quad (3.56)$$

The three sets of relationships derived all have their actual physical significance, corresponding to the critical exponents β, γ, δ . The critical exponents are independent of the specific physical system and are only related to the system's dimension, correlation length, and spin dimension. Experimentally measured values are $\alpha \sim -0.1 - 0.1$, $\beta \sim 0.33$, $\gamma \sim 1.3$, $\delta \sim 4 - 5$, and they are divided into complete universality classes according to the system's symmetry and dimension

Table 7

$$C_p \propto |T - T_c|^{-\alpha}, \quad (3.57a)$$

$$v_G - v_L \simeq (T_e - T)^\beta, \quad (3.57b)$$

$$\kappa \simeq (T - T_c)^{-\gamma}, \quad (3.57c)$$

$$p - p_c \simeq (v - v_c)^{-\delta} \quad (3.57d)$$

There are two relations between the critical exponents

$$\text{Rushbrooke relation: } \alpha + 2\beta + \gamma \geq 2 \quad (3.58a)$$

$$\text{Griffith relation: } \alpha + \beta(\delta + 1) \geq 2 \quad (3.58b)$$

Below is a proof of the Rushbrooke relation Eq. 3.58a for magnetic systems, based on

$$\begin{aligned} C_H - C_M &= T \left(\frac{\partial M}{\partial T} \right)_H^2 / \left(\frac{\partial M}{\partial H} \right)_T \\ C_M &\geq 0 \Rightarrow C_H \geq T \chi^{-1} \left(\frac{\partial M}{\partial T} \right)_H^2 \end{aligned} \quad (3.59)$$

Used for the critical exponent relation

$$C_H \propto |T - T_c|^{-\alpha}, \quad \chi \propto |T - T_c|^{-\gamma}, \quad M \propto |T - T_c|^\beta \quad (3.60)$$

It is obtained that

$$\begin{aligned} C_1 |T - T_c|^{-\alpha} &\geq C_2 |T - T_c|^\gamma \left[|T - T_c|^{\beta-1} \right]^2 \\ -\alpha &\leq \gamma + 2\beta - 2 \Rightarrow \alpha + 2\beta + \gamma \geq 2 \end{aligned} \quad (3.61)$$

In experiments, the equality can be obtained.

3.4.3 Metastable Equilibrium: Under-cooling/Overheating Phenomenon

In physics, metastable state represents an intermediate energy state within a dynamical system, rather than the minimum energy state of the system, as shown in Fig. 25 where the position of the 1st ball is if the disturbance exceeds the 2nd ball, it returns to the stable state 3rd position. In thermodynamics, a common metastable state is over-heating (boiling delay) and under-cooling

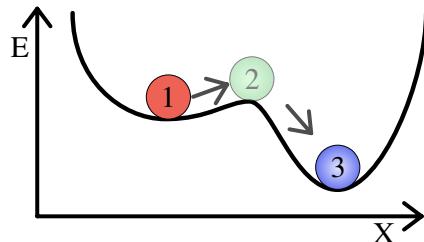


Fig. 25: 1st metastable state, 3rd stable state

Consider the energy of the unit area A

$$U(T, A) = u(T)A, \quad F(T, A) = f(T)A \quad (3.62)$$

Give the unit work

$$dU = Q - W = TdS + \sigma(T)dA \quad (3.63)$$

So we get the unit internal energy and free energy

$$\begin{aligned} f &= \frac{F}{A} = \left(\frac{\partial F}{\partial A} \right)_T = \sigma(T) \\ u &= \frac{U}{A} = \left(\frac{\partial U}{\partial A} \right)_T = \left(\frac{\partial F}{\partial A} \right)_T + T \left(\frac{\partial S}{\partial A} \right)_T = \sigma + T \left(\frac{\partial \sigma}{\partial T} \right)_A = \sigma - T \frac{d\sigma}{dT} \end{aligned} \quad (3.64)$$

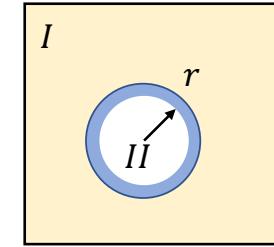


Fig. 26: II phase nucleation in I phase

(solidification delay), where the liquid is cooled below the freezing point temperature and solidifies. We will discuss the phenomenon of nucleation in the solid-liquid transition

So the total free energy

$$F = F_I + F_{II} + Af_A = V_I f_I + V_{II} f_{II} + A\sigma \quad (3.65)$$

Under $V_{II} = 0$, assume a II phase with radius r :

$$\begin{aligned} \Delta V_{II} &= 4\pi r^3/3 \quad \Delta V_I = -\Delta V_{II} = -4\pi r^3/3 \quad \Delta A = 4\pi r^2 \\ \Delta F &= f_I \Delta V_I + f_{II} \Delta V_{II} + \sigma \Delta A = (f_{II} - f_I) 4\pi r^3/3 + 4\pi r^2 \sigma \end{aligned} \quad (3.66)$$

Consider obtaining possible radius by differentiation

$$\frac{\partial \Delta F}{\partial r} = 4\pi (f_{II} - f_I) r^2 + 8\pi r \sigma \quad (3.67)$$

Radius obtained

$$r_0 = \frac{2\sigma}{f_I - f_{II}} \quad (3.68)$$

- $r < r_0, \frac{\partial \Delta F}{\partial r} > 0, r = 0$ metastable system completely in I phase, free energy minimum
- $r = r_0$, maximum, unstable
- $r > r_0, \frac{\partial \Delta F}{\partial r} < 0, r = \infty$ stable system completely in II phase, free energy minimum

Similarly, in the case of over-heating, the same physical description exists.

In general, metastable phase is easy to appear near the phase transition point, but after the temperature deviates from the phase transition point, due to the spontaneous fluctuation of the system, can destroy metastable phase, impurities/defects can also destroy metastable phase.

3.4.4 Clapeyron Equation

On the pressure-temperature ($p - T$) diagram, for any phase transition, the line separating the two phases is called the coexistence curve, according to the phase equilibrium equation

$$\begin{aligned}\mu_I(T + \Delta T, p + \Delta p) &= \mu_I(T, p) - s_I \Delta T + v_I \Delta p \\ &= \mu_{II}(T + \Delta T, p + \Delta p) = \mu_{II}(T, p) - s_{II} \Delta T + v_{II} \Delta p\end{aligned}\quad (3.69)$$

Clapeyron gave the slope of this curve, used to describe the rate of change of gas pressure with temperature in the equilibrium of a single component system.

$$\frac{dp}{dT} = \frac{L}{T \Delta v} = \frac{\Delta s}{\Delta v} \quad (3.70)$$

where $L = T \Delta s$ is the latent heat of phase transition, and the entropy change $\Delta s = s_{II} - s_I$, the change in molar volume (specific volume $v = \frac{V}{n}$) is $\Delta v = v_{II} - v_I$.

When the phase transition occurs between gas and condensed phase (liquid or solid), and it occurs at a temperature much lower than the critical temperature of the substance, the specific volume of the gas v_g is much larger than that of the condensed phase v_c . Therefore, the change in specific volume is approximately

$$\Delta v = v_g \left(1 - \frac{v_c}{v_g}\right) \simeq v_g \quad (3.71)$$

At low temperatures, if the pressure is also very low, the gas can be approximated by the ideal gas law, thus

$$v_g = \frac{RT}{p}, \quad (3.72)$$

Substituting back into the Clapeyron equation Eq. 3.70

$$\frac{dp}{dT} = \frac{L}{T \Delta v}, \quad (3.73)$$

yields the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{PL}{T^2 R} \quad (3.74)$$

3.5 Second-order Phase Transition

3.5.1 λ Transition

^4He can form a superfluid, and the formation of a superfluid is related to the formation of a Bose-Einstein condensate. Each atom of ^4He is a boson, while each atom of ^3He is a fermion. Below is the phase diagram of ^4He .

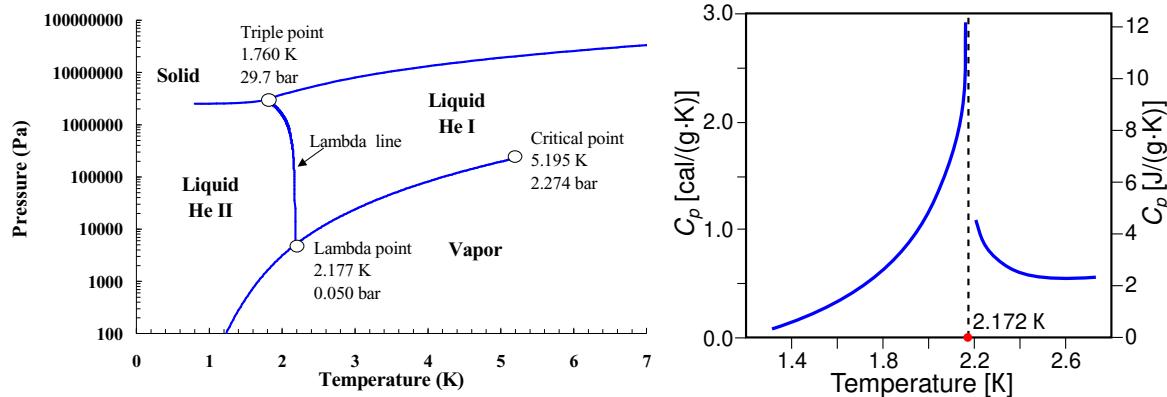


Fig. 27: ^4He phase diagram, heat capacity relationship

^4He cannot become solid under normal pressure due to weak interactions and strong zero-point motion. At the critical point: $T_C = 5.19 \text{ K}$, $p_C = 2.24 \text{ atm}$, it divides into two types of liquids: LHe-I (normal liquid) and LHe-II (superfluid). The boundary line between these two liquids is the λ transition line. The λ transition is a continuous (second-order) phase transition.

At the λ point, it is the gas / LHe-I / LHe-II triple point, $T_\lambda = 2.17 \text{ K}$, $p_\lambda = 0.05 \text{ atm}$

Near the λ point, the change in heat capacity is

$$C \simeq B_\pm + A_\pm |1 - T/T_C|^{-\alpha}, \quad \alpha \simeq -0.0127 \quad (3.75)$$

In the superfluid state, the viscosity coefficient η is zero, so the superfluid can flow without resistance. The thermal conductivity is infinite, and the two states have different appearances: He-I keeps boiling; He-II is usually calm and only evaporates on the surface.

3.5.2 Critical Phenomena of Continuous Phase Transition

Thomas Andrews systematically studied the liquefaction behavior of CO₂ and found:

- $T < 31^\circ\text{C}$, CO₂ can be liquefied by simply increasing the pressure ($p \sim 70$ atm). At the phase transition point, the two phases coexist, and both the gas and liquid are homogeneous and transparent; there is a clear interface separating the liquid and gas.
- $T > 31^\circ\text{C}$, it cannot be liquefied by increasing the pressure.
- Near $T \approx 31^\circ\text{C}$, the gas-liquid interface becomes blurred when the two phases coexist; at $T = T_c = 31^\circ\text{C}$, $p = p_c = 73$ atm, the interface completely disappears: (T_c, p_c) represents the critical point of CO₂.

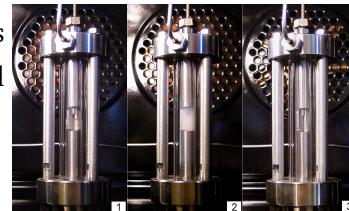


Fig. 28: Critical opalescence of ethane

At the critical point, the system becomes a gas-liquid mixture, with droplets of various sizes suspended in the gas. These droplets scatter light strongly at visible wavelengths, turning the system milky white and producing the phenomenon of critical opalescence.

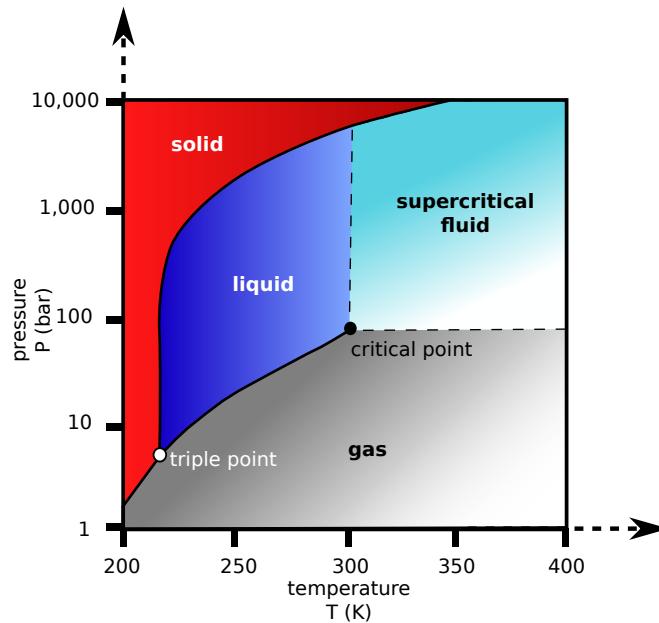


Fig. 29: Phase diagram of CO₂

3.5.3 Landau's Theory of Second-order Phase Transitions

Landau pointed out that all phase transitions involve changes in the degree of order, which can be described by one or a set of parameters (order parameters). Different systems have differ-

ent order parameters. Below are the order parameters for different systems:

- Gas-liquid phase transition: density;
- Paramagnetic transition: magnetic moment, which can be a scalar magnetic moment M or a vector magnetic moment \mathbf{M} ;
- Alloy order/disorder: $N_A^X - N_B^X$;
- Superconductor/normal conductor: energy gap $\Delta(\mathbf{k})e^{i\theta}$; macroscopic wave function $\Psi = \sqrt{\rho(\mathbf{r})}e^{i\theta}$; superfluid density: n_s ; superconducting electron density: $\rho = |\Psi|^2$.

Below, we discuss Landau's theory of second-order phase transitions using a uniaxial ferromagnetic system as an example. The paramagnetic transition requires the magnetic moment as the order parameter, considering the Gibbs free energy as a function of temperature, magnetic moment, and magnetic field strength: $G(T, H, M)$. Since

- Critical point: keeping pressure constant, $T = T_C, H = H_C = 0$;
- $T > T_c$ is paramagnetic, with no spontaneous magnetic moment when $H = 0, M = 0$;
- $T < T_c$ is ferromagnetic, with spontaneous magnetic moment when $H = 0, M \neq 0$. The spontaneous magnetic moment M reflects magnetic order, $\xi = M$.

Thus, we retain the lowest effective terms

$$G(T, H, M) = G_0(T) + a_1(T)HM + a_2(T)M^2 + a_4(T)M^4 + \dots \quad (3.76)$$

$$(1) \text{ Equilibrium condition: extremum point, } \left(\frac{\partial G}{\partial M} \right)_{TH} = 0$$

$$0 = a_1(T)H + 2a_2(T)M + 4a_4(T)M^3 + \dots \quad (3.77)$$

Critical point $H = H_c = 0$

$$2M [a_2(T) + 2a_4(T)M^2 + \dots] = 0 = \begin{cases} M = 0 & , T > T_C \\ M^2 = -\frac{a_2(T)}{2a_4(T)} & , T < T_C \end{cases} \quad (3.78)$$

$$(2) \text{ Stability condition: minimum point, } \left(\frac{\partial^2 G}{\partial M^2} \right)_{TH} > 0$$

$$0 < 2a_2(T) + 12a_4(T)M^2 = \begin{cases} 2a_2(T) & , M = 0 \\ -4a_2(T) & , M^2 = -\frac{a_2(T)}{2a_4(T)} \end{cases} , T < T_c \quad (3.79)$$

Next, we discuss the coefficients of each order, $\alpha > 0$, because

$$\left. \begin{array}{ll} T > T_c & a_2(T) > 0 \\ T < T_c & a_2(T) < 0 \end{array} \right\} \Rightarrow a_2(T) \simeq \alpha \times (T - T_c) \quad (3.80)$$

$\beta > 0$, because

$$\begin{aligned} T < T_c \Rightarrow M^2 = -\frac{a_2(T)}{2a_4(T)} > 0 \Rightarrow a_4(T) \simeq a_4(T_c) = \beta/2 \\ \Rightarrow M^2 = -\alpha(T - T_c)/\beta \end{aligned} \quad (3.81)$$

For $T > T_c$, according to Curie's law

$$\begin{aligned} \left(\frac{\partial G}{\partial M} \right)_{TH} &= 0 = a_1(T)H + 2\alpha(T - T_c)M + \dots \\ M &\simeq -\frac{a_1(T)}{2(T - T_c)}H = -\frac{a_1(T_c)}{2(T - T_c)}H = \frac{C}{T - T_c}H \end{aligned} \quad (3.82)$$

Thus, the Gibbs free energy of the system is obtained, representing a spontaneous symmetry breaking

$$G = G(T, H, M) = G_0(T) - 2CHM + \alpha(T - T_c)M^2 + \frac{\beta M^4}{2} \quad (3.83)$$

Under the condition $H = 0$, the second term can be removed.

3.6 Conventional Superconductors

Meissner Effect: Perfect diamagnetism, when $H < H_C(T)$,

$$G_n(T, H = 0) - G_S(T, H = 0) = \frac{\mu_0 H_c^2(T)}{2} \quad (3.84)$$

In general, phase transitions are first-order, but the transition at $H = 0, T = T_C$ is generally considered a second-order phase transition. The normal/superconducting transition of conventional superconductors is the only one that conforms to the Ehrenfest definition of a second-order phase transition. At the phase transition point, there is a jump in the heat capacity of the two phases.

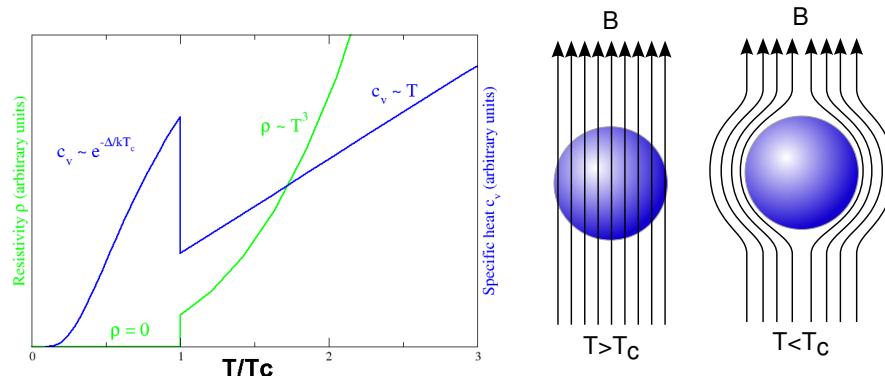


Fig. 30: Zero resistance effect, Meissner effect

In electromagnetism, there is a formula relating magnetization and magnetic field strength

$$M = \chi H \quad (3.85)$$

In the normal phase, a superconductor is paramagnetic ($\chi = 0$), and in the superconducting phase, it is diamagnetic ($\chi = -1$). When $T < T_C$ (critical temperature), a magnetic field H is

applied until $H_c(T)$ (critical field), at which point it transitions from the superconducting phase to the normal phase. Below, the work done by the external field is calculated

$$W = B \, dM = \mu_0 H \chi \, dH \quad (3.86)$$

The differential of the chemical potential during the phase transition process is

$$d\mu = -S \, dT - M \, dB \quad (3.87)$$

Rearranging terms gives the entropy

$$S = -M \frac{dB}{dT} - \frac{d\mu}{dT} \quad (3.88)$$

At the superconducting critical point (T_c), the chemical potential remains unchanged

$$\Delta S = S_N - S_S = -\mu_0 (\chi_N - \chi_S) H_c \frac{dH_c}{dT} = -\mu_0 H_c \frac{dH_c}{dT} \quad (3.89)$$

The expression for heat capacity can also be given

$$\begin{aligned} C &= \frac{T \, dS}{dT} = T \left(-\frac{dM}{dT} \frac{dB}{dT} - M \frac{d^2B}{dT^2} - \frac{d^2\mu}{dT^2} \right) \\ &= -T \left(\mu_0 \chi \left(\frac{dH}{dT} \right)^2 + \mu_0 \chi H \frac{d^2H}{dT^2} - \frac{d^2\mu}{dT^2} \right) \end{aligned} \quad (3.90)$$

3.6.1 Bardeen-Cooper-Schrieffer Theory

Two electrons tend to overlap in phase space, forming a pair of quasiparticles with opposite momentum, symmetric wave function, and antisymmetric spin ($\mathbf{k} \uparrow, -\mathbf{k} \downarrow$), known as Cooper pairs. The weak phonon-mediated attraction can cause electrons above the Fermi energy to form Cooper pairs, lowering the energy below the Fermi energy, destabilizing the Fermi sea, and promoting the formation of Cooper pairs ($\mathbf{k} \uparrow, -\mathbf{k} \downarrow$). Specific heat: In the superconducting state, $C_S(T) =$

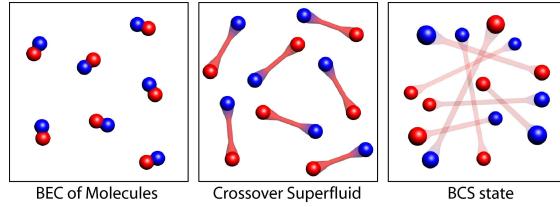


Fig. 31: Transition from BEC to BCS

$V\alpha T^3$; in the normal state, $C_N(T) = V [\beta T^3 + \gamma T]$. Here, V is the volume, and α, β, γ are constants. Using the third law of thermodynamics, the entropy functions of the superconducting and normal states $S_S(T), S_N(T)$ can be solved.

$$S_S(T) = \int_0^T \frac{C_S(T)}{T} \, dT = \int_0^T V \alpha T^2 \, dT = \frac{1}{3} V \alpha T^3 \quad (3.91a)$$

$$S_N(T) = \int_0^T \frac{C_N(T)}{T} \, dT = \int_0^T V [\beta T^2 + \gamma] \, dT = \frac{1}{3} V \beta T^3 + V \gamma T \quad (3.91b)$$

Considering the case of zero external field, the entropy is continuous at T_c :

$$\frac{1}{3}V\alpha T_c^3 = \frac{1}{3}V\beta T_c^3 + V\gamma T_c \quad (3.92)$$

The transition temperature is obtained as

$$T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}} \quad (3.93)$$

For both states, the internal energy at 0 K differs due to the formation of Cooper pairs. The internal energy of the superconducting state at 0 K is $E_S(T = 0) = E_0 - V\Delta$; the internal energy of the normal state at 0 K is $E_N(T = 0) = E_0$. E_0 is a constant, and Δ is the energy gap function. It can be seen that $V\Delta$ is the reduced energy. Using the above relationships, the internal energies $E_S(T), E_N(T)$ of the two states are calculated.

$$E_S(T) = E_0 - V\Delta + \int_0^T T \cdot dS_S = E_0 - V\Delta + \int_0^T V\alpha T^3 dT = E_0 - V\Delta + \frac{1}{4}V\alpha T^4 \quad (3.94a)$$

$$E_N(T) = E_0 + \int_0^T T \cdot dS_N = E_0 + \int_0^T (V\beta T^3 + V\gamma T) dT = E_0 + \frac{1}{4}V\beta T^4 + \frac{1}{2}V\gamma T^2 \quad (3.94b)$$

Using the equality of chemical potential at the superconducting transition temperature

$$\begin{aligned} G_S(T_c) &= G_N(T_c) \\ E_0 - V\Delta - \frac{1}{12}V\alpha T_c^4 &= E_0 - \frac{1}{12}V\beta T_c^4 - \frac{1}{2}V\gamma T_c^2 \end{aligned} \quad (3.95)$$

The energy gap is obtained.

$$\Delta = \frac{1}{2}\gamma T_c^2 + \frac{1}{12}(\beta - \alpha)T_c^4 = \frac{3}{4}\frac{\gamma^2}{\alpha - \beta} \quad (3.96)$$

Considering the external field, the expression for internal energy changes

$$dE = T dS + B dM \quad (3.97)$$

The superconducting phase exhibits complete diamagnetism, with internal magnetic polarization completely shielding the internal magnetic field lines. Therefore, $M_S = -\frac{VB}{4\pi}$. In general, the normal state of superconducting metals is considered to be mostly non-magnetic, following Matthias's rule. Therefore, $M_N = 0$. It can be proven that the critical field satisfies

$$B_c(T) = B_0 \left(1 - \frac{T^2}{T_c^2} \right) \quad (3.98)$$

Considering the chemical potential

$$d\mu = -S dT - M dB \quad (3.99)$$

For both phases

$$d\mu_S = -S_S dT - \left(\frac{-VB}{4\pi} \right) dB = -\frac{1}{3}V\alpha T^3 dT + \frac{VB}{4\pi} dB = d \left(-\frac{1}{12}V\alpha T^4 + \frac{V}{8\pi}B^2 + C_1 \right) \quad (3.100a)$$

$$d\mu_N = -S_N dT = - \left(\frac{1}{3}V\beta T^3 + V\gamma T \right) dT = d \left(-\frac{1}{12}V\beta T^4 - \frac{1}{2}V\gamma T^2 + C_2 \right) \quad (3.100b)$$

At the boundary between the two phases

$$\mu_S = \mu_N, \quad d(\mu_S - \mu_N) = 0 \quad (3.101)$$

That is

$$\begin{aligned} -\frac{1}{12}V\alpha T^4 + \frac{V}{8\pi}B^2 + C_1 - \left(-\frac{1}{12}V\beta T^4 - \frac{1}{2}V\gamma T^2 + C_2 \right) &= 0 \\ \frac{V}{8\pi}B^2 &= \frac{1}{12}V(\alpha - \beta)T^4 - \frac{1}{2}V\gamma T^2 + C \end{aligned} \quad (3.102)$$

Thus, the change in the magnetic field is

$$\begin{aligned} B^2 &= 8\pi(\alpha - \beta) \left(\frac{1}{12}T^4 - \frac{1}{6}T_c^2 T^2 + \frac{1}{12}T_c^4 \right) \\ &= \frac{2\pi(\alpha - \beta)}{3} (T^2 - T_c^2)^2 \end{aligned} \quad (3.103)$$

And B_0 is

$$B_0 = \sqrt{\frac{2\pi}{3} \cdot (\alpha - \beta) \cdot \frac{9\gamma^2}{(\alpha - \beta)^2}} = \sqrt{\frac{6\pi\gamma^2}{\alpha - \beta}} \quad (3.104)$$

3.6.2 Ginzburg-Landau Theory

Based on the experimental facts at the time, Landau ingeniously proposed a mean-field model to describe second-order phase transitions, which involves a perturbative expansion of the free energy in response to external fields/order parameters under the mean-field approximation. Based on this approximation, the theory can describe spontaneous symmetry breaking (where certain physical quantities exhibit multivalued phenomena). Ginzburg and Landau established the following phenomenological model: Suppose we set the magnetic field in the normal state as $B_0 = \mu_0 H$, as a constant external field, and assume the magnetic field in the superconducting state as B , while considering the paramagnetic term $dW = -\mu_0 H dM$. The difference in free energy between the superconducting and normal states is:

$$f_{GL} = \frac{1}{2m}|(-i\hbar\nabla - q\vec{A})\phi(r)|^2 + a(T)|\phi(r)|^2 + \frac{b(T)}{2}|\phi(r)|^4 + \frac{B^2}{2\mu_0} - \frac{\mu_0 H^2}{2} - \mu_0 H \cdot M \quad (3.105)$$

Consider variations with respect to ϕ^* and \vec{A} to make the free energy F_{GL} reach an extremum: Taking the variation with respect to ϕ^* , using the above relations, yields the first GL equation

$$\begin{aligned} \frac{1}{2m}(-i\hbar\nabla - q\vec{A}) \cdot [(-i\hbar\nabla - q\vec{A})\phi] + a(T)\phi + b(r)\phi^2\phi^* &= 0 \\ \frac{1}{2m}(-i\hbar\nabla - q\vec{A})^2\phi + a(T)\phi + b(T)|\phi|^2\phi &= 0 \end{aligned} \quad (3.106)$$

Taking the variation with respect to A , using the above relations, noting that H is a constant field, yields the second GL equation

$$\begin{aligned} \frac{1}{2m}(-q\phi^*) \cdot [(-i\hbar\nabla - q\vec{A})\phi] + \frac{1}{2m} \left[(i\hbar\nabla - q\vec{A})\phi^* \right] \cdot (-q\phi) + \frac{1}{\mu_0} \nabla \times (\nabla \times \vec{A}) - \nabla \times H &= 0 \\ \frac{iq\hbar}{2m}(\phi^*\nabla\phi - \phi\nabla\phi^*) + \frac{q^2\vec{A}}{m}|\phi|^2 + \frac{1}{\mu_0} \nabla \times \vec{B} &= 0 \\ -\frac{iq\hbar}{2m}(\phi^*\nabla\phi - \phi\nabla\phi^*) - \frac{q^2\vec{A}}{m}|\phi|^2 &= j_s \end{aligned} \quad (3.107)$$

Assuming that within a certain locality, the spatial distribution of superconducting electrons is uniform,

$$\phi(r) = \sqrt{n_s} \exp(i\theta(r)) \quad (3.108)$$

Note that $|\phi|^2 = n_s$ is defined as the superconducting electron density, which is a constant. In this case, for an isolated superconductor, n_s is constant, the charge distribution is uniform, and the current j_s for an isolated superconductor is 0. Substituting Eq. 3.108 into the wave function

$$\frac{-iq\hbar}{2m} (n_s i \nabla \theta(r) + n_s i \nabla \theta(r)) - \frac{q^2}{m} \vec{A} n_s = 0 \quad \Rightarrow \quad \vec{A} = \frac{\hbar}{q} \nabla \theta(r) \quad (3.109)$$

This results in magnetic flux quantization

$$\begin{aligned} \Phi &= \oint \vec{B} \cdot d\vec{S} = \oint \nabla \times \vec{A} \cdot d\vec{S} \\ &= \oint_L \vec{A} \cdot d\vec{l} = \oint_L \frac{\hbar}{q} \nabla \theta(r) \cdot d\vec{l} = \frac{\hbar}{q} \Delta\theta \\ &= \frac{\hbar \cdot 2\pi n}{q} = n \frac{\hbar}{q} = n \frac{h}{2e} \end{aligned} \quad (3.110)$$

Where, due to the single-valued nature of the wave function, the change in angle after a loop can only be an integer multiple of 2π , i.e., $\Delta\theta = 2\pi n$, the charge carriers in the superconductor are Cooper pairs $q = 2e$. For the second GL equation, multiplying both sides by $\nabla \times$, the result is

$$\begin{aligned} -\frac{1}{\mu_0} \nabla^2 \vec{B} &= -\frac{q^2}{m} \vec{B} n_s \\ \nabla^2 \vec{B} &= \frac{1}{\frac{m}{\mu_0 n_s q^2}} \vec{B} = \frac{1}{\lambda^2} \vec{B} \end{aligned} \quad (3.111)$$

This is the London equation, where the penetration depth λ is

$$\lambda = \sqrt{\frac{m}{\mu_0 n_s q^2}} \quad (3.112)$$

3.7 Multicomponent Equilibrium

3.7.1 Characteristic Functions

Consider a homogeneous system containing k components, where the chemical parameters, particle numbers N_1, N_2, \dots, N_k , need to be adjusted accordingly. The various thermodynamic characteristic functions change accordingly to

$$U = U(S, V, N_1, N_2, \dots, N_k) \quad (3.113a)$$

$$F = F(T, V, N_1, N_2, \dots, N_k) = U - TS \quad (3.113b)$$

$$G = G(T, p, N_1, N_2, \dots, N_k) = F + pV \quad (3.113c)$$

Thus, the differential of internal energy is

$$dU = TdS - pdV + \mu_1 dN_1 + \mu_2 dN_2 + \dots + \mu_k dN_k \quad (3.114)$$

From this, various thermodynamic parameters are

$$T(S, V, \{N_i\}) = \left(\frac{\partial U}{\partial S} \right)_{V\{N_i\}} \quad (3.115a)$$

$$p(S, V, \{N_i\}) = - \left(\frac{\partial U}{\partial V} \right)_{S,\{N_i\}} \quad (3.115b)$$

$$\mu_i(S, V, \{N_j\}) = \left(\frac{\partial U}{\partial N_i} \right)_{S,V,\{N_j \neq i\}} \quad (3.115c)$$

Based on the differential of Helmholtz free energy,

$$dF = -SdT - pdV + \sum_i \mu_i dN_i \quad (3.116)$$

A set of Maxwell relations is given

$$\left(\frac{\partial S}{\partial V} \right)_{T\{N_i\}} = \left(\frac{\partial p}{\partial T} \right)_{V\{N_i\}} \quad (3.117a)$$

$$\left(\frac{\partial S}{\partial N_i} \right)_{TV\{N_j \neq i\}} = - \left(\frac{\partial \mu_i}{\partial T} \right)_{V\{N_j\}} \quad (3.117b)$$

$$\left(\frac{\partial p}{\partial N_i} \right)_{TV\{N_j \neq i\}} = - \left(\frac{\partial \mu_i}{\partial V} \right)_{T\{N_j\}} \quad (3.117c)$$

$$\left(\frac{\partial \mu_i}{\partial N_j} \right)_{TV\{N_k \neq j\}} = \left(\frac{\partial \mu_j}{\partial N_i} \right)_{TV\{N_k \neq i\}} \quad (3.117d)$$

Based on the differential of Gibbs free energy

$$dG = -SdT + Vdp + \sum_i \mu_i dN_i \quad (3.118)$$

Another set of Maxwell relations is given

$$\left(\frac{\partial S}{\partial p} \right)_{T\{N_i\}} = - \left(\frac{\partial V}{\partial T} \right)_{p\{N_i\}} \quad (3.119a)$$

$$\left(\frac{\partial S}{\partial N_i} \right)_{Tp\{N_j \neq i\}} = - \left(\frac{\partial \mu_i}{\partial T} \right)_{p\{N_j\}} \quad (3.119b)$$

$$\left(\frac{\partial V}{\partial N_i} \right)_{Tp\{N_j \neq i\}} = \left(\frac{\partial \mu_i}{\partial p} \right)_{T\{N_j\}} \quad (3.119c)$$

$$\left(\frac{\partial \mu_i}{\partial N_j} \right)_{Tp\{N_k \neq j\}} = \left(\frac{\partial \mu_j}{\partial N_i} \right)_{Tp\{N_k \neq i\}} \quad (3.119d)$$

Given the proportion of the amount of substance

$$x_i = \frac{N_i}{N}, \quad \sum_i x_i = 1 \quad (3.120)$$

According to the Gibbs-Duhem relation,

$$\begin{aligned} dU &= Ndu + udN = TdS - pdV + \sum_i \mu_i dN_i \\ &= NTds - Npdv + N \sum_i \mu_i dx_i + \left(Ts - pv + \sum_i x_i \mu_i \right) dN \end{aligned} \quad (3.121)$$

Comparing with Eq. 3.20, the new molar internal energy and its differential are obtained

$$u = u(s, v, \{x_i\}) = Ts - pv + \sum_i x_i \mu_i, \quad du = Tds - pdv + \sum_i \mu_i dx_i \quad (3.122)$$

For Helmholtz free energy,

$$dF = -SdT - pdV + \sum_i \mu_i dN_i \quad (3.123)$$

Considering a local Legendre transformation of the above equation, a new physical quantity—the grand potential—is obtained, mainly used for systems in contact with particle sources (such as the grand canonical ensemble)

$$J = J(T, V, \{\mu_i\}) = F - \sum_i N_i \mu_i \quad (3.124)$$

In fact, the grand potential can be transformed into

$$\begin{aligned} J &= F - \sum_i N_i \mu_i = F - G = F - (F + pV) = -pV \\ &= -p(T, V, \{\mu_i\}) V \end{aligned} \quad (3.125)$$

Its differential is

$$dJ = -SdT - pdV - \sum_i N_i d\mu_i \quad (3.126)$$

Similarly, the Maxwell relations for molar physical quantities can be obtained.

3.7.2 Ideal Gas Mixture

Ideal gas mixture, with the law of partial volumes

$$p \left(\sum_i V_i \right) = pV = \left(\sum_i N_i \right) RT = NRT \quad (3.127)$$

and Dalton's law of partial pressures

$$p = \sum_i p_i = \sum_i \frac{N_i RT}{V} = \sum_i x_i \frac{NRT}{V} = \frac{NRT}{V} \quad (3.128)$$

For each gas undergoing free expansion, an entropy increase occurs, which accumulates to give the mixing entropy (corresponding to an information entropy)

$$\Delta S_{mix} = \sum_i N_i R \ln \frac{V}{V_i} = NR \sum_i \frac{N_i}{N} \ln \frac{N}{N_i} = -NR \sum_i x_i \ln x_i \quad (3.129)$$

It can also be derived from

$$\mu_i^0(T, p) = g_i(T, p) = \phi_i(T) + RT \ln p \quad (3.130)$$

Rewrite the chemical potential of the i-th component as

$$\mu_i(T, p, \{x_j\}) = g_i(T, p) + RT \ln x_i \quad (3.131)$$

3.7.3 Multicomponent Phase Equilibrium

Consider a system with k components and ϕ phases, where each phase is homogeneous. Each phase has the same pressure corresponding to mechanical equilibrium, and the same temperature corresponding to thermal equilibrium. The variables are: $T, p, V^\sigma, \{N_i^\sigma\}$, $\sigma = I, \dots, \phi; i = 1, \dots, k$, among which, Independent variables: T, p, N_i^σ , totaling $2 + \phi \times k$ independent variables.

The total extensive quantity is the sum of the extensive quantities of each phase, so the system can be divided into infinitesimal subsystems for summation. For example, free energy

$$\begin{aligned} dG &= \sum_{\sigma} dG^{\sigma} = \sum_{\sigma} \left[-S^{\sigma} dT + V^{\sigma} dp + \sum_i \mu_i^{\sigma} dN_i^{\sigma} \right] \\ &= -SdT + Vdp + \sum_{\sigma i} \mu_i^{\sigma} dN_i^{\sigma} \end{aligned} \quad (3.132)$$

At equilibrium, due to the conservation of particle number

$$\delta N_i = 0 = \sum_{\sigma} \delta N_i^{\sigma} \Rightarrow \delta N_i^I = - \sum_{\sigma=II}^{\phi} \delta N_i^{\sigma} \quad (3.133)$$

The variation of chemical potential is zero

$$\begin{aligned} \delta G &= \sum_{i=1}^k \sum_{\sigma=I}^{\phi} \mu_i^{\sigma} \delta N_i^{\sigma} = \sum_{i=1}^k \left[-\mu_i^I \sum_{\sigma=II}^{\phi} \delta N_i^{\sigma} + \sum_{\sigma=II}^{\phi} \mu_i^{\sigma} \delta N_i^{\sigma} \right] \\ &= \sum_i^k \sum_{\sigma=II}^{\phi} (\mu_i^{\sigma} - \mu_i^I) \delta N_i^{\sigma} \end{aligned} \quad (3.134)$$

This is the equilibrium condition for multicomponent phases, which can be expanded into $(\phi - 1) \times k$ conditions

$$\delta G = \sum_i^k \sum_{\sigma=II}^{\phi} (\mu_i^{\sigma} - \mu_i^I) \delta N_i^{\sigma} \quad (3.135a)$$

$$\mu_i^I = \mu_i^{II} = \dots = \mu_i^{\phi} \quad i = 1, 2, \dots, k \quad (3.135b)$$

In which, the chemical potential of each component is the same in all phases; the chemical potential of different components in one phase can be different.

Gibbs Phase Rule: For a system with k components and ϕ phases, the degrees of freedom are:

$$D = 2 + k - \phi \quad (3.136)$$

Specific component discussion

(1) Single component $k = 1 \Rightarrow D = 3 - \phi$

- Single phase $\phi = 1, D = 2$: Both temperature T and pressure p can change independently. Two phases $\phi = 2, D = 1$:
- Two-phase coexistence, only one of T or p can change freely; melting/boiling point: $T^*(p)$ or saturated vapor pressure: $p^*(T)$

- Three phases $\phi = 3, D = 0$: When three phases coexist, both temperature and pressure are determined, Triple point: $T = T_{tp}, p = p_{tp}$

(2) Two components $k = 2 \Rightarrow D = 4 - \phi$, e.g., saline solution

- Single phase $\phi = 1, D = 3$

Independent variables T, p , concentration $x = x_{\text{salt}} = \frac{N_{\text{salt}}}{N_{\text{salt}} + N_{\text{water}}}$

Water proportion: $x_{\text{water}} = 1 - x = 1 - x_{\text{salt}} = \frac{N_{\text{water}}}{N_{\text{salt}} + N_{\text{water}}}$

- Two phases $\phi = 2, D = 2$

(a) Saturated solution + salt

Independent variables T, p : Saturation concentration $x^s = x^s(T, p)$

(b) Solution + ice (no salt in ice)

Independent variables $p, x : T = T(p, x)$, freezing point changes with pressure and solution concentration or $T, x : p = p(T, x)$

(c) Solution + vapor

Independent variables $p, x : T = T(p, x)$, boiling point changes with pressure and solution concentration; or $T, x : p = p(T, x)$, saturated vapor pressure changes with temperature and solution concentration

- Three phases $\phi = 3, D = 1$

(a) Solution + ice + vapor

Independent variable x , triple point changes with concentration $T = T_t(x), p = p_t(x)$

(b) Saturated solution + salt + ice (or vapor)

- Four phases $\phi = 4 D = 0$. Saturated solution + salt + ice + vapor: Temperature, pressure, and concentration are all determined

Osmotic pressure equilibrium is a good example of multiphase equilibrium. According to the equality of chemical potential (x is the solute molar concentration), there is a small pressure perturbation Δp

$$g_w(T, p) = g_w(T, p + \Delta p) + RT \ln x_w = g_w(T, p) + v_w \Delta p + RT \ln x_w \quad (3.137)$$

The pressure difference is obtained

$$\Delta p = -\frac{RT}{v_w} \ln x_w = -RT \rho_w \ln(1 - x) = \rho g h \simeq RT \rho_w x \quad (3.138)$$

The boiling point of the solution is also affected by the solute concentration x . When solid and solution coexist: considering the chemical potential of water, the melting point temperature has a small perturbation $\Delta T = T - T^*$

$$g_s(T, p) = \mu_s(T, p) = \mu_l(T, p, x) = g_l(T, p) + RT \ln(1 - x) \quad (3.139)$$

Considering the change in chemical potential before and after, we get

$$\begin{aligned} g_s(T^* + \Delta T, p) &= g_l(T^* + \Delta T, p) + RT \ln(1 - x) \\ g_s(T^*, p) - s_s \Delta T &= g_l(T^*, p) - s_l \Delta T + R(T^* + \Delta T) \ln(1 - x) \\ [s_l - s_s - R \ln(1 - x)] \Delta T &= RT^* \ln(1 - x) \end{aligned} \quad (3.140)$$

The melting point temperature perturbation is obtained

$$\begin{aligned} \Delta T &= \frac{RT^* \ln(1 - x)}{(s_l - s_s - R \ln(1 - x)} = \frac{RT^{*2} \ln(1 - x)}{T^*(s_l - s_s) - RT^* \ln(1 - x)} \\ &= \frac{RT^{*2} \ln(1 - x)}{L - RT^* \ln(1 - x)} \simeq -\frac{RT^* x}{L + RT^* x} T^* \end{aligned} \quad (3.141)$$

Similarly, the boiling point temperature perturbation can also be obtained

$$\Delta T = \frac{RT^{*2} \ln(1 - x)}{-L - RT^* \ln(1 - x)} \simeq \frac{RT^* x}{L - RT^* x} T^* \quad (3.142)$$

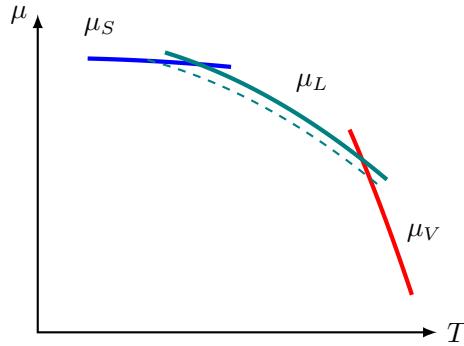


Fig. 32: Chemical potential phase diagram of water's three phases and impurity-containing solution (dashed line)

3.7.4 Chemical Equilibrium

Move the reactants to the left to write the reaction equation $2\text{NH}_3 - \text{N}_2 - 3\text{H}_2 = 0$, Formally given as,

$$\sum_i v_i A_i = 0 \quad (3.143)$$

where A_i is the molecular formula of the i -th component, v_i is the stoichiometric coefficient, and the degree of reaction is defined as $\xi = \Delta N_i / v_i$. The direction of the reaction and equilibrium condition at constant temperature and pressure are derived as

$$\Delta G = \sum_i \mu_i \Delta N_i = \left(\sum_i v_i \mu_i \right) \xi = -A\xi \leq 0 \quad (3.144)$$

where the chemical affinity is defined as

$$A = - \sum_i v_i \mu_i \quad (3.145)$$

- $A > 0 \Rightarrow \xi > 0$: Forward reaction, products increase, reactants decrease
- $A < 0 \Rightarrow \xi < 0$: Reverse reaction, products decrease, reactants increase
- $A = 0 \Rightarrow \xi$: Arbitrary reaction equilibrium

Assuming all components are ideal gases, the chemical potential satisfies Eq. 3.131

$$\begin{aligned} A &= -\sum_i v_i \mu_i = -\sum_i v_i g_i(T, p) - RT \sum_i v_i \ln x_i \\ &= -\sum_i v_i g_i(T, p) - RT \ln \left(\prod_i x_i^{v_i} \right) \end{aligned} \quad (3.146)$$

Define the equilibrium constant K , at equilibrium $A = 0$, the larger K , the more products

$$K = \prod_i x_i^{v_i}, \quad \ln K = \ln K(T, p) = -\frac{\sum_i v_i g_i(T)}{RT} \quad (3.147)$$

The derivative of the equilibrium constant with respect to temperature can determine the direction of endothermic or exothermic reactions

$$\begin{aligned} \left(\frac{\partial \ln K}{\partial T} \right)_p &= -\frac{1}{RT} \sum_i v_i \left(\frac{\partial g_i}{\partial T} \right)_p + \frac{1}{RT^2} \sum_i v_i g_i \\ &= \frac{1}{RT^2} \sum_i v_i (T s_i + g_i) = \frac{\sum_i v_i h_i}{RT^2} = \frac{\Delta h}{RT^2} \end{aligned} \quad (3.148)$$

Define the reaction heat as

$$\Delta h = \sum_i v_i h_i \quad (3.149)$$

- $\Delta h > 0$ Endothermic reaction: Temperature increases, K increases, forward reaction
- $\Delta h < 0$ Exothermic reaction: Temperature increases, K decreases, reverse reaction

The derivative of the equilibrium constant with respect to pressure can derive Le Chatelier's principle

$$\left(\frac{\partial \ln K}{\partial p} \right)_T = -\sum_i \frac{v_i}{RT} \left(\frac{\partial g_i}{\partial p} \right)_T = -\sum_i \frac{v_i v_i}{RT} = -\frac{\sum_i v_i}{p} \quad (3.150)$$

- Reaction with volume increase: Pressure increases, K decreases, reverse reaction; Pressure decreases, K increases, forward reaction
- Reaction with volume decrease: Pressure increases, K increases, forward reaction; Pressure decreases, K decreases, reverse reaction

Chapter 4 Classical Statistical Theory

4.1 Fundamentals of Statistical Thinking

4.1.1 Probability Theory

A random event (abbreviated as event) refers to a set of things assigned a probability, which is a subset of the sample space. When the sample space is infinite, defining a probability space often requires removing certain subsets of the sample space, stipulating that they cannot become events. **Classical Probability Model** describes the situation where the sample space is finite, and each basic event in the experiment has the same likelihood of occurring. Thus, for a total of Ω events, the probability satisfies

$$p_i = \frac{1}{\Omega}, \quad \sum_i p_i = 1 \quad (4.1)$$

Probability theory's core is Kolmogorov's three axioms: non-negativity, normalization, and additivity, mathematically expressed as:

$$P(E) \in \mathbb{R}, \quad P(E) \geq 0, \quad \forall E \in F \quad (4.2a)$$

$$P(\Omega) = \sum_i p_i = 1 \quad (4.2b)$$

$$P\left(\bigcup_{i=1}^{\infty} E_i\right) = \sum_{i=1}^{\infty} P(E_i) \quad (4.2c)$$

For a series of results from multiple experiments, there may be different distributions. If we define the events of one experiment as the **microscopic states**, then repeatedly performing the same experiment can observe that each event produces some common features, and we define the collection of microscopic states with these common features as **macroscopic states**. For example, when throwing a coin N times (assuming only two possible outcomes), and n times heads, just knowing this macroscopic result (N, n) , we cannot deduce the specific orientation of each throw, but we can know how many possible microscopic states $\Omega(N, n)$ exist

$$\Omega(N, n) = \frac{N!}{n!(N-n)!} = \binom{N}{n} \quad (4.3)$$

When N is very large, $\Omega(N, n)$ is also very large. To facilitate analysis, we seek the most probable macroscopic state by taking the natural logarithm of the number of microscopic states:

$$\begin{aligned} \ln \Omega(N, n) &= \ln N! - \ln n! - \ln(N-n)! \\ &\simeq N(\ln N - 1) - n(\ln n - 1) - (N-n)[\ln(N-n) - 1] \\ &\simeq N \ln N - n \ln n - (N-n) \ln(N-n), \end{aligned} \quad (4.4)$$

where the second step uses Stirling's formula: $\ln N! \simeq N(\ln N - 1)$, the proof of which is as follows, based on the area integral relationship

$$\begin{aligned} \int_1^N \ln(x) dx &< \ln N! < \int_2^{N+1} \ln(x) dx \\ \ln N! &\simeq N \ln N - N \end{aligned} \quad (4.5)$$

We can also obtain the standard formula for approximating the factorial of n using Stirling's formula

$$n! = \sqrt{2\pi n} \left(\frac{n}{e}\right)^n \left[1 + O\left(\frac{1}{n}\right)\right] \quad (4.6)$$

Taking the derivative of $\ln \Omega(N, n)$ with respect to n

$$\frac{\partial \ln \Omega}{\partial n} = -\ln n + \ln(N-n) = \ln \frac{N-n}{n} = 0, \Rightarrow n = \frac{N}{2} \quad (4.7)$$

we get $n = \frac{N}{2}$, i.e., the most probable macroscopic state is $(N, \frac{N}{2})$, so the probability of the most probable macroscopic state occurring is:

$$P(N, \frac{N}{2}) = \binom{N}{\frac{N}{2}} \left(\frac{1}{2}\right)^N \quad (4.8)$$

Taking the logarithm, we get

$$\ln P(N, \frac{N}{2}) \simeq N(\ln N - 1) - N(\ln \frac{N}{2} - 1) - N \ln 2 = 0 \quad (4.9)$$

i.e., $P \simeq 1$, i.e., the probability of the most probable macroscopic state occurring is basically 100%, and the probability of other macroscopic states occurring is basically 0. We can also prove this from another angle, assuming that the macroscopic state has deviated by $\Delta n = 1$ to $(N, \frac{N}{2} - 1)$, corresponding to

$$\frac{\partial^2 \ln \Omega}{\partial n^2} \Big|_{n=\frac{N}{2}} = -\frac{1}{n} - \frac{1}{(N-n)} = -\frac{4}{N} \quad (4.10)$$

Performing a Taylor expansion, we get:

$$\ln \Omega(N, \frac{N}{2} - \Delta n) = \ln \Omega(N, \frac{N}{2}) + \frac{1}{2} \frac{\partial^2 \ln \Omega}{\partial n^2} (\Delta n)^2 = \ln \Omega(N, \frac{N}{2}) - \frac{2}{N} \quad (4.11)$$

Thus

$$\frac{\Omega(N, \frac{N}{2} - 1)}{\Omega(N, \frac{N}{2})} = \exp\left(-\frac{2}{N}\right) \rightarrow 0 \quad (4.12)$$

This also shows that the most probable macroscopic state is indeed the true macroscopic state. In a thermodynamic system, the macroscopic quantity averaged over a long time and large scale is the ensemble average.

4.1.2 Physical Thinking

A common way of thinking in physics is **reductionism**, which is to reduce the complex to the simple (top-down) and attribute all the various phenomena in complex systems to the basic rules governing the behavior of the most basic components and the determining elements, and then build the complex from the simple. The history of exploration from molecular atoms to particle quarks demonstrates the application of this way of thinking.

However, each level also has its own basic laws in addition to a certain degree of coupling between levels, and the basic rules at each level are still present, so building the complex from the simple is not as easy as imagined. When faced with the dual challenge of scale and complexity,

considering how a large number of basic elements (agents) construct a complex system and exhibit a variety of unexpected complex physical properties at each different aggregation level (bottom-up) is called **emergent/evolutionary theory**.

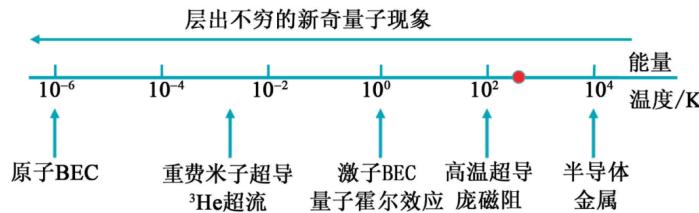


Fig. 33: Novel physical properties of condensed matter systems at different scales

A phase transition represents a change from one disordered phase to another ordered phase in a physical system. In describing phase transitions, physicists developed the concept of "mean-field theory", which replaces the average energy of the mutual interaction that a particle receives from other particles. However, it cannot describe the fluctuation phenomena near the critical point well, so the renormalization group was developed: consider describing a physical system in parameter space, and classify parameters into relevant and irrelevant parameters based on whether they move towards or away from the saddle point. A "universal class" is formed by a system that controls a region of parameter space from the same saddle point, and the renormalization group gives the condition that mean-field theory only holds in more than four dimensions, and the critical exponents only depend on the spatial dimension, the number of internal degrees of freedom, and the short or long range of the interaction force.

A typical discussion of a many-body system can discuss an evolutionary model of collective excitation, namely elementary excitation, which has different types of elementary excitations in different systems, such as phonons, excitons, spin waves, polarons, magnons, etc.

4.2 Systems Composed of Nearly Independent Subsystems

A macroscopic system is composed of microscopic particles or quasi-particles. For systems composed of nearly independent subsystems, we can consider the system's motion, and divide the system into different subsystems. These subsystems interact with each other, and the average energy of their mutual interaction can be ignored for equilibrium states. Let the Hamiltonian of the i th subsystem be \hat{h}_i , N be the number of subsystems in the system, then the Hamiltonian of the system is

$$\hat{H} = \sum_{i=1}^N \hat{h}_i(\mathbf{r}_i, \mathbf{p}_i) + H_I \simeq \sum_{i=1}^N h_i(\mathbf{r}_i, \mathbf{p}_i) \quad (4.13)$$

For example

$$\hat{H} = \sum_i \frac{\mathbf{p}_i^2}{2M} + \sum_i \frac{\mathbf{L}_i^2}{2I} + \sum_i \hat{h}_{iv} \quad (\text{polyatomic molecule}) \quad (4.14\text{a})$$

$$\hat{H} = \sum_i \frac{p_i^2}{2m} + \sum_{i < j} V(\mathbf{r}_{ij}) \simeq E_0 + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} |n_{\mathbf{q}}\rangle \langle n_{\mathbf{q}}| \quad (\text{phonon system}) \quad (4.14\text{b})$$

4.2.1 Quantum Description of Microscopic States

For physical quantities in thermodynamic equilibrium, we can consider them as stationary states, or energy eigenstates, because of the condition of nearly independent systems, we can separately calculate the eigenstates and wavefunctions of each single particle, and then superpose them to obtain the system's. We can also say that we separate the variables in the Schrödinger equation for the system, and obtain the Schrödinger equation for a single particle. The subscript l represents the particle's energy level, α represents the α th quantum state belonging to the energy ε_l , and ω_l is the degeneracy of the energy level $\varepsilon_l(V)$. To consider how many particles occupy each level/state, we often look at the sequence of particle numbers as a distribution function a_l constructed from a sequence of particle numbers.

$$\hat{h} |\psi_s\rangle = \varepsilon_s |\psi_s\rangle = \varepsilon_l |\psi_{l\alpha}\rangle \quad (4.15)$$

For the level distribution a_1, a_2, \dots, a_l (state distribution a_s), energy levels $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_l$, degeneracies $\omega_1, \omega_2, \dots, \omega_l$, and wavefunctions satisfy

$$\langle \psi_s | \psi_{s'} \rangle = \delta_{ss'} \quad \langle \psi_{l\alpha} | \psi_{l'\alpha'} \rangle = \delta_{ll'} \delta_{\alpha\alpha'} \quad (4.16)$$

with particle number and energy constraints

$$\sum_l a_l = N, \quad \sum_l a_l \varepsilon_l = E = \langle \Psi | \hat{H} | \Psi \rangle \quad (4.17)$$

and the particle number density expressed as

$$\rho(\mathbf{r}) = \left\langle \Psi \left| \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right| \Psi \right\rangle = \sum_{i=1}^N |\psi_{s_i}(\mathbf{r})|^2 = \sum_s a_s |\psi_s(\mathbf{r})|^2 \quad (4.18)$$

(1) Non-identical particles: The eigenfunction of the system is the simple tensor product of single-particle states

$$|\Psi_S(1, 2, \dots, N)\rangle = |\psi_{s_1}(1)\rangle \otimes |\psi_{s_2}(2)\rangle \cdots \otimes |\psi_{s_N}(N)\rangle = |\psi_{l_1\alpha_1}(1)\psi_{l_2\alpha_2}(2)\cdots\psi_{l_N\alpha_N}(N)\rangle \quad (4.19\text{a})$$

$$\hat{H} |\Psi_S\rangle = E_S |\Psi_S\rangle = \sum_i \varepsilon_{s_i} |\Psi_S\rangle = \sum_i \varepsilon_{l_i} |\Psi_S\rangle \quad (4.19\text{b})$$

$$E_S = \sum_i \varepsilon_{s_i} = \sum_i \varepsilon_{l_i} \quad (4.19\text{c})$$

(2) Identical particles: The eigenfunction of the system is the simple tensor product of single-particle wavefunctions, then symmetrized (Bose) or antisymmetrized (Fermi). The system wavefunction (where P is the exchange operator)

$$|\Psi_S\rangle = \frac{1}{C} \sum_P (\pm)^P |\psi_{s_1}(1)\psi_{s_2}(2) \cdots \psi_{s_N}(N)\rangle \quad (4.20)$$

1. Fermi systems: Systems composed of identical fermions with half-integer spin are called, the wavefunction is antisymmetric, Consider a system composed of N fermions, the wavefunction is written in Slater determinant form, for simplicity, use k_i to represent a complete set of quantum numbers for a single-particle state, and ξ_i to represent the collection of position and spin coordinates of the i th particle

$$\psi_A(\xi_1, \xi_2, \dots, \xi_N) = \frac{1}{\sqrt{N!}} \sum_P \delta_P \hat{P} \prod_{i=1}^N \psi_{k_i}(\xi_i) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(\xi_1) & \cdots & \psi_{k_1}(\xi_N) \\ \psi_{k_2}(\xi_1) & \cdots & \psi_{k_2}(\xi_N) \\ \vdots & & \vdots \\ \psi_{k_N}(\xi_1) & \cdots & \psi_{k_N}(\xi_N) \end{vmatrix} \quad (4.21)$$

where $\frac{1}{\sqrt{N!}}$ is the normalization constant, \hat{P} is the two-particle exchange operator, and $\sum_P \delta_P \hat{P} \prod_{i=1}^N \psi_{k_i}(\xi_i)$ represents the sum over all possible two-particle exchanges, starting from the standard arrangement $\psi_{k_1}(\xi_1) \psi_{k_2}(\xi_2) \cdots \psi_{k_N}(\xi_N)$, if an odd number of exchanges is needed to reach $\hat{P}[\psi_{k_1}(\xi_1) \psi_{k_2}(\xi_2) \cdots \psi_{k_N}(\xi_N)]$, this \hat{P} is called an odd permutation, $\delta_P = -1$; if an even number of exchanges is needed to reach $\hat{P}[\psi_{k_1}(\xi_1) \psi_{k_2}(\xi_2) \cdots \psi_{k_N}(\xi_N)]$, this \hat{P} is called an even permutation, $\delta_P = +1$. In the total of $N!$ permutations, even permutations and odd permutations each occupy half, so in the sum in Eq. 4.21, half are positive terms, and half are negative terms. From the antisymmetry of the Fermi system wavefunction, it is easy to prove that the Fermi system obeys the following theorem:

Theorem 4.1 (Pauli Exclusion Principle). *An occupied quantum state by a fermion cannot have more than one.*

If fermion 1 and 2 occupy the same quantum state, take $k_1 = k_2$ in Eq. 4.21, then the first and second rows of the determinant are completely the same, $\Psi_A = 0$. Therefore, two identical fermions cannot occupy the same quantum state. The wavefunction of two fermions is

$$|\Psi\rangle = \frac{1}{\sqrt{2}} [|\psi_1(1)\psi_2(2)\rangle - |\psi_1(2)\psi_2(1)\rangle] \quad (4.22)$$

Since each state can be occupied by at most one electron, for the energy level ε_l , we must have $a_l \leq \omega_l$, so the number of microstates of a Fermi system

$$\Omega_F(\{a_l\}) = \prod_l \frac{\omega_l!}{a_l!(\omega_l - a_l)!} \quad (4.23)$$

2. Bose systems: Systems composed of identical bosons with zero or integer spin, the wavefunction is symmetric. For a system composed of N bosons, it does not follow the Pauli Exclusion

Principle, and any number of bosons can occupy the same quantum state. Let N bosons have n_1 in state k_1 , n_2 in state k_2 , \dots , n_i in state k_i , and the sum of n_i is the total number of particles, i.e., $\sum_i n_i = N$, n_i can be 0 or a positive integer. The system wavefunction is represented as

$$\sum_P \hat{P} [\varphi_{k_1}(\xi_1) \cdots \varphi_{k_1}(\xi_{n_1}) \varphi_{k_2}(\xi_{n_1+1}) \cdots \varphi_{k_2}(\xi_{n_1+n_2}) \cdots \varphi_{k_N}(\xi_{N-n_N+1}) \cdots \varphi_{k_N}(\xi_N)] \quad (4.24)$$

where \hat{P} is the exchange of only those bosons in different states, and the wavefunctions of different states are orthogonal to each other, this exchange has $\frac{N!}{n_1!n_2!\cdots n_N!} = \frac{N!}{\prod n_i!}$ kinds, so the normalized wavefunction of the Bose system is

$$\psi_S(\xi_1, \xi_2, \dots, \xi_N) = \sqrt{\frac{\prod n_i!}{N!}} \sum_P \hat{P} [\varphi_{k_1}(\xi_1) \cdots \varphi_{k_N}(\xi_N)] \quad (4.25)$$

The wavefunction of two bosons is

$$|\Psi\rangle = \frac{1}{\sqrt{2}} [|\psi_1(1)\psi_2(2)\rangle + |\psi_1(2)\psi_2(1)\rangle] \quad (4.26)$$

Remark 4.1. *Indistinguishable particles in a non-local system must follow the indistinguishability principle; distinguishable particles in a local system can be distinguished.*

The number of microstates of a Bose system requires considering the possible permutations of a_l indistinguishable particles and ω_l quantum states, which can be calculated as

$$\Omega_B(\{a_l\}) = \prod_l \frac{(a_l + \omega_l - 1)!}{a_l!(\omega_l - 1)!} \quad (4.27)$$

3. Boltzmann systems: Boltzmann systems/local systems, particles are distinguishable, the system does not follow the indistinguishability principle, nor does it need to follow the Pauli Exclusion Principle. The wavefunction of the system can be expressed as the product of the wavefunctions of each single particle

$$\psi(\xi_1, \xi_2, \dots, \xi_N) = \prod_{i=1}^N \psi_{k_i}(\xi_i) \quad (4.28)$$

For any of the a_l distinguishable particles, it can occupy any of the ω_l quantum states on the energy level ε_l , so there are $\omega_l^{a_l}$ ways for a_l particles, and a total of $\prod_l \omega_l^{a_l}$ ways for the distribution $\{a_l\}$.

The total number of exchanges is $N!$, and the number of exchanges among a_l particles in the same energy level is $a_l!$, these exchanges will not change the distribution $\{a_l\}$, so subtract from the total, and still need to multiply by the factor $\frac{N!}{\prod_l a_l!}$, then the number of microstates of a Boltzmann system

$$\Omega_{\text{Bol}} = \frac{N!}{\prod_l a_l!} \prod_l \omega_l^{a_l} \quad (4.29)$$

4. Classical limit: If in a Bose/Fermi system, for all energy levels ε_l have

$$\frac{a_l}{\omega_l} \ll 1 \quad (4.30)$$

then the number of microstates of a Bose or Fermi system can be approximated as (where $N!$ comes from the indistinguishability of identical particles)

$$\Omega_B \simeq \Omega_F \simeq \prod_l \frac{\omega_l^{a_l}}{a_l!} = \frac{\Omega_{\text{Bol}}}{N!} \quad (4.31)$$

4.2.2 Three Distributions

The equilibrium state is the most probable state, we can consider the most probable distribution of a Boltzmann system, assuming the particle number a_l is large (using Stirling's formula)

$$\begin{aligned} \ln \Omega &= \ln N! - \sum_l \ln a_l! + \sum_l a_l \ln \omega_l \\ &= N \ln N - N - \sum_l (a_l \ln a_l - a_l) + \sum_l a_l \ln \omega_l \\ &= \left(\sum_l a_l \right) \ln \left(\sum_l a_l \right) - \sum_l a_l (\ln a_l - \ln \omega_l) \end{aligned} \quad (4.32)$$

Take the variation δa_l of the distribution, and use $(x \ln x)' = \ln x + 1$, subject to the constraints

$$\delta \ln \Omega = \left[\ln \left(\sum_l a_l \right) + 1 \right] \sum_l \delta a_l - \sum_l (\ln a_l + 1 - \ln \omega_l) \delta a_l = \sum_l \left[\ln N - \ln \frac{a_l}{\omega_l} \right] \delta a_l = 0 \quad (4.33a)$$

$$\delta N = \sum_l \delta a_l = 0, \quad \delta E = \sum_l \varepsilon_l \delta a_l = 0 \quad (4.33b)$$

We need to use the method of Lagrange multipliers to discuss the relationship between these physical quantities, the idea is as follows: to find the local maximum/minimum of a function $f(x)$ subject to multiple constraint equations such as $g(x) = 0$, add Lagrange multiplier λ , form the Lagrangian function

$$\mathcal{L}(x, \lambda) \equiv f(x) + \lambda \cdot g(x) \quad (4.34)$$

where the stable point (saddle point) we need to find satisfies

$$\frac{\partial \mathcal{L}}{\partial x} = 0, \quad \frac{\partial \mathcal{L}}{\partial \lambda} = 0 \quad (4.35)$$

Generalize to n variables, it is

$$\nabla_{x_1, \dots, x_n, \lambda} \mathcal{L}(x_1, \dots, x_n, \lambda) = 0 \quad (4.36)$$

Then for Eq. 4.33a, Eq. 4.33b three variations, introduce $\tilde{\alpha}, \beta$ as undetermined Lagrange multipliers after assuming a_l is independent, so we have the variational equation

$$\begin{aligned} \delta \ln \Omega - \beta \delta E - \tilde{\alpha} \delta N &= 0 \\ \sum_l \left[\ln N - \ln \frac{a_l}{\omega_l} - \tilde{\alpha} - \beta \varepsilon_l \right] \delta a_l &= 0 \\ \Rightarrow \ln \frac{a_l}{\omega_l} - \ln N + \tilde{\alpha} + \beta \varepsilon_l &= 0 \end{aligned} \quad (4.37)$$

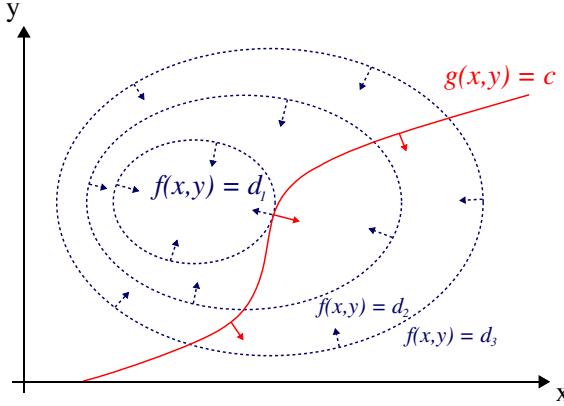


Fig. 34: Lagrange undetermined multiplier method for gradient descent to find

Using $\alpha = \tilde{\alpha} - \ln N$, we can derive the most probable distribution (called the Maxwell-Boltzmann distribution) as

$$\bar{a}_l = N\omega_l e^{-\tilde{\alpha}-\beta\varepsilon_l} = \omega_l e^{\ln N-\tilde{\alpha}-\beta\varepsilon_l} = \omega_l e^{-\alpha-\beta\varepsilon_l}, \quad \bar{a}_s = e^{-\alpha-\beta\varepsilon_s} \quad (4.38)$$

The corresponding energy and total particle number are

$$E = \sum_l a_l \varepsilon_l = \sum_l \varepsilon_l \omega_l e^{-\alpha-\beta\varepsilon_l}, \quad N = \sum_l a_l = \sum_l \omega_l e^{-\alpha-\beta\varepsilon_l} \quad (4.39)$$

From Eq. 4.37 we get the physical meaning of α, β , respectively related to the rate of change of particle number and energy: From Eq. 4.37, the physical meanings of α and β are given, which are related to the rate of change of particle number and energy, respectively:

$$\tilde{\alpha} = \left. \frac{\delta \ln \Omega}{\delta N} \right|_{\delta E=0, \delta V=0}, \quad \beta = \left. \frac{\delta \ln \Omega}{\delta E} \right|_{\delta N=0, \delta V=0} \quad (4.40)$$

For the Bose distribution

$$\ln \Omega_B (\{a_l\}) \simeq \sum_l \{(a_l + \omega_l) \ln (a_l + \omega_l) - a_l \ln a_l - \omega_l \ln \omega_l\} \quad (4.41)$$

Similarly, using the method of Lagrange multipliers, we obtain

$$\ln \Omega_B (\{a_l\}) \simeq \sum_l \{(a_l + \omega_l) \ln (a_l + \omega_l) - a_l \ln a_l - \omega_l \ln \omega_l\} \quad (4.42)$$

Similarly, using the method of Lagrange multipliers, we obtain

$$\begin{aligned} \delta \ln \Omega_B - \alpha \delta N - \beta \delta E &= \sum_l \left\{ \ln \left(\frac{\omega_l}{a_l} + 1 \right) - \alpha - \beta \varepsilon_l \right\} \delta a_l = 0 \\ \Rightarrow \quad \ln \left(\frac{\omega_l}{a_l} + 1 \right) - \alpha - \beta \varepsilon_l &= 0 \end{aligned} \quad (4.43)$$

Thus, the Bose distribution is actually

$$a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} - 1} \quad (4.44)$$

Therefore, the particle number and energy of the Einstein-Bose distribution are

$$N = \sum_l \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} - 1}, \quad E = \sum_l \frac{\varepsilon_l \omega_l}{e^{\alpha+\beta\varepsilon_l} - 1} \quad (4.45)$$

For the Fermi distribution, similarly consider

$$\ln \Omega_F = \sum_l \{ \omega_l \ln \omega_l - a_l \ln a_l - (\omega_l - a_l) \ln (\omega_l - a_l) \} \quad (4.46)$$

Using the method of Lagrange multipliers, we have

$$\delta \ln W_F - \alpha \delta N - \beta \delta E = \sum_l \left\{ \ln \left(\frac{\omega_l}{a_l} - 1 \right) - \alpha - \beta \varepsilon_l \right\} \delta a_l = 0 \quad (4.47)$$

Thus, the Fermi distribution is

$$a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} + 1} \quad (4.48)$$

Therefore, the particle number and energy of the Fermi-Dirac distribution are

$$N = \sum_l \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} + 1}, \quad E = \sum_l \frac{\varepsilon_l \omega_l}{e^{\alpha+\beta\varepsilon_l} + 1} \quad (4.49)$$

For the E-B distribution or F-D distribution, introducing the average particle number as a physical quantity, it is uniformly written as

$$f_s = \frac{a_l}{\omega_l} = \frac{1}{e^{\alpha+\beta\varepsilon_l} \pm 1} \quad (4.50)$$

It is observed that if $e^{\alpha+\beta\varepsilon_l} \gg 1$, then the E-B distribution and F-D distribution revert to the Maxwell-Boltzmann distribution.

4.2.3 Partition Function

The origin of the partition function can be derived from the Jaynesian maximum entropy method, first according to the Gibbs entropy expression Eq. 4.82

$$S = -k_B \sum_i \rho_i \ln \rho_i \quad (4.51)$$

According to probability normalization and energy conservation

$$\sum_i \rho_i = 1, \quad \langle E \rangle = \sum_i \rho_i E_i \equiv U \quad (4.52)$$

Using the method of Lagrange multipliers

$$\mathcal{L} = \left(-k_B \sum_i \rho_i \ln \rho_i \right) + \lambda_1 \left(1 - \sum_i \rho_i \right) + \lambda_2 \left(U - \sum_i \rho_i E_i \right) \quad (4.53)$$

Perform variation

$$\begin{aligned}
0 &= \delta \mathcal{L} \\
&= \delta \left(-\sum_i k_B \rho_i \ln \rho_i \right) + \delta \left(\lambda_1 - \sum_i \lambda_1 \rho_i \right) + \delta \left(\lambda_2 U - \sum_i \lambda_2 \rho_i E_i \right) \\
&= \sum_i [\delta(-k_B \rho_i \ln \rho_i) + \delta(\lambda_1 \rho_i) + \delta(\lambda_2 E_i \rho_i)] \\
&= \sum_i \left[\frac{\partial}{\partial \rho_i} (-k_B \rho_i \ln \rho_i) \delta(\rho_i) + \frac{\partial}{\partial \rho_i} (\lambda_1 \rho_i) \delta(\rho_i) + \frac{\partial}{\partial \rho_i} (\lambda_2 E_i \rho_i) \delta(\rho_i) \right] \\
&= \sum_i [-k_B \ln \rho_i - k_B + \lambda_1 + \lambda_2 E_i] \delta(\rho_i).
\end{aligned} \tag{4.54}$$

The probability expression is obtained as

$$\rho_i = \exp \left(\frac{-k_B + \lambda_1 + \lambda_2 E_i}{k_B} \right) \tag{4.55}$$

According to the normalized probability, we can obtain

$$1 = \sum_i \rho_i = \exp \left(\frac{-k_B + \lambda_1}{k_B} \right) \sum_i \exp \left(\frac{\lambda_2}{k_B} E_i \right) = \exp \left(\frac{-k_B + \lambda_1}{k_B} \right) Z \tag{4.56}$$

The constant generated in this operation is defined as the **canonical ensemble partition function**, according to $\lambda_1 = -k_B \ln(Z) + k_B$, $\lambda_2 = \frac{1}{T}$, and according to Eq. 4.64, the standard form of the partition function is

$$Z = \sum_i e^{-\beta E_i} \tag{4.57}$$

Another understanding of the partition function considers the most probable distribution under the Boltzmann distribution, where the number of microstates is a function of E, N, \bar{a}_l

$$\bar{\Omega} = \Omega(E, N, \{\bar{a}_l\}) = \frac{N!}{\prod_l \bar{a}_l} \prod_l \omega_l^{\bar{a}_l} \tag{4.58}$$

To better determine $\alpha/\tilde{\alpha}, \beta$, change the variables to β, N, \bar{a}_l using a Legendre transform, and write a function Z

$$\begin{aligned}
\ln Z &= \ln Z(\beta, N, a_l) = \ln \bar{\Omega} - \beta E = N \ln N - \sum_l a_l \left(\ln \frac{a_l}{\omega_l} + \beta \varepsilon_l \right) \\
&= N \ln N + \alpha e^{-\alpha} \sum_l \omega_l e^{-\beta \varepsilon_l} = N \ln N + \alpha e^{-\alpha} z
\end{aligned} \tag{4.59}$$

Where $z(\beta, a_l)$ is defined as the single-particle partition function, the third and fourth equations hold only for the Boltzmann distribution

$$z = z(\beta, a_l) = \sum_l \omega_l e^{-\beta \varepsilon_l} = \sum_l a_l e^\alpha = N e^\alpha \tag{4.60}$$

Substituting back into Eq. 4.59, we can obtain the partition function for N particles

$$\ln Z = \ln z^N, \quad Z = \left(\sum_l \omega_l e^{-\beta \varepsilon_l} \right)^N \tag{4.61}$$

The density of states, partition function, particle number, and internal energy integrals provide an analogy

$$g(\varepsilon) = \omega_s \int \frac{d\mathbf{p}d\mathbf{r}}{h^d} \delta(\varepsilon - \varepsilon(\mathbf{p}, \mathbf{r})), \quad z = \omega_s \int \frac{d\mathbf{p}d\mathbf{r}}{h^d} e^{(-\beta\varepsilon(\mathbf{p}, \mathbf{r}))}, \quad N = \int_0^\varepsilon g(\varepsilon) d\varepsilon, \quad U = \int_0^{+\infty} \varepsilon g(\varepsilon) f(\varepsilon) d\varepsilon \quad (4.62)$$

4.2.4 Statistical Significance of Thermodynamic Laws

The partition function is an important key in statistical mechanics, possessing rich physical meanings. It can serve as the probability of partitioning distributions, as a moment-generating function to derive various thermodynamic parameters, and can also be used to obtain the density of states $g(\varepsilon)$ through a Laplace transform. Below, we explain the physical significance of the major thermodynamic laws from the partition function and derive various thermodynamic quantities.

Consider two systems exchanging energy through thermal contact to reach a new thermal equilibrium, then the total number of microstates changes

$$\delta \ln \Omega = \beta_1 \delta E_1 + \beta_2 \delta E_2 = (\beta_1 - \beta_2) \delta E_1 \quad (4.63)$$

Therefore, at thermodynamic equilibrium, $\beta_1 = \beta_2$, according to Theorem 1.1 the zeroth law of thermodynamics can define temperature through thermal equilibrium $T \propto \frac{1}{\beta}$, introducing a proportionality factor k , which can be proven to be the Boltzmann constant, thus defining a new physical quantity, the reciprocal of temperature, coldness β

$$\beta = \frac{1}{k_B T} = \frac{1}{\tau} \quad (4.64)$$

Next, according to Theorem 1.2 the first law of thermodynamics, the relationship between internal energy, work, and heat, first, internal energy is a state function, expressed using the partition function

$$\begin{aligned} U &= \bar{E} = \sum_l a_l \varepsilon_l = \sum_l \omega_l e^{-\alpha - \beta \varepsilon_l} \varepsilon_l \\ &= e^{-\alpha} \sum_l \varepsilon_l \omega_l e^{-\beta \varepsilon_l} = \frac{N}{z} \sum_l \omega_l \left(-\frac{\partial e^{-\beta \varepsilon_l}}{\partial \beta} \right)_V \\ &= -\frac{N}{z} \left(\frac{\partial}{\partial \beta} \sum_l \omega_l e^{-\beta \varepsilon_l} \right)_V = -\frac{N}{z} \left(\frac{\partial z}{\partial \beta} \right)_V = -N \left(\frac{\partial \ln z}{\partial \beta} \right)_V \\ &= - \left(\frac{\partial \ln Z}{\partial \beta} \right)_{NV} \end{aligned} \quad (4.65)$$

According to the expression of β Eq. 4.64, internal energy is transformed into a more commonly used calculation formula

$$\begin{aligned} U &= -N \left(\frac{\partial \ln z}{\partial T} \right)_V \left(\frac{\partial T}{\partial \beta} \right) = -N \left(\frac{\partial \ln z}{\partial T} \right)_V \cdot (-k_B T^2) \\ &= N k_B T^2 \left(\frac{\partial \ln z}{\partial T} \right)_V = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{NV} \end{aligned} \quad (4.66)$$

According to $U = Q - W = Q + W_{\text{ext}}$, and the generalized work Eq. 1.29, expand the differential expression of internal energy to correspond

$$dU = \sum_l \varepsilon_l da_l + \sum_l a_l d\varepsilon_l = Q + Y dy \quad (4.67)$$

Then the energy change Q caused by the change in particle number da_l due to heat absorption, the adjustment of energy levels $d\varepsilon_l(V)$ corresponds to generalized displacement, causing the external generalized force to do work W , the statistical expression of the external generalized force Y is

$$Y = \sum_l a_l \frac{d\varepsilon_l}{dy} \quad (4.68)$$

When the generalized displacement is taken as volume V , $Y = -p$, giving the pressure expression

$$\begin{aligned} p &= - \sum_l a_l \left(\frac{\partial \varepsilon_l}{\partial V} \right) = - \sum_l \omega_l e^{-\alpha-\beta\varepsilon_l} \left(\frac{\partial \varepsilon_l}{\partial V} \right) \\ &= e^{-\alpha} \sum_l \omega_l \frac{1}{\beta} \left(\frac{\partial}{\partial V} e^{-\beta\varepsilon_l} \right)_\beta = \frac{N}{z} \frac{1}{\beta} \left(\frac{\partial}{\partial V} \sum_l \omega_l e^{-\beta\varepsilon_l} \right)_\beta \\ &= \frac{N}{z} \frac{1}{\beta} \left(\frac{\partial z}{\partial V} \right)_\beta = \frac{N}{\beta} \left(\frac{\partial \ln z}{\partial V} \right)_\beta = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)_{\beta N} \\ &= Nk_B T \left(\frac{\partial \ln z}{\partial V} \right)_T = k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_{TN} \end{aligned} \quad (4.69)$$

The expression for entropy considers the relationship between entropy and Q , $S = k_B \beta Q$, where

$$\begin{aligned} \beta Q &= \beta \sum_l \varepsilon_l da_l = \sum_l [d(\beta \varepsilon_l a_l) - a_l d(\beta \varepsilon_l)] \\ &= d \left(\sum_l \beta \varepsilon_l a_l \right) - \sum_l a_l d(\beta \varepsilon_l) = d(\beta U) - \sum_l e^{-\alpha} \omega_l e^{-\beta \varepsilon_l} d(\beta \varepsilon_l) \\ &= d(\beta U) + \frac{N}{z} \sum_l \omega_l d(e^{-\beta \varepsilon_l}) = d(\beta U) + \frac{N}{z} d \left(\sum_l \omega_l e^{-\beta \varepsilon_l} \right) \\ &= d(\beta U) + \frac{N}{z} dz = d(\beta U + N \ln z) \end{aligned} \quad (4.70)$$

Therefore, entropy is expressed as (where Z_1 represents the single-particle partition function)

$$S = \frac{U}{T} + Nk_B \ln z = k_B \left[-N\beta \left(\frac{\partial \ln z}{\partial \beta} \right)_V + N \ln z \right] \quad (4.71)$$

For systems with indistinguishable particles, $W = W_{\text{Bol}}/N!$, thus the expression for entropy is rewritten as

$$S = Nk \left(\ln Z_1 - \beta \frac{\partial \ln Z_1}{\partial \beta} \right) - k \ln N! \quad (4.72)$$

The corresponding free energy is expressed as $F = U - TS$, and the Helmholtz free energy (or $Z = e^{-\beta F}$) is written as

$$F = -NkT \ln Z_1 + kT \ln(N!) \quad (4.73)$$

Then, using differential relations, the expression for the chemical potential μ is derived

$$\begin{aligned} T d \left(Nk \left(\ln Z_1 - \beta \frac{\partial}{\partial \beta} \ln Z_1 \right) - k \ln N! \right) &= -d \left(N \frac{\partial \ln Z_1}{\partial \beta} \right) + \frac{N}{\beta} \frac{\partial \ln Z_1}{\partial y} dy - \mu dN \\ \Rightarrow d(NkT \ln Z_1 - kT \ln N!) &= NkT d \ln Z_1 - \mu dN \\ \Rightarrow kT \ln Z_1 dN - kT \ln N dN &= -\mu dN \\ \Rightarrow \mu &= -\frac{\alpha}{\beta} \end{aligned} \quad (4.74)$$

Thus, another important parameter α is obtained

$$\alpha = -\mu\beta = -\frac{\mu}{k_B T} = \frac{\ln Z_1}{N} \quad (4.75)$$

After obtaining the expressions for α and β , the specific forms of the F-D/B-E distributions (corresponding to \pm respectively) can be given

$$a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} \pm 1} = \frac{\omega_l}{\exp\left(-\frac{\varepsilon_l-\mu}{k_B T}\right) \pm 1} \quad (4.76)$$

And the specific form of the Boltzmann distribution

$$a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}} = \omega_l \exp\left(-\frac{\varepsilon_l-\mu}{k_B T}\right) \quad (4.77)$$

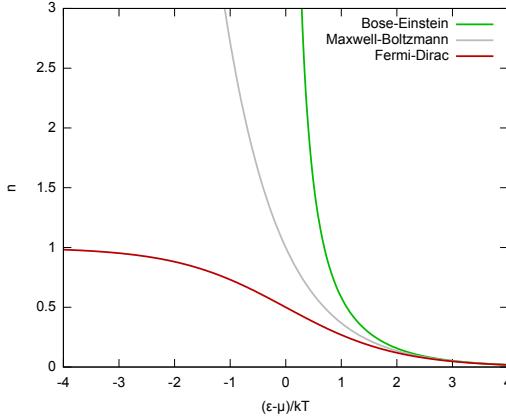


Fig. 35: Fermi-Dirac distribution, Bose-Einstein distribution, Maxwell-Boltzmann distribution

Another expression for entropy is derived from the generalized form of the total differential expression of internal energy Eq. 3.12, obtaining

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{NV} \quad (4.78)$$

Combined with Eq. 4.40, the expression for Boltzmann entropy can be given

$$S = k_B \ln \Omega \quad (4.79)$$

Theorem 1.3 The second law of thermodynamics can be explained by this expression: the degree of disorder of a system corresponds to the number of microstates, and entropy is a measure of the degree of disorder of a system. According to the maximum entropy of an isolated system at equilibrium, the number of microstates of an isolated system at equilibrium is the largest.

An equivalent expression to Boltzmann entropy is Gibbs entropy, assuming the probability of each microstate $n_i, i = 1, 2, \dots, s$ is $P_i = \frac{n_i}{N} = \frac{n_i}{\sum_i n_i}$, due to the existence of more refined micro-entropy S_{micro} that cannot be measured due to system selection constraints, it is written as the statistical average of each macrostate

$$S_{\text{micro}} = \langle S_i \rangle = \sum_{i=1}^s P_i S_i = k_B \sum_{i=1}^s P_i \ln n_i \quad (4.80)$$

Boltzmann entropy is written as

$$S = S_{\text{tol}} - S_{\text{micro}} \quad (4.81)$$

Thus, Gibbs entropy is written as

$$S = k_B \left(\ln N - \sum_{i=1}^s P_i \ln n_i \right) = k_B \sum_{i=1}^s P_i (\ln N - \ln n_i) = -k_B \sum_{i=1}^s P_i \ln P_i, \quad (4.82)$$

From the perspective of information theory, there is also an information entropy (Shannon entropy), introducing the quantitative definition of information quantity Q , and its relationship with the probability P of the occurrence of a microstate (the occurrence of this information):

$$Q = -k \log P \quad (4.83)$$

If $k = 1, \log = \log_2$, the unit of information quantity is bit; for $k = k_B, \log = \ln$, it describes the information of a thermodynamic system. Thus, Shannon entropy is defined as the average value of information quantity

$$S = \langle Q_i \rangle = \sum_i Q_i P_i = -k \sum_i P_i \log P_i \quad (4.84)$$

Similarly, for quantum systems, the statistical information of the system is in the density matrix $\hat{\rho}$, introducing the von Neumann entropy of the quantum ensemble:

$$S(\hat{\rho}) = \langle -\hat{\rho} \log \hat{\rho} \rangle = -\text{Tr}(\hat{\rho} \log \hat{\rho}) \quad (4.85)$$

If the eigenvalues of the density matrix $\hat{\rho}$ are $\lambda_i, i = 1, 2, \dots$, then the von Neumann entropy is:

$$S(\hat{\rho}) = - \sum_i \lambda_i \log \lambda_i \quad (4.86)$$

Table 3: Relationship between Thermodynamic Characteristic Functions and Partition Functions

State Function	Statistical Mechanics Expression
U	$-\frac{\partial \ln Z}{\partial \beta} = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{NV}$
F	$-k_B T \ln Z$
$S = - \left(\frac{\partial F}{\partial T} \right)_V = \frac{U - F}{T}$	$k_B \ln Z + k_B T \left(\frac{\partial \ln Z}{\partial T} \right)_V$
$p = - \left(\frac{\partial F}{\partial V} \right)_T$	$k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_T$
$H = U + pV$	$k_B T \left[T \left(\frac{\partial \ln Z}{\partial T} \right)_V + V \left(\frac{\partial \ln Z}{\partial V} \right)_T \right]$
$G = F + pV = H - TS$	$k_B T \left[-\ln Z + V \left(\frac{\partial \ln Z}{\partial V} \right)_T \right]$
$C_V = \left(\frac{\partial U}{\partial T} \right)_V$	$k_B T \left[2 \left(\frac{\partial \ln Z}{\partial T} \right)_V + T \left(\frac{\partial^2 \ln Z}{\partial T^2} \right)_V \right]$

4.2.5 Characteristic Temperature

According to the distribution number of states Eq. 4.38, and the single-particle partition function Eq. 4.60

$$a_s = e^{-\alpha - \beta \varepsilon_s} = \frac{N}{z} e^{-\beta \varepsilon_s} \quad (4.87)$$

Thus, the probability of a single-particle state $|s\rangle$ being occupied can be obtained

$$P = \frac{a_s}{N} = \frac{1}{z} e^{-\beta \varepsilon_s} \quad (4.88)$$

The ground state energy of a single particle ε_g , has no effect on the calculation of a_s , and can be set to zero; the characteristic excitation energy of a certain degree of freedom is $\Delta\varepsilon$, and the probability of this degree of freedom being excited is P_S

$$p \propto e^{-\beta \Delta \varepsilon} = e^{-\Delta \varepsilon / k_B T} = e^{-\Theta / T} \quad (4.89)$$

Thus, the characteristic temperature can be defined

$$\Theta = \frac{\Delta \varepsilon}{k_B} \quad (4.90)$$

$T \ll \Theta, P \sim 0$, particles are all in the ground state of this degree of freedom, almost no particles in the excited state: energy quantization leads to the freezing of degrees of freedom, this degree of freedom has no effect on the thermodynamic properties of the system; $T \gg \Theta$, the probability of low-energy excited states $P \sim 1$, degrees of freedom are fully excited (particles are all in the excited state): classical results, satisfying the principle of energy equipartition, using the Boltzmann constant, temperature can be mapped to energy

$$k_B = 1.380649 \times 10^{-23} \text{ J/K}, \quad k_B \cdot 1 \text{ K} = 8.6 \times 10^{-5} \text{ eV} \simeq 9 \times 10^{-5} \text{ eV} \quad (4.91)$$

Therefore, different degrees of freedom correspond to different characteristic temperatures: Diatomic vibrational degrees of freedom $\Theta_v \sim 10^2 - 10^3$ K; diatomic rotational degrees of freedom $\Theta_r \sim 10$ K; atomic translational degrees of freedom $\Theta_t \sim 10^{-12}$ K.

We consider the simplest system: a system composed of non-interacting two-level subsystems

$$\hat{h}|0\rangle = 0|0\rangle, \quad \hat{h}|1\rangle = \varepsilon|1\rangle = k_B\Theta|1\rangle \quad (4.92)$$

Thus, the distribution number

$$\begin{cases} a_0 = \frac{N}{z}e^{-\beta\varepsilon_0} = \frac{N}{1+e^{-\beta\varepsilon}} = \frac{N}{1+e^{-\Theta/T}} \\ a_1 = \frac{N}{z}e^{-\beta\varepsilon_1} = \frac{Ne^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{Ne^{-\Theta/T}}{1+e^{-\Theta/T}} \end{cases} \quad (4.93)$$

The partition function of the system is

$$z = \sum_s e^{-\beta\varepsilon_s} = 1 + e^{-\beta\varepsilon} = 1 + e^{-\Theta/T} \quad (4.94)$$

Some thermodynamic parameters are written as

$$U = a_0\varepsilon_0 + a_1\varepsilon_1 = a_1\varepsilon = -N \left(\frac{\partial \ln z}{\partial \beta} \right) = Nk_B T^2 \left(\frac{\partial \ln z}{\partial T} \right) = N\varepsilon \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{N\varepsilon}{e^{\Theta/T}+1} \quad (4.95a)$$

$$C = \left(\frac{\partial U}{\partial T} \right) = Nk_B \left(\frac{\varepsilon}{k_B T} \right)^2 \frac{e^{\beta\varepsilon}}{(e^{\beta\varepsilon}+1)^2} = Nk_B \left(\frac{\Theta}{T} \right)^2 \frac{e^{\Theta/T}}{(e^{\Theta/T}+1)^2} \quad (4.95b)$$

$$S = \frac{U}{T} + Nk_B \ln z = Nk_B \frac{\Theta/T}{e^{\Theta/T}+1} + Nk_B \ln [1 + e^{-\Theta/T}] \quad (4.95c)$$

In the low-temperature limit ($T \ll \Theta$), $z \simeq 1$, $a_0 \simeq N$, $a_1, U, C, V \simeq 0$, thus $\Omega \simeq 1$;

In the high-temperature limit ($T \gg \Theta$), $z \simeq 2$, $a_0 \simeq a_1 \simeq N/2$, $U \simeq N\varepsilon/2$, $C \simeq Nk_B \left(\frac{\Theta}{2T} \right)^2 \rightarrow 0$, $S \simeq Nk_B \ln 2$, $\Omega \simeq 2^N$, indicating that at high temperatures, the probability of being in the ground state and excited state is the same.

Remark 4.2. Schottky anomaly: At low and high temperatures, the heat capacity tends to zero, and the heat capacity shows a peak with temperature, with the peak position at $T \approx 0.416\Theta$, approximately half of the excitation energy level, at which point $C_V \approx 0.44Nk_B$. The reason for the Schottky anomaly is that the number of states (energy) of the system has an upper limit.

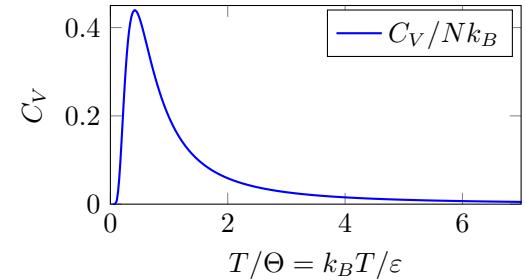


Fig. 36: Heat capacity of solids as a function of temperature changes

When examining the changes in physical states corresponding to points in phase space, we often consider Hamilton's canonical equations.

$$\dot{q}_\alpha(t) = \frac{\partial H}{\partial p_\alpha}, \quad \dot{p}_\alpha(t) = -\frac{\partial H}{\partial q_\alpha}. \quad (4.96)$$

Through the discussion of the Hamiltonian, we discuss the system's wave function, energy eigenstates, and corresponding partition functions.

4.3 Ideal Classical Gas

In classical systems, the discussion is about distinguishable particles, i.e., N points in μ space \leftrightarrow the microscopic state of the system at a certain moment; in quantum systems, the discussion is about indistinguishable particles, discussing the number of particles in each quantum state, i.e., the microscopic state of the system at a certain moment.

4.3.1 Ideal Monatomic Gas

Treat the atom as a whole, with single-particle energy including the energy of the nucleus, the energy of electrons outside the nucleus, and their interactions.

$$\hat{h}_t = \frac{p^2}{2m} + u(\mathbf{r}) + \sum_{i \in \text{electrons}} \left[\frac{\mathbf{p}_i^2}{2m_e} + u_e(\mathbf{r}_i) - \frac{Ze^2}{\varepsilon_0 |\mathbf{r}_i - \mathbf{r}|} + \sum_{j < i} \frac{e^2}{\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \right] \quad (4.97)$$

Since the electron energy difference $\Delta\varepsilon_e \sim 1 - 10\text{eV} \sim 10^{4-5} \text{ K}$, degrees of freedom are frozen at general temperatures, indicating that only the translational motion of the center of mass needs to be considered. We discuss within a deep potential well of volume $V(L_x, L_y, L_z)$, where $u(\mathbf{r}) = 0$, giving the wave function (where $n_x, n_y, n_z = 1, 2, 3, \dots$)

$$\psi_{n_x n_y n_z}(\mathbf{r}) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z), \quad \psi_{n_x}(x) = \sqrt{\frac{2}{L_x}} \sin \frac{n_x \pi x}{L_x} \quad (4.98)$$

The corresponding energy eigenvalues

$$\varepsilon_{n_x n_y n_z} = \varepsilon_{n_x}^x + \varepsilon_{n_y}^y + \varepsilon_{n_z}^z, \quad \varepsilon_{n_x}^x = \frac{\hbar^2 \pi^2 n_x^2}{2m L_x^2} \quad (4.99)$$

Energy determines the corresponding partition function (each degree of freedom can be considered independent and unaffected), for a gas molecule

$$z = \sum_{n_x, n_y, n_z} e^{-\beta \varepsilon_{n_x n_y n_z}} = z_x z_y z_z \quad (4.100)$$

Taking z_x as an example

$$\begin{aligned} z_x &= \sum_{n_x=1}^{\infty} e^{-\beta \varepsilon_{n_x}} \simeq \int_0^{\infty} e^{-\frac{\beta \hbar^2 \pi^2}{2m L_x^2} n_x^2} dn_x = \sqrt{\frac{2m L_x^2}{\beta \hbar^2 \pi^2}} \int_0^{\infty} e^{-x^2} dx \\ &= \sqrt{\frac{2m L_x^2}{\beta \hbar^2 \pi^2}} \int_0^{\infty} \frac{1}{2} e^{-t} t^{-\frac{1}{2}} dt = \sqrt{\frac{2m L_x^2}{\beta \hbar^2 \pi^2}} \frac{1}{2} \Gamma\left(\frac{1}{2}\right) \\ &= \sqrt{\frac{2m L_x^2}{\beta \hbar^2 \pi^2}} \frac{\sqrt{\pi}}{2} = L_x \left(\frac{2\pi m k_B T}{\hbar^2}\right)^{\frac{1}{2}} \end{aligned} \quad (4.101)$$

Here, the technique of integral table transformation and the second type of Euler integral (i.e., the definition of the Gamma function) is used.

$$\Gamma(z) = \int_0^{\infty} t^{z-1} e^{-t} dt \quad (4.102)$$

Some basic Gamma functions are given

$$\Gamma(\alpha + 1) = \alpha\Gamma(\alpha), \quad \Gamma(n + 1) = n!, \quad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \quad (4.103)$$

Thus, the partition function of a monatomic gas

$$z = L_x L_y L_z \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} = V \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}}, \quad Z = z^N \quad (4.104)$$

Under periodic boundary conditions

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + L_x \hat{e}_x) = \psi(\mathbf{r} + L_y \hat{e}_y) = \psi(\mathbf{r} + L_z \hat{e}_z) \quad (4.105)$$

The wave function uses boundary conditions, and energy

$$\psi_{\mathbf{k}=(k_x, k_y, k_z)}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}, \quad \varepsilon(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m} \quad (4.106)$$

The partition function can also be calculated by integration (the form does not change)

$$\begin{aligned} z &= \sum_{k_x k_y k_z} e^{-\beta\varepsilon(\mathbf{k})} = \int_{-\infty}^{+\infty} \frac{dk_x}{2\pi/L_x} \frac{dk_y}{2\pi/L_y} \frac{dk_z}{2\pi/L_z} e^{-\beta\varepsilon(\mathbf{k})} = L_x L_y L_z \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{-\beta\varepsilon(\mathbf{k})} = V \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{-\beta\varepsilon(\mathbf{k})} \\ &= \frac{V}{(2\pi)^3} \int_0^\infty k^2 dk \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi e^{-\beta\hbar^2 k^2/(2m)} = \frac{4\pi V}{(2\pi)^3} \int_0^\infty e^{-\hbar^2 k^2/(2mk_B T)} k^2 dk \\ &= \frac{4\pi V}{(2\pi)^3} \left(\frac{2mk_B T}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty e^{-x^2} x^2 dx = \frac{4\pi V}{(2\pi)^3} \left(\frac{2mk_B T}{\hbar^2} \right)^{\frac{3}{2}} \cdot \frac{1}{2} \Gamma\left(\frac{3}{2}\right) = V \left(\frac{2\pi m k_B T}{\hbar^2} \right)^{\frac{3}{2}} \end{aligned} \quad (4.107)$$

According to the thermodynamic De Broglie wavelength of particles

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} = \sqrt{\frac{2\pi \hbar^2}{mk_B T}} \quad (4.108)$$

Thus, the simplified form of the single-particle partition function

$$z = \frac{V}{\lambda_T^3} \quad (4.109)$$

We derive thermodynamic quantities from another perspective, the system's free energy is:

$$F(N, T, V) = -Nk_B T \ln Z_1 = -Nk_B T \ln \left(\frac{V}{\lambda_T^3} \right) \quad (4.110)$$

According to the full differential expression of free energy: $dF = -S dT - p dV + \mu dN$, the system's pressure is obtained:

$$p = - \left(\frac{\partial F}{\partial V} \right)_{N,T} = \frac{Nk_B T}{V} \quad (4.111)$$

Corresponding to the ideal gas equation of state, then the system's entropy is:

$$S = - \left(\frac{\partial F}{\partial T} \right)_{N,V} = Nk_B \left(\ln \frac{V}{\lambda_T^3} + \frac{3}{2} \right) \quad (4.112)$$

And the chemical potential of a single particle is:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \ln \frac{V}{\lambda_T^3} \quad (4.113)$$

According to the Legendre transformation, the expressions for the system's internal energy, enthalpy, and Gibbs free energy can be obtained. The system's internal energy is:

$$U = F + TS = \frac{3}{2} N k_B T \quad (4.114)$$

The system's enthalpy is:

$$H = F + TS + pV = \frac{5}{2} N k_B T \quad (4.115)$$

The system's Gibbs free energy is:

$$G = F + pV = N k_B T \left(1 - \ln \frac{V}{\lambda_T^3} \right) = N \mu + N k_B T \quad (4.116)$$

Note that the entropy and Gibbs free energy $G \neq N\mu$ do not satisfy the requirement of extensivity, which Gibbs explains through the indistinguishability of particles. In the previous discussion, $Z = z^N$ was assumed to be the requirement of distinguishability. If considering indistinguishability, the partition function should be

$$Z = \frac{z^N}{N!} \quad (4.117)$$

In the case of indistinguishability, the system's free energy is:

$$F(T, V, N) = -k_B T \ln \left[\frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N \right] = N k_B T [\ln(n\lambda_T^3) - 1] \quad (4.118)$$

According to the full differential relationship of F , the expressions for the system's entropy, Gibbs free energy, and chemical potential are obtained (satisfying extensivity)

$$S = - \left(\frac{\partial F}{\partial T} \right)_{N,V} = N k_B \left[\frac{5}{2} - \ln(n\lambda_T^3) \right], \quad (4.119a)$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = k_B T \ln(n\lambda_T^3), \quad (4.119b)$$

$$G = F + pV = N k_B T \ln(n\lambda_T^3) = N\mu, \quad (4.119c)$$

The indistinguishability of microscopic particles can also be understood from the perspective of Gibbs' paradox, i.e., the diffusion entropy of identical gas molecules remains unchanged.

4.3.2 Ideal Diatomic Gas

Diatomeric gas, in addition to the 3 translational degrees of freedom of a monatomic gas, also adds two molecular rotational degrees of freedom and two vibrational degrees of freedom, for a total of 7 degrees of freedom. The principle of energy equipartition tells us that the theoretical heat capacity of diatomic molecules is $C_V = \frac{7}{2}nR$. In experiments, it is found that discussing the change in heat capacity requires considering the quantum effects of frozen degrees of freedom.

The Hamiltonian of a diatomic molecule is given

$$h = \frac{p_A^2}{2M_A} + \frac{p_B^2}{2M_B} + V(|\mathbf{R}_A - \mathbf{R}_B|) \quad (4.120)$$

The effective potential energy is a function of relative motion, which can be taken as a harmonic potential, and the Morse potential can be introduced to more accurately describe molecular vibrations

$$V(|\mathbf{R}_A - \mathbf{R}_B|) = \frac{Z_A Z_B e^2}{\varepsilon_0 |\mathbf{R}_A - \mathbf{R}_B|} + E_e^g(|\mathbf{R}_A - \mathbf{R}_B|) \quad (4.121)$$

Separate the motion of the center of mass, where reduced mass: $\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B}$

$$\begin{aligned} h &= \frac{\mathbf{P}_c^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + V(R) = \frac{\mathbf{P}_c^2}{2M} - \frac{\hbar^2}{2\mu} \left[\partial_R^2 + \frac{2}{R} \partial_R \right] + V(R) - \frac{\hbar^2}{2\mu R^2} \left[\left(\frac{1}{\sin \theta} \partial_\theta \right)^2 + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right] = h_t + h_{v,r} \\ V(R) &= V(R_0) + \frac{1}{2} \mu \omega^2 (R - R_0)^2 + \dots, \quad h_v = -\frac{\hbar^2}{2\mu} \partial_x^2 + \frac{1}{2} \mu \omega^2 x^2 + V_0, \quad h_r = -\frac{\hbar^2}{2I} \left[\left(\frac{1}{\sin \theta} \partial_\theta \right)^2 + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right] \end{aligned}$$

where, $x = R - R_0$, $I = \mu R_0^2$

(4.122)

According to the energy levels of the hydrogen atom

$$E_{n,j} \approx -\frac{\mu c^2 \alpha^2}{2n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right], \quad j = \left| \ell \pm \frac{1}{2} \right| \quad (4.123)$$

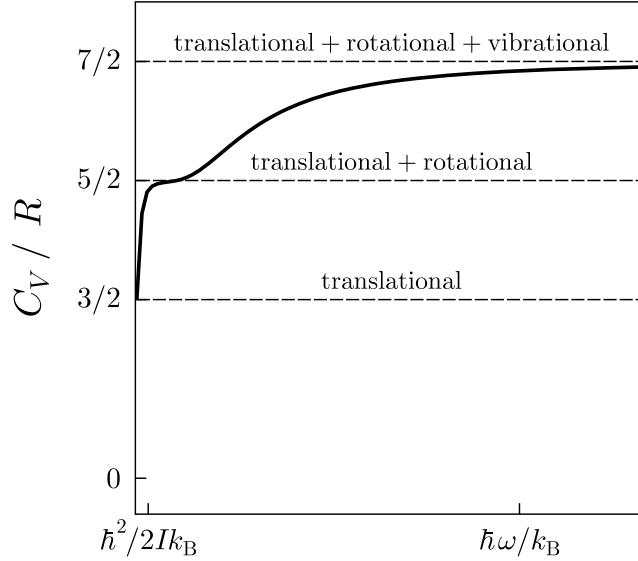


Fig. 37: From low to high temperature, the heat capacity increases, and the frozen vibrational and rotational degrees of freedom are successively thawed

We consider the temperature range where vibrational and rotational energy levels are not locked

$$\begin{aligned}\Theta_v &= [E_{n+1,l} - E_{n,l}] / k_B \sim 1000 \text{ K} \\ \Theta_r &= [E_{n,l+1} - E_{n,l}] / k_B \sim 1 - 10 \text{ K}\end{aligned}\quad (4.124)$$

Starting from the high-temperature vibrational state, according to the form of Eq. 4.122, the energy eigenstate is given

$$\varepsilon_n = (n + \frac{1}{2})\hbar\omega + V_0, \quad n = 0, 1, 2, \dots, \omega_n = 1 \quad (4.125)$$

The vibrational energy level partition function is obtained

$$z_v = \sum_n e^{-\beta\varepsilon_n} = e^{-\beta(\hbar\omega/2+V_0)} \sum_{n=0}^{\infty} e^{-n\beta\omega_n} = \frac{e^{-\beta(\hbar\omega/2+V_0)}}{1 - e^{-\beta\hbar\omega}} \quad (4.126)$$

From this, the vibrational internal energy and heat capacity are obtained

$$U = -N \left(\frac{\partial \ln z}{\partial \beta} \right) = N \left(V_0 + \frac{\hbar\omega}{2} \right) + \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1} = N \left(V_0 + \frac{\hbar\omega}{2} \right) + \frac{Nk_B\Theta_v}{e^{\Theta_v/T} - 1} \quad (4.127a)$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V = \frac{Nk_B\Theta_v^2}{T^2} \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2} = \frac{Nk_B\Theta_v^2}{4T^2 \sinh^2(\Theta_v/2T)} \quad (4.127b)$$

In the high-temperature limit $T \gg \Theta_v$, it follows the result of the classical energy equipartition theorem

According to $x \rightarrow 0$, $\sinh x = \frac{e^x - e^{-x}}{2} \simeq x$, the vibrational heat capacity

$$C_v = \frac{Nk_B\Theta_v^2}{4T^2 \sinh^2(\Theta_v/2T)} = \frac{Nk_B\Theta_v^2}{4T^2 (\Theta_v/2T)^2} = Nk_B \quad (4.128)$$

In the low-temperature limit $T \ll \Theta_v$, $T \rightarrow 0$, energy quantization begins to manifest

According to $x \rightarrow +\infty$, $\sinh x \simeq e^x/2$, the vibrational heat capacity

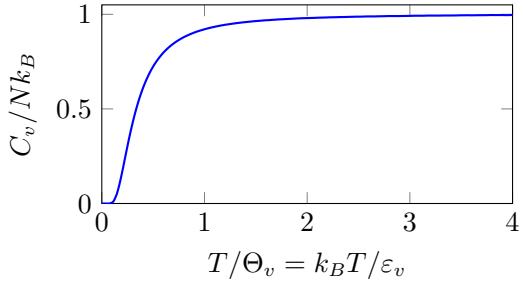


Fig. 38: Temperature Dependence of Vibrational heat capacity

$$C_v \simeq Nk_B \frac{\Theta_v^2}{T^2} e^{-\Theta_v/T} \rightarrow 0 \quad (4.129)$$

Next, we discuss the rotational states of A-B type molecular gases. Without considering the case of complete symmetry, all states can appear according to the eigenvalue equation

$$h_r |\psi_{lm}\chi(A, B)\rangle = \varepsilon_l |\psi_{lm}\rangle |S_A S_z^A\rangle |S_B S_z^B\rangle \quad (4.130)$$

where the Hamiltonian and energy are

$$h_r = \frac{\hat{L}^2}{2I}, \quad h_r \varepsilon_l = \frac{\hbar^2 l(l+1)}{2I} = l(l+1)k_B\Theta_r, \quad \Theta_r = \frac{\hbar^2}{2Ik_B} \quad (4.131)$$

At this time, the total number of energy states

$$\omega_l = (2l+1)(2S_A+1)(2S_B+1) = \omega_S(2l+1) \quad (4.132)$$

The corresponding rotational partition function

$$z_r = \sum_{l=0}^{\infty} \omega_l e^{-l(l+1)\Theta_r/T} = \omega_S \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\Theta_r/T} \quad (4.133)$$

In the high-temperature limit $T \gg \Theta_r$, it follows the result of the classical energy equipartition theorem

$$z_r(A - B) = \omega_S \int_0^{\infty} (2l+1) e^{-l(l+1)\Theta_r/T} dl \simeq \omega_S \int_0^{\infty} e^{-l(l+1)\Theta_r/T} d[l(l+1)] = \omega_S T / \Theta_r \quad (4.134)$$

$$\ln z_r \simeq \ln \omega_S + \ln T - \ln \Theta_r$$

The corresponding rotational internal energy and heat capacity

$$U = Nk_B T^2 \left(\frac{\partial \ln z_r}{\partial T} \right) = Nk_B T, \quad C_r = \left(\frac{\partial U}{\partial T} \right)_V = Nk_B \quad (4.135)$$

In the low-temperature limit $T \ll \Theta_r, T \rightarrow 0$, energy quantization begins to manifest, and the partition function changes to

$$\begin{aligned} z_r &= \omega_S [1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + 7e^{-12\Theta_r/T} + \dots] \\ \ln z_r &\simeq \ln \omega_S + 3e^{-2\Theta_r/T} + \dots \end{aligned} \quad (4.136)$$

The corresponding rotational internal energy and heat capacity

$$U = Nk_B T^2 \left(\frac{\partial \ln z_r}{\partial T} \right) = 6Nk_B \Theta_r e^{-2\Theta_r/T}$$

$$C_r = \left(\frac{\partial U}{\partial T} \right)_V = 12Nk_B \frac{\Theta_r^2}{T^2} e^{-2\Theta_r/T} = 3Nk_B \left(\frac{2\Theta_r}{T} \right)^2 e^{-2\Theta_r/T} \quad (4.137)$$

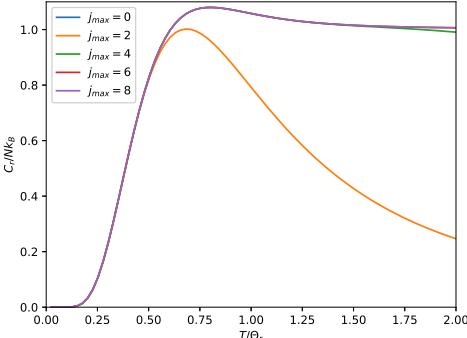


Fig. 39: Temperature Dependence of Rotational heat capacity

It can be seen that the low-temperature rotational heat capacity is similar to a two-level system or vibrational heat capacity, but the first excited state is triply degenerate, making it three times larger.

Next, we focus on the rotational heat capacity of hydrogen molecules: H₂ is the diatomic molecule with the smallest moment of inertia. Since its $k_B \Theta_r = \hbar^2/(2I) \sim 100$ K \gg boiling point 21 K, it is the only gas that can observe rotational quantization effects at normal pressure. Moreover, due to issues of quantization, complete symmetry, and metastable states, the rotational heat capacity of H₂ is relatively complex.

Since the nucleus of a hydrogen atom has only one proton, with spin $\frac{1}{2}$, it is a Fermion and follows exchange antisymmetry

$$\chi(A, B) = (-)^{l+1} \chi(B, A) \quad (4.138)$$

Therefore, the form of the H wave function depends on the angular momentum quantum number l , determining orthohydrogen and parahydrogen based on the parity of l :

Ortho-hydrogen: Angular momentum wave function is odd, $l \in \{1, 3, 5, \dots\}$, spin wave function is even, degeneracy: $\omega_l = 3 \times (2l + 1)$

$$|\chi(A, B)\rangle = |\chi(B, A)\rangle = \begin{cases} |\uparrow\uparrow\rangle & S = 1, S_z = 1 \\ \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle] & S = 1, S_z = 0, \text{ spin triplet} \\ |\downarrow\downarrow\rangle & S = 1, S_z = -1 \end{cases} \quad (4.139)$$

Para-hydrogen: Angular momentum wave function is even, $l \in \{0, 2, 4, \dots\}$, spin wave function is odd, degeneracy: $\omega_l = 1 \times (2l + 1)$

$$|\chi(A, B)\rangle = -|\chi(B, A)\rangle = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle], \quad S = S_z = 0, \text{ spin singlet} \quad (4.140)$$

We will first discuss the heat capacity of H₂ in equilibrium, giving its partition function

$$\begin{aligned} z_r &= \sum_l \omega_l e^{-\beta \varepsilon_l} = z_p + z_o \\ &= \sum_{l=0,2,4,\dots} 1 \times (2l + 1) e^{-l(l+1)\Theta_r/T} + \sum_{l=1,3,5,\dots} 3 \times (2l + 1) e^{-l(l+1)\Theta_r/T} \end{aligned} \quad (4.141)$$

In the high-temperature limit, $T \gg \Theta_r$, the partition function can be expanded into an infinite series, based on the integral

$$\int_0^{+\infty} (2x + 1) e^{-ax(x+1)} dx = -\frac{1}{a} e^{-x(x+1)} \Big|_0^{+\infty} = \frac{1}{a} \quad (4.142)$$

In the high-temperature limit, the partition function (equivalent to $l = 0$, $\omega_l = 4$), analogous to Eq. 4.134

$$z_r = z_p + z_o = \frac{1}{2} \frac{T}{\Theta_r} + \frac{3}{2} \frac{T}{\Theta_r} = 2 \frac{T}{\Theta_r}, \quad z_r(A - B) = 4 \frac{T}{\Theta_r} \quad (4.143)$$

Thus, the rotational internal energy and heat capacity are

$$U = Nk_B T, \quad C_r = Nk_B \quad (4.144)$$

In the low-temperature limit, the partition function

$$z_r = 1 + 9e^{-2\Theta_r/T} + \dots, \quad \ln z_r \simeq 9e^{-2\Theta_r/T}, \quad z_r(A - B) = 4(1 + 3e^{-2\Theta_r/T} + \dots) \quad (4.145)$$

Therefore, in the low-temperature limit, the rotational internal energy and heat capacity are

$$\begin{aligned} U &= 9Nk_B (2\Theta_r) e^{-2\Theta_r/T} \\ C_r &= 9Nk_B \left(\frac{2\Theta_r}{T}\right)^2 e^{-2\Theta_r/T}, \quad C_r(A - B) = 3Nk_B \left(\frac{2\Theta_r}{T}\right)^2 e^{-\frac{-2\Theta_r}{T}} \end{aligned} \quad (4.146)$$

Next, we discuss normal H₂. Normal hydrogen is a metastable mixture of orthohydrogen and parahydrogen obtained by cooling at room temperature, with the ratio given by the partition function ratio of equilibrium hydrogen $\frac{n_o}{n_p} = \frac{z_o}{z_p} = 3$. The conversion rate between orthohydrogen

and parahydrogen is very slow.

The partition function of the orthohydrogen part of normal hydrogen

$$\begin{aligned} z_o &= \sum_{l=1,3,\dots} \omega_l e^{-\beta \varepsilon_l} = 3 [3e^{-2\Theta_r/T} + 7e^{-12\Theta_r/T} + \dots] = 9e^{-2\Theta_r/T} [1 + 7/3e^{-10\Theta_r/T} + \dots] \\ \ln z_o &\simeq \ln 9 - 2 \frac{\Theta_r}{T} + \frac{7}{3} e^{-10\Theta_r/T} + \dots \end{aligned} \quad (4.147)$$

The internal energy and heat capacity corresponding to orthohydrogen

$$\begin{aligned} U_o &= Nk_B T^2 \left(\frac{\partial \ln z_o}{\partial T} \right) = Nk_B \left[2\Theta_r + \frac{7}{3} \times 10\Theta_r e^{-10\Theta_r/T} + \dots \right] \\ C_o &= \left(\frac{\partial U_o}{\partial T} \right)_V = \frac{7}{3} Nk_B \left(\frac{10\Theta_r}{T} \right)^2 e^{-10\Theta_r/T} \end{aligned} \quad (4.148)$$

The partition function of the parahydrogen part of normal hydrogen

$$z_p = \sum_{l=0,2,\dots} \omega_l e^{-\beta \varepsilon_l} = 1 + 5e^{-6\Theta_r/T} + \dots, \quad \ln z_p = 5e^{-6\Theta_r/T} + \dots \quad (4.149)$$

The internal energy and heat capacity corresponding to parahydrogen

$$\begin{aligned} U_p &= Nk_B T^2 \left(\frac{\partial \ln z_p}{\partial T} \right) = Nk_B \times 5 \times 6\Theta_r e^{-6\Theta_r/T} \\ C_p &= 5Nk_B \left(\frac{6\Theta_r}{T} \right)^2 e^{-6\Theta_r/T} \end{aligned} \quad (4.150)$$

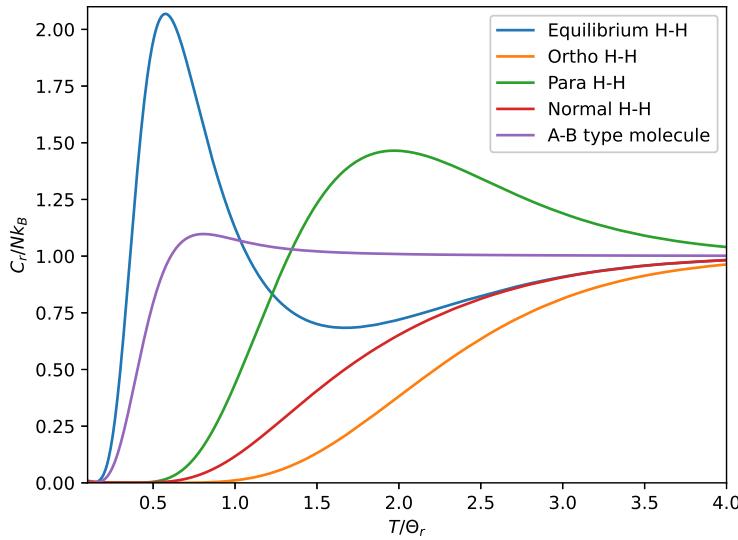


Fig. 40: Heat capacity of hydrogen in different states

According to the proportional relationship, the heat capacity of normal hydrogen is

$$C_r = \frac{1}{4} C_p + \frac{3}{4} C_o \quad (4.151)$$

For the heat capacity of diatomic molecular gases, as the temperature rises, the degrees of freedom are thawed, and at ultra-high temperatures, electronic and nuclear degrees of freedom may appear

$$C = \frac{3R}{2} \xrightarrow{T > \Theta_r \sim 10^K} \frac{5R}{2} \xrightarrow{T > \Theta_v \sim 10^4 K} \frac{7R}{2} \xrightarrow[T > \Theta_e \sim 10^{4-5} K]{(N_e + 7)} R \xrightarrow{T > \Theta_M \sim 1 MeV/k_B = 10^7 K} \frac{N_e + N_c + 7}{2} R \quad (4.152)$$

So, under what conditions can the temperature be considered the limit temperature? It can be estimated based on

$$\frac{dU}{dT} = C_v \simeq Nk_B/2 \simeq \frac{U}{2Mc^2} k_B \quad (4.153)$$

Thus, the maximum temperature is related to the Planck density $\rho_{Planck} = c^5/(\hbar G^2)$

$$T \simeq \frac{2Mc^2}{k_B} \ln \frac{U}{V} = \frac{2Mc^2}{k_B} \ln \rho c^2 \quad (4.154)$$

4.4 Basic Laws

The description of a single particle state can be obtained by the point \mathbf{r}, \mathbf{p} in phase space, knowing its position and momentum. However, in quantum mechanics, microscopic particles have wave-particle duality, meaning position and momentum cannot be accurately measured simultaneously. Δp_i is the uncertainty of the conjugate momentum corresponding to Δq_i , and the uncertainty principle of quantum mechanics gives

$$\Delta q_i \Delta p_i \sim h \quad (4.155)$$

where h is the Planck constant. When the Planck constant $h \rightarrow 0$, quantum effects can be ignored, and quantum mechanics returns to classical mechanics. In quantum mechanics, the state of a one-dimensional moving particle does not correspond to a point in phase space but corresponds to a small region of size h . A state of a particle with d degrees of freedom corresponds to a volume element (phase cell) of size h^d . In phase space, the number of phase cells, i.e., the number of microscopic states contained in a macroscopically small volume element $d\omega = dq_1 dq_2 \cdots dq_d dp_1 dp_2 \cdots dp_d$, is equal to

$$\frac{d\omega}{h^d} = \frac{1}{h^d} \cdot dq_1 dq_2 \cdots dq_d dp_1 dp_2 \cdots dp_d \quad (4.156)$$

In the classical Boltzmann distribution, the physical quantities discussed are regarded as the quantum statistical form of discrete energy levels (discretized phase space), while in the classical distribution, the physical quantities discussed are regarded as continuous forms, i.e.,

$$\sum_s f(s) \Rightarrow \sum_i f(\mathbf{r}_i, \mathbf{p}_i) = \int \frac{d\mathbf{r} d\mathbf{p}}{h^d} f(\mathbf{r}, \mathbf{p}) \quad (4.157)$$

Therefore, the partition function under the quasi-classical approximation is written as

$$z = \sum_s e^{-\beta \varepsilon_s} \Rightarrow z_c = \int \frac{d\mathbf{r} d\mathbf{p}}{h^d} e^{-\beta h(\mathbf{r}, \mathbf{p})} \quad (4.158)$$

4.4.1 Maxwell-Boltzmann Velocity Distribution Law

According to the quasi-classical approximation Eq. 4.158, the single-particle partition function Eq. 4.100 is rewritten, with the potential energy still being zero in an infinitely deep potential well,

$$\begin{aligned} z_c &= \int \frac{d\mathbf{r} d\mathbf{p}}{h^3} e^{-\beta h(\mathbf{r}, \mathbf{p})} = \frac{1}{h^3} \int_{Box} d\mathbf{r} \int d\mathbf{p}^3 e^{-\beta \mathbf{p}^2/(2m)} \\ &= \frac{4\pi V}{h^3} \int_0^\infty dp p^2 e^{-p^2/(2mk_B T)}, \quad u^2 = p^2/(2mk_B T) \rightarrow t = u^2 \\ &= \frac{4\pi V}{h^3} (2mk_B T)^{\frac{3}{2}} \int_0^\infty e^{-u^2} u^2 du, \quad \int_0^\infty e^{-t} t dt^{\frac{1}{2}} = \frac{1}{2} \int_0^\infty e^{-t} t^{\frac{1}{2}} dt \\ &= 4\pi V \left(\frac{2mk_B T}{h^2} \right)^{\frac{3}{2}} \frac{1}{2} \Gamma\left(\frac{3}{2}\right) = V \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}} = z \end{aligned} \quad (4.159)$$

Under classical limit conditions, the kinetic energy ε of molecules can be regarded as a quasi-continuous function of molecular momentum. In volume V , the number of microstates of molecules within the range $dp_x dp_y dp_z$ is $\frac{V}{h^3} dp_x dp_y dp_z$, and the average number of molecules per state is $e^{-\alpha-\beta\varepsilon}$. Therefore, the number of molecules within the range $dp_x dp_y dp_z$ in volume V is

$$dN_p = \frac{V}{h^3} e^{-\alpha - \frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)} dp_x dp_y dp_z = N \left(\frac{1}{2\pi mk_B T} \right)^{\frac{3}{2}} e^{-\frac{1}{2mk_B T}(p_x^2 + p_y^2 + p_z^2)} dp_x dp_y dp_z \quad (4.160)$$

where $e^\alpha = \frac{z}{N} = \frac{V}{N} \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}}$, Using $\mathbf{p} = m\mathbf{v}$, the number of gas molecules within the range $dv_x dv_y dv_z$ is

$$dN_v = N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{m}{2k_B T}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \quad (4.161)$$

The probability distribution function of a molecule's speed within $v \sim v + dv$ is $f_M(\mathbf{v}) = f_M(\mathbf{r}, \mathbf{v}) = m^3 f_B(\mathbf{r}, m\mathbf{v})$

$$f_M(\mathbf{v}) = f(v_x, v_y, v_z) dv_x dv_y dv_z = \frac{dN_v}{N} = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{m}{2k_B T}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \quad (4.162)$$

This is the Maxwell velocity distribution law, satisfying the normalization condition

$$\int_{-\infty}^{+\infty} f_M(\mathbf{v}) dv = \iiint_{-\infty}^{+\infty} f(v_x, v_y, v_z) dv_x dv_y dv_z = 1, \quad \int_0^\infty v^2 e^{-mv^2/2k_B T} dv = \frac{1}{4} \sqrt{\frac{2\pi k_B T}{m^3}} \quad (4.163)$$

Considering the distribution of speed magnitude, we can introduce spherical coordinates v, θ, φ in velocity space, where the volume element in velocity space is $dv_x dv_y dv_z = v^2 dv d\Omega = v^2 dv \sin \theta d\theta d\varphi$. After integrating over angles θ and φ , the number of molecules within the range $v \sim v + dv$ per unit volume satisfies the Maxwell speed distribution law

$$f(v) dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{m}{2k_B T} v^2} dv \quad (4.164)$$

This gives the number of molecules per unit volume (n is the number of molecules per unit volume)

$$nf(v) dv \frac{d\Omega}{4\pi} = nf(v) dv \frac{1}{2} \sin \theta d\theta \quad (4.165)$$

The number of molecules colliding with a unit area of the wall per unit time at angle θ is

$$v \cos \theta \cdot n f(v) dv \frac{1}{2} \sin \theta d\theta \quad (4.166)$$

The change in vertical momentum of molecules colliding with the wall is $2mv \cos \theta$, from which the relationship between pressure and the mean square speed can be obtained

$$\begin{aligned} p &= \int_0^\infty \int_0^{\pi/2} (2mv \cos \theta) \left(v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta \right) \\ &= mn \int_0^\infty dv v^2 f(v) \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta = \frac{1}{3} nm \langle v^2 \rangle \end{aligned} \quad (4.167)$$

1. Most probable speed, satisfying the maximum of the Maxwell speed distribution function,

$$\frac{d}{dv} \left(e^{-\frac{m}{2k_B T} v^2} v^2 \right) \Big|_{v_m} = 0 \Rightarrow v_m = \sqrt{\frac{2k_B T}{m}} \quad (4.168)$$

2. Average speed

$$\begin{aligned} \bar{v} &= \frac{\int_0^\infty v f(v) dv}{\int_0^\infty f(v) dv} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty v e^{-\frac{m}{2k_B T} v^2} v^2 dv \\ &= \sqrt{\frac{8k_B T}{\pi m}} \int_0^\infty x^3 e^{-x^2} dx = \sqrt{\frac{2k_B T}{\pi m}} \int_0^\infty t e^{-t} dt = \sqrt{\frac{8k_B T}{\pi m}} \end{aligned} \quad (4.169)$$

3. Root mean square speed

$$\begin{aligned} v_s &= \sqrt{\bar{v}^2} = \frac{\int_0^\infty v f(v) dv}{\int_0^\infty f(v) dv} = \sqrt{4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty v^2 e^{-\frac{m}{2k_B T} v^2} v^2 dv} \\ &= \sqrt{\frac{8k_B T}{\sqrt{\pi m}} \int_0^\infty x^4 e^{-x^2} dx} = \sqrt{\frac{4k_B T}{\sqrt{\pi m}} \int_0^\infty t^{\frac{3}{2}} e^{-t} dt} = \sqrt{\frac{3k_B T}{m}} \end{aligned} \quad (4.170)$$

Based on the root mean square speed, the expression for pressure can be obtained

$$pV = \frac{1}{3} n V m \langle v^2 \rangle = \frac{1}{3} N m \frac{3k_B T}{m} = N k_B T \quad (4.171)$$

The number of moles of molecules $n = N/N_A$, then the ideal gas equation of state (universal gas constant $R = N_A k_B = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) is

$$pV = n_m R T = N k_B T, \quad p = n k_B T \quad (4.172)$$

The ratio of the values of the three characteristic speeds is expressed in units of $\sqrt{\frac{k_B T}{m}}$

$$v_m : \bar{v} : v_s = 1 : \frac{2}{\sqrt{\pi}} : \sqrt{\frac{3}{2}} \approx 1 : 1.128 : 1.225 \quad (4.173)$$

4.4.2 Equipartition Theorem

Assume that the kinetic and potential energy of microscopic particles in the system are both quadratic terms of generalized momentum and generalized coordinates, where d is the degree of freedom:

$$\varepsilon = \varepsilon_p + \varepsilon_q = \frac{1}{2} \sum_{\alpha=1}^d a_\alpha p_\alpha^2 + \frac{1}{2} \sum_{\alpha=1}^d b_\alpha q_\alpha^2 \quad (4.174)$$

The coefficients a_α, b_α are all positive, and the energy of the particles follows the Boltzmann distribution $f(\varepsilon) = e^{-\beta\varepsilon}$, so the average value of the kinetic energy term is:

$$\begin{aligned} \left\langle \frac{1}{2}a_n p_n^2 \right\rangle &= \frac{\int \cdots \int \frac{1}{2}a_n p_n^2 f(\varepsilon) \frac{dq_1 \cdots dq_1 dp_1 \cdots dp_2}{h^d}}{\int \cdots \int f(\varepsilon) \frac{dq_1 \cdots dq_0 dp_n \cdots dp_2}{h^d}} = \frac{1}{2\beta} = \frac{1}{2}k_B T \\ \int_{-\infty}^{+\infty} \frac{1}{2}a_n p_n^2 e^{-\beta a_n p_n^2/2} dp_n &= -\frac{p_n}{2\beta} e^{-\beta a_n p_n^2/2} \Big|_{-\infty}^{+\infty} + \frac{1}{2\beta} \int_{-\infty}^{+\infty} e^{-\beta a_n p_n^2/2} dp_n = \frac{1}{2\beta} \int_{-\infty}^{+\infty} e^{-\beta a_n p_n^2/2} dp_n \end{aligned} \quad (4.175)$$

Similarly, the average value of the potential energy term is:

$$\left\langle \frac{1}{2}b_n q_n^2 \right\rangle = \left\langle \frac{1}{2}a_n p_n^2 \right\rangle = \frac{1}{2\beta} = \frac{1}{2}k_B T \quad (4.176)$$

Therefore, the internal energy of the system is as follows, with different degrees of freedom freezing at different temperatures, as discussed in Subsubsec. 4.3.2

$$U = \frac{d}{2}Nk_B T \quad (4.177)$$

4.5 Solids

In solids, to describe the collective properties of the lattice, phonons are introduced to describe the elementary excitations of lattice vibrations. The heat capacity of a phonon gas is discussed below. Phonons can be regarded as massless bosons, and the energy of these quasiparticles follows the reduced Bose-Einstein distribution, i.e., the Planck distribution (chemical potential $\mu = 0$, n represents the average value of the quantum number):

$$f_p(\omega) = \langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1} = \frac{\sum_s s \exp(-s\beta\hbar\omega)}{\sum_s \exp(-s\beta\hbar\omega)} \quad (4.178)$$

Considering the influence of wave vector k and polarization p on the frequency $\omega_{k,p}$, the internal energy is

$$U = \sum_k \sum_p \frac{\hbar\omega_{k,p}}{\exp(\beta\hbar\omega_{k,p}) - 1} \quad (4.179)$$

where $g_p(\omega)d\omega$ gives the number of modes of polarization p in the frequency domain $\omega \sim \omega + d\omega$.

Let $x = \beta\hbar\omega = \hbar\omega/k_B T$, then the heat capacity is

$$C_{\text{lat}} = \frac{\partial U}{\partial T} = k_B \sum_p \int d\omega g_p(\omega) \frac{x^2 \exp x}{(\exp x - 1)^2} \quad (4.180)$$

The number of modes for each polarization direction is N , and the total number of modes is $3N$, therefore

$$N = \int g(\omega) f(\omega) d\omega \quad (4.181)$$

4.5.1 Density of States

For a one-dimensional monoatomic chain, the frequency $\omega_{k,p}$ has a certain dispersion relation with the wave vector k , and a specific wave vector contains three polarization directions, two transverse

waves, and one longitudinal wave. Under the periodic boundary condition of the lattice (Born-Karman), the displacement $u_s = u(0) \exp [i(ska - \omega_k t)]$, where a is the atomic spacing, L is the length of the monoatomic chain, and since the adjacent wave vector $\Delta k = \frac{2\pi}{L}$, the number of modes is (the coefficient is multiplied by 2 due to the equivalence of positive and negative k directions)

$$g_1(\omega) d\omega = \frac{L}{\pi} \frac{dk}{d\omega} d\omega = \frac{L}{\pi} \cdot \frac{d\omega}{d\omega/dk} \quad (4.182)$$

Therefore, the solution of the density of states depends on the dispersion relation. Due to the dispersion relation of a one-dimensional monoatomic chain

$$\omega = 2\sqrt{\frac{\beta}{m}} \left| \sin \frac{1}{2}ak \right| = \omega_m \left| \sin \frac{1}{2}ak \right|, \quad \frac{d\omega}{dk} = \frac{a}{2}\omega_m \cos \left(\frac{ka}{2} \right) \quad (4.183)$$

we have

$$g_1(\omega) = \frac{L}{\pi} \cdot \frac{dk}{d\omega} = \frac{2N}{\pi \sqrt{\omega_m^2 - \omega^2}} \quad (4.184)$$

The dispersion relation and density of states for one-dimensional elastic waves are

$$\omega = v_s k, \quad g_1(\omega) = \frac{1}{v_s} \cdot \frac{L}{\pi} \quad (4.185)$$

In three dimensions, the wave vector satisfies the periodic boundary condition

$$\exp [i(k_x x + k_y y + k_z z)] = \exp \{i[k_x(x + L) + k_y(y + L) + k_z(z + L)]\} \quad (4.186)$$

Thus, the volume of the unit momentum space becomes

$$\left(\frac{L}{2\pi} \right)^3 = \frac{V}{8\pi^3} \quad (4.187)$$

Therefore, the number of vibrational modes is

$$g_3(\omega) d\omega = \left(\frac{L}{2\pi} \right)^3 \int_{\text{shell}} d^3k = \left(\frac{V}{8\pi^3} \right) 4\pi k^2 \int dS_\omega dk_\perp \quad (4.188)$$

where S_ω is the area element of the constant frequency surface, and k_\perp is the wave vector component perpendicular to the constant frequency surface, satisfying

$$|\nabla_{\mathbf{k}}\omega| dk_\perp = d\omega \quad (4.189)$$

The three-dimensional density of states is obtained as

$$g_3(\omega) = \frac{V}{(2\pi)^3} \int \frac{dS_\omega}{|\nabla_{\mathbf{k}}\omega|} = \frac{V}{(2\pi)^3} \int \frac{dS_\omega}{v_g} \quad (4.190)$$

where $v_g = |\nabla_{\mathbf{k}}\omega|$ is the group velocity of phonons perpendicular to the constant frequency surface.

Similarly, considering the dispersion relation of an elastic wave $\omega = v_s k$, the density of states is

$$g_3(\omega) = \frac{V}{(2\pi)^3} \cdot \frac{4\pi q^2}{\nabla_{\mathbf{k}}\omega} = \frac{V}{2\pi^2} \cdot \frac{q^2}{v_s} = \frac{V\omega^2}{2\pi^2 v_s^3} \quad (4.191)$$

Another derivation considers the three-dimensional spherical vibrational mode

$$N = \left(\frac{L}{2\pi}\right)^3 \frac{4}{3} \pi k^3 = \frac{V}{8\pi^3} \frac{4}{3} \pi \left(\frac{\omega}{v_s}\right)^3 \quad (4.192)$$

The density of states can be given by the differential of the vibrational mode

$$g_3(\omega) = \frac{dN}{d\omega} = \frac{V}{2\pi^2} \frac{\omega^2}{v_s^3} \quad (4.193)$$

Another type of density of states describes the number of electronic states per unit energy interval, called the density of states $g(E)$

$$g(E) = \frac{1}{V} \sum_{i=1}^N \delta(E - E(\mathbf{k}_i)) \quad (4.194)$$

Considering continuous energy levels, and $(\Delta k)^d = \left(\frac{2\pi}{L}\right)^d$, the density of states for continuous energy levels is

$$g(E) = \int_{\mathbb{R}^d} \frac{d^d k}{(2\pi)^d} \cdot \delta(E - E(\mathbf{k})) \quad (4.195)$$

Discussing the one-dimensional harmonic oscillator case, for discrete energy levels, the density of states is

$$g(E) = \sum_{n=0}^{\infty} \delta[E - (n + 1/2)\hbar\omega] \simeq \int_0^{\infty} \delta[E - (n + 1/2)\hbar\omega] dn = \frac{1}{\hbar\omega} \quad (4.196)$$

The density of states for continuous energy levels is

$$\begin{aligned} g(E) &= \int \delta\left(E - \frac{p^2}{2m} - \frac{m\omega^2 x^2}{2}\right) \frac{dp dx}{h} \\ &= \frac{1}{h} \int_{-\infty}^{\infty} \frac{dx}{|p/m|_{p=\pm\sqrt{2mE-m^2\omega^2x^2}}} = 2\frac{m}{h} \int_{-\sqrt{2E/(m\omega^2)}}^{\sqrt{2E/(m\omega^2)}} \frac{dx}{\sqrt{2mE - m^2\omega^2x^2}} \\ &= \frac{2}{h\omega} \int_{-\sqrt{2mE}}^{\sqrt{2mE}} \frac{dx}{\sqrt{2mE - x^2}} = \frac{2}{h\omega} \int_{-1}^1 \frac{dx}{\sqrt{1-x^2}} = \frac{2\pi}{h\omega} = \frac{1}{\hbar\omega} \end{aligned} \quad (4.197)$$

This utilizes the properties of the Dirac- δ function

$$\delta(f(x)) = \sum_n |f'(x_n)|^{-1} \delta(x - x_n), \quad \text{where } f(x_n) = 0, f'(x_n) \neq 0 \quad (4.198a)$$

$$\delta(x^2 - \alpha^2) = \frac{1}{2|\alpha|} [\delta(x + \alpha) + \delta(x - \alpha)] \Rightarrow \int \delta\left(E - \frac{p^2}{2m}\right) dp = \frac{1}{|p/m|_{p=\pm\sqrt{2mE}}} \quad (4.198b)$$

The corresponding partition function is

$$z = \int dE g(E) e^{-\beta E} = \int_0^{\infty} e^{-\beta E} \frac{dE}{\hbar\omega} = \frac{1}{\beta\hbar\omega} = \frac{k_B T}{\hbar\omega} \quad (4.199)$$

If we only discuss the density of states for translational degrees of freedom, in the three-dimensional case, the spin degree of freedom ω_S is generally: $\omega_S = (2S + 1)$, for example, for electrons

$S = \frac{1}{2}$, $\omega_S = 2$; for photons: $S = 1$, but $\omega_S = 2$.

$$\begin{aligned} g_3(E) &= \sum_S \delta(E - E_S) = \omega_S \int \delta[E - h(\mathbf{r}, \mathbf{p})] \frac{d\mathbf{r} d\mathbf{p}}{h^3} = \frac{\omega_S V}{h^3} \int \delta\left(E - \frac{p^2}{2m}\right) p^2 dp d\Omega \\ &= \frac{4\pi V \omega_S}{h^3} \frac{p^2}{p/m} \Big|_{p=\sqrt{2mE}} = \frac{4m\pi V \omega_S}{h^3} \sqrt{2mE} = 2\pi V \omega_S \left(\frac{2m}{h^2}\right)^{3/2} \sqrt{E} \end{aligned} \quad (4.200)$$

Similarly, for two-dimensional and one-dimensional cases, it can be found that the two-dimensional density of states is independent of energy, and the d -dimensional density of states can be found in Eq. B.8.

$$g_2(E) = \pi A \omega_S \frac{2m}{h^2}, \quad g_1(E) = \omega_S L \sqrt{\frac{m}{2h^2 E}} \quad (4.201)$$

4.5.2 Debye/Einstein Model

The Debye model assumes that the crystal is a continuous elastic medium, and each elastic wave vibration mode is equivalent to a harmonic oscillator, with energy quantized. The total degrees of freedom/vibration modes in the crystal are $3N$, so

$$\int_0^{\omega_D} g(\omega) d\omega = 3N, \quad g(\omega) = 3 \frac{dN}{d\omega} = \frac{3V}{2\pi^2} \frac{\omega^2}{v_s^3} \quad (4.202)$$

According to Eq. 4.193, the highest cutoff frequency (Debye frequency) ω_D can be calculated, where v is treated as a constant sound speed, often written as $v = \sqrt{Y/\rho}$

$$\omega_D = \sqrt[3]{6\pi^2 v^3 \frac{N}{V}} \quad (4.203)$$

The corresponding cutoff wave vector (Debye wave vector) k_D is (degeneracy taken as 1, for cases where degeneracy is not 1, see Eq. B.6)

$$k_D = \frac{\omega_D}{v} = \sqrt[3]{6\pi^2 \frac{N}{V}} \quad (4.204)$$

For convenience in subsequent calculations, we define the Debye temperature Θ_D as

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v k_D}{k_B} = \frac{\hbar v}{k_B} \sqrt[3]{\frac{6\pi^2 N}{V}} \quad (4.205)$$

Let $x = \beta\hbar\omega = \hbar\omega/k_B T$, $x_D = \Theta_D/T$, then the internal energy ($D_3(x)$) is the third Debye function)

$$\begin{aligned} U &= \int \hbar\omega g(\omega) f(\omega) d\omega = \int_0^{\omega_D} \left(\frac{V\omega^2}{2\pi^2 v^3} \right) \left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right) d\omega \\ &= \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} = \frac{3V k_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1} \\ &= 9Nk_B T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1} = 3T D_3 \left(\frac{T_D}{T} \right) \end{aligned} \quad (4.206)$$

The corresponding Debye heat capacity is

$$C_V = \frac{\partial U}{\partial T} = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \quad (4.207)$$

In the low-temperature limit, $T \ll \Theta_D$, i.e., $x \gg 1$, $\omega_D \approx \infty$, using series expansion

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \int_0^\infty dx x^3 \sum_{s=1}^\infty \exp(-sx) = 6 \sum_1^\infty \frac{1}{s^4} = \frac{\pi^4}{15} \quad (4.208)$$

The internal energy and heat capacity are

$$U \approx \frac{3}{5} \pi^4 N k_B \frac{T^4}{\Theta_D^3}, \quad C_V \approx \frac{12}{5} \pi^4 N k_B \left(\frac{T}{\Theta_D} \right)^3 \quad (4.209)$$

This is known as the Debye- T^3 law, reflecting that at low temperatures, only low-frequency acoustic modes are excited, while high-energy ones are frozen.

In the high-temperature limit, $T \gg \Theta_D$, i.e., $x \ll 1$, using the expansion $e^x \approx 1 + x$, the internal energy and heat capacity are

$$U \approx 9Nk_B T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\frac{\Theta_D}{T}} x^2 dx = 3Nk_B T, \quad C_V \approx 3Nk_B \quad (4.210)$$

This result is consistent with the Dulong-Petit law (solid heat capacity is constant) and also with the Einstein model discussed later Eq. 4.218, because at high temperatures all modes are excited.

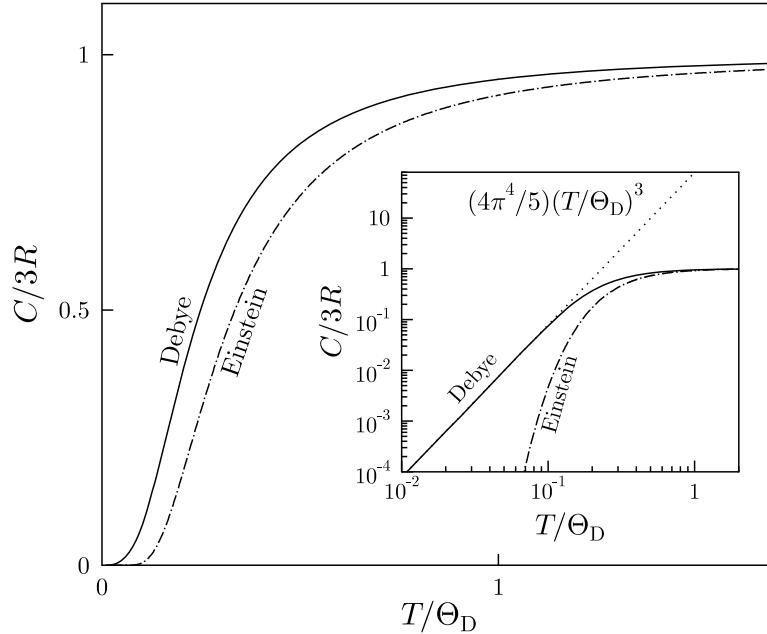


Fig. 41: Schematic diagram of Debye and Einstein heat capacity, choosing $\Theta_D = 500$ K, $\Theta_E = 200$ K

The internal energy of the Einstein model can be derived from two perspectives, from the perspective of discrete energy levels, the energy of each vibration mode is

$$\varepsilon_i = \left(n_i + \frac{1}{2} \right) \hbar \omega_i \quad (4.211)$$

The average energy of the harmonic oscillator is

$$\bar{\varepsilon}_i = \left(\langle n \rangle + \frac{1}{2} \right) \hbar\omega = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} + \frac{1}{2}\hbar\omega \quad (4.212)$$

Einstein assumed that all atoms in the crystal vibrate at the same frequency ω_E , the total vibrational energy is

$$U = \sum_{i=1}^{3N} \bar{\varepsilon}_i = \frac{3N\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1} + \frac{3N}{2}\hbar\omega_E \quad (4.213)$$

Another method is to start from the partition function, the single-particle partition function of the Einstein model is

$$Z_1 = \sum_{n=0}^{\infty} e^{-(n+1/2)\beta\hbar\omega_E} = \frac{e^{-\beta\hbar\omega_E/2}}{1 - e^{-\beta\hbar\omega_E}} \quad (4.214)$$

The free energy of the system is:

$$F(N, T, V) = -3Nk_B T \ln Z_1 = \frac{3}{2}N\hbar\omega_E + 3Nk_B T \ln \left(1 - e^{-\frac{\hbar\omega_E}{k_B T}} \right) \quad (4.215)$$

According to the total differential relationship of free energy $dF = -S dT - p dV + \mu dN$, the entropy of the system is:

$$S = - \left(\frac{\partial F}{\partial T} \right)_{N, V} = 3Nk_B \left[-\ln \left(1 - e^{-\frac{\hbar\omega_E}{k_B T}} \right) + \frac{\hbar\omega_E}{k_B T} \frac{e^{-\hbar\omega_E/k_B T}}{1 - e^{-\hbar\omega_E/k_B T}} \right] \quad (4.216)$$

The expression for internal energy can also be obtained

$$U = F + TS = \frac{3}{2}N\hbar\omega_E + \frac{3N\hbar\omega_E}{e^{\hbar\omega_E/k_B T} - 1} \quad (4.217)$$

Differentiating the above expression gives the heat capacity

$$C_V = \frac{\partial U}{\partial T} = 3Nk_B \left(\frac{\hbar\omega_E}{k_B T} \right)^2 \frac{e^{\hbar\omega_E/k_B T}}{(e^{\hbar\omega_E/k_B T} - 1)^2} = 3Nk_B \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1 \right)^2} \quad (4.218)$$

where the Einstein temperature $\Theta_E = \hbar\omega_E/k_B$ is defined, $x = T_E/T$, and $f_E(x) = \frac{e^x}{(e^x - 1)^2}$ is the Einstein heat capacity function.

At high temperatures, $T \gg \Theta_E$, $x \ll 1$, we have $e^x \approx 1 + x$, $f_E(x) \approx 1$, $C_V \approx 3Nk_B$;

At low temperatures, $T \ll \Theta_E$, $x \gg 1$, we have $e^x \gg 1$, $f_E(x) \approx e^{-x}$, $C_V \approx 3Nk_B \left(\frac{\Theta_E}{T} \right)^2 e^{-\frac{\Theta_E}{T}}$, as seen in Fig. 41, C_V decreases exponentially with temperature, which does not match experimental results because it ignores the main contribution of low-frequency acoustic branches.

4.5.3 Paramagnetic Solids

The classical theory of paramagnetic solids assumes that there are N atomic magnetic moments in the system, without considering interactions, the energy of a single magnetic moment in an external field is

$$\varepsilon = -\mu \cdot \mathbf{B} = -\mu B \cos \theta \quad (4.219)$$

where μ is the magnetic moment, θ is the angle between the magnetic moment and the external magnetic field, and B is the strength of the external magnetic field. Since the orientation of the magnetic moment is random, the partition function of the system is

$$Z_1(T, B) = \int d\Omega e^{\beta \mu B \cos \theta} = \int d\phi d \cos \theta e^{\beta \mu B \cos \theta} = 4\pi \frac{\sinh(\beta \mu B)}{\beta \mu B} \quad (4.220)$$

The free energy of the system is:

$$F(T, B, N) = -Nk_B T \ln \left[4\pi \frac{\sinh(\beta \mu B)}{\beta \mu B} \right] \quad (4.221)$$

Since the total magnetic moment of the paramagnetic medium can only be aligned along the external magnetic field, according to the total differential relationship of free energy: $dF = -S dT - M dB$, the total magnetic moment of the system is:

$$M = - \left(\frac{\partial F}{\partial B} \right)_T = N\mu \left[\coth(\beta \mu B) - \frac{1}{\beta \mu B} \right] \equiv N\mu L(x) \quad (4.222)$$

where the Langevin function $L(x)$ is defined as:

$$L(x) = \coth(x) - \frac{1}{x} = \frac{1}{3}x - \frac{1}{45}x^3 + \frac{2}{945}x^5 - \frac{1}{4725}x^7 + \dots \quad (4.223)$$

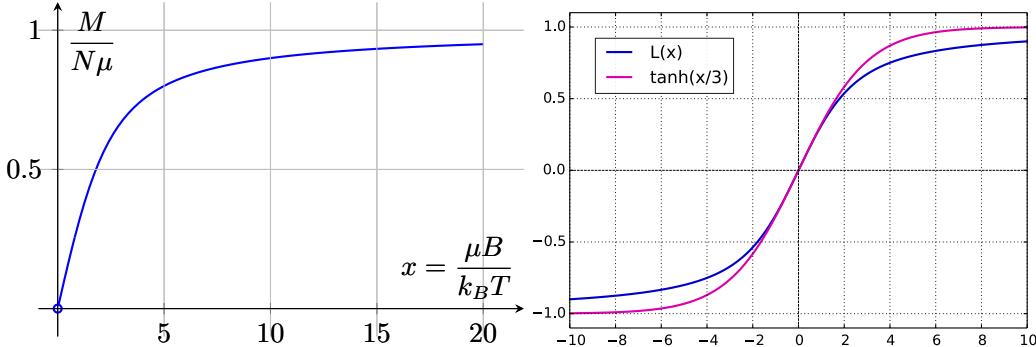


Fig. 42: Total magnetic moment variation with $x = \frac{\mu B}{k_B T}$ and the Langevin function

In the case of low temperature or weak magnetic field, $x \gg 1$, $L(x) \simeq 1$, almost all atomic magnetic moments are aligned along the external magnetic field, and the system reaches magnetic saturation; in the case of high temperature or weak magnetic field, $x \ll 1$, $L(x) \simeq \frac{x}{3} + \dots$, the total magnetic moment of the system is:

$$M \simeq \frac{N\mu^2}{3k_B T} B \equiv C \frac{B}{T} \quad (4.224)$$

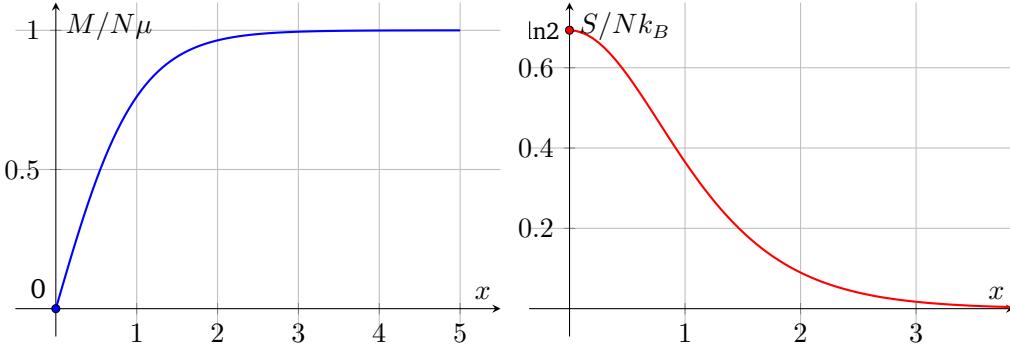


Fig. 43: Magnetization and entropy of the two-level system as a function of $x = \frac{\mu B}{k_B T}$

where $C = \frac{N\mu^2}{3k_B T}$ is the Curie coefficient of the paramagnet. The entropy of the system is obtained through the free energy Eq. 4.221:

$$S = - \left(\frac{\partial F}{\partial T} \right)_B = Nk_B \left\{ \ln \left[4\pi \frac{\sinh(x)}{x} \right] - xL(x) \right\} \quad (4.225)$$

A frequently discussed model—the **two-level system**, where the magnetic moment only has two states: aligned or anti-aligned with the magnetic field, with an energy difference of $2\mu B$, the partition function is:

$$Z_1(T, B) = \sum_s e^{-\beta \varepsilon_s} = e^{-\beta \mu B} + e^{\beta \mu B} = 2 \cosh \left(\frac{\mu B}{k_B T} \right) \quad (4.226)$$

Where the external magnetic field B can be regarded as a generalized displacement, the free energy of the system is:

$$F(N, T, B) = -Nk_B T \ln Z_1 = -Nk_B T \left[\ln 2 + \ln \cosh \left(\frac{\mu B}{k_B T} \right) \right] \quad (4.227)$$

Similarly, the entropy and magnetization are obtained through differential relations

$$S = Nk_B \left[\ln 2 + \ln \cosh \left(\frac{\mu B}{k_B T} \right) - \left(\frac{\mu B}{k_B T} \right) \tanh \left(\frac{\mu B}{k_B T} \right) \right] \quad (4.228a)$$

$$M = N\mu \tanh \left(\frac{\mu B}{k_B T} \right) \quad (4.228b)$$

Thus, the internal energy is obtained:

$$U = F + TS = -N\mu B \tanh \left(\frac{\mu B}{k_B T} \right) = -MB \quad (4.229)$$

In the weak field or high temperature limit, $\mu B \ll k_B T$, $\tanh(\mu B/k_B T) \simeq \mu B/k_B T$, $\ln [\cosh(\mu B/k_B T)] \sim$

$(\mu B/k_B T)^2 / 2$, thus

$$F \simeq -Nk_B T \left[\ln 2 + \frac{1}{2} \left(\frac{\mu B}{k_B T} \right)^2 \right], \quad (4.230a)$$

$$M \simeq N\mu \frac{\mu B}{k_B T} \equiv \chi H, \quad \text{Curie's Law} \quad (4.230b)$$

$$S \simeq Nk_B \ln 2 = Nk_B \ln 2, \quad \text{maximum entropy} \quad (4.230c)$$

where the magnetic susceptibility $\chi = N\mu^2/k_B T_0$; in the strong field or low temperature limit, $\mu B \gg k_B T, e^{\mu B/k_B T} \gg e^{-\mu B/k_B T}, \cosh(\mu B/k_B T) \simeq e^{\mu B/k_B T/2}$. Thus, the physical quantities

$$F \simeq -N\mu B, \quad (4.231a)$$

$$M \simeq N\mu, \quad (4.231b)$$

$$S \simeq 0 \quad (4.231c)$$

Therefore, in the strong field or low temperature limit, the magnetic moments are mostly aligned along the magnetic field direction, and the microscopic state of each magnetic moment is determined, so the total number of microscopic states of the system is 1, and the entropy of the system is 0.

Next, consider the generation of negative temperature. If at low temperature, the direction of the external magnetic field is suddenly reversed, then the number of excited state particles N_+ is greater than the number of ground state particles N_- , i.e., $N_+ - N_- > 0$. At this time, if the internal energy of the system is increased, more particles will transition to the excited state, the system becomes more ordered and the entropy decreases. Such a state is called a negative temperature state.

$$\frac{N_+}{N_-} = e^{-\frac{2\mu B}{k_B T}} > 1, \quad \frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_N < 0 \quad (4.232)$$

The total number of particles and internal energy of the system are:

$$N = N_- + N_+, \quad U = N_- \varepsilon_- + N_+ \varepsilon_+ = \mu B (N_+ - N_-) \quad (4.233)$$

Thus, the number of excited state and ground state particles

$$N_{\pm} = \frac{1}{2} \left(N \pm \frac{U}{\mu B} \right) \quad (4.234)$$

The entropy of the system

$$S = k_B \ln \Omega = k_B \ln \frac{N!}{N_+! N_-!} \simeq N \ln N - N_+ \ln N_+ - N_- \ln N_- \quad (4.235)$$

where the approximation conditions $N_+ \gg 1$ and $N_- \gg 1$ are used.

Substituting Eq. 4.234 into the above equation, the specific entropy $s \equiv S/Nk_B$ is obtained as a function of the unit particle internal energy $u \equiv U/N\mu B$

$$s = \ln 2 - \frac{1}{2}(1+u) \ln(1+u) - \frac{1}{2}(1-u) \ln(1-u) \quad (4.236)$$

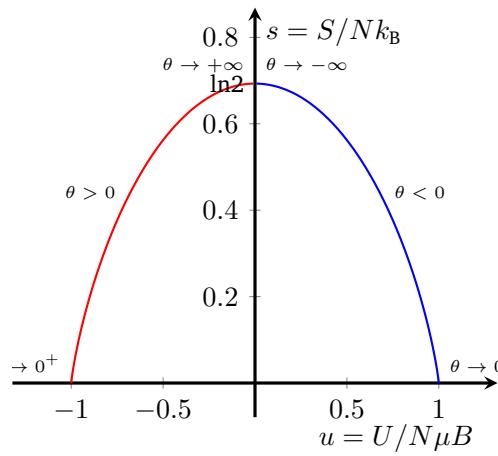


Fig. 44: Specific entropy-unit particle internal energy function, slope is the reciprocal of dimensionless temperature $\frac{1}{\theta}$

Thus, the dimensionless temperature θ of the system is given by:

$$\theta = \frac{1}{\left(\frac{\partial s}{\partial u}\right)_N} = \frac{2}{\ln\left(\frac{1-u}{1+u}\right)} = \begin{cases} 0^+, & u = -1, \\ +\infty, & u = 0^-, \\ -\infty, & u = 0^+, \\ 0^-, & u = 1. \end{cases} \quad (4.237)$$

From this, three conditions for the occurrence of negative temperature are obtained: the system must have an upper energy limit, particle number inversion, and the system must be adiabatic with the outside (otherwise, particles in the excited state will transition to the ground state).

Chapter 5 Quantum Statistical Theory

5.1 Grand Partition Function

Starting from the form of the Bose distribution given by Eq. 4.76, we need to select an appropriate thermodynamic potential to generate various thermodynamic parameters. For a classical ideal gas, the free energy $F(T, V, N)$ is chosen as the thermodynamic potential because, in Boltzmann statistics, the chemical potential and the number of particles satisfy

$$Ne^\alpha = Z_1(T, V) \quad (5.1)$$

However, in Bose/Fermi statistics, there is no simple algebraic relationship between the chemical potential (μ) and the number of particles (N), so the grand thermodynamic potential $J(\mu, T, V)$ must be chosen as the thermodynamic potential. For Bose statistics, we will discuss starting from the grand partition function Ξ , according to the Legendre transformation:

$$\begin{aligned} \delta \ln \Omega &= \alpha \delta N + \beta \delta E \\ \ln \Xi &= \ln \Xi(\beta, \alpha, V) = \ln \bar{\Omega} - \alpha N - \beta E \end{aligned} \quad (5.2)$$

Through the Legendre transformation, the free parameters are changed from (E, V, N) to $(T, V, \mu) \Leftrightarrow (\beta, V, \alpha)$. This is equivalent to changing from an isolated system to an open system: the system is in contact with a large heat source and a large particle source, maintaining constant temperature and chemical potential. Substituting the expression for the microstate number of the Bose system Eq. 4.27, we have

$$\begin{aligned} \ln \Xi &= \ln \Xi(\beta, \alpha, V) = \ln \bar{\Omega} - \alpha N - \beta E \\ &= \sum_l \{ [(\omega_l + a_l) \ln (\omega_l + a_l) - (\omega_l + a_l)] - (a_l \ln a_l - a_l) - (\omega_l \ln \omega_l - \omega_l) - (\alpha + \beta \varepsilon_l) a_l \} \\ &= \sum_l \left\{ \omega_l \ln \frac{\omega_l + a_l}{\omega_l} + a_l \ln \frac{\omega_l + a_l}{a_l} - (\alpha + \beta \varepsilon_l) a_l \right\} \\ &= \sum_l \left[\omega_l \ln (1 - e^{-\alpha - \beta \varepsilon_l})^{-1} + a_l (\alpha + \beta \varepsilon_l) - a_l (\alpha + \beta \varepsilon_l) \right] = - \sum_l \omega_l \ln (1 - e^{-\alpha - \beta \varepsilon_l}) \end{aligned} \quad (5.3)$$

Among them, using $\frac{\omega_l + a_l}{\omega_l} = \frac{1}{1 - e^{-\alpha - \beta \varepsilon_l}}$, $\frac{\omega_l + a_l}{a_l} = e^{\alpha + \beta \varepsilon_l}$, we obtain the grand partition function

$$\Xi = \prod_l \Xi_l = \prod_l (1 - e^{-\alpha - \beta \varepsilon_l})^{-\omega_l} \quad (5.4)$$

For Fermi statistics, similarly using Eq. 5.2 to discuss from the grand partition function Ξ , substituting the expression for the microstate number of the Fermi system Eq. 4.23, we have

$$\begin{aligned}\ln \Xi &= \ln \Xi(\beta, \alpha, V) = \ln \bar{\Omega} - \alpha N - \beta E \\ &= \sum_l \{ \omega_l \ln \omega_l - \omega_l - (a_l \ln a_l - a_l) - [(\omega_l - a_l) \ln (\omega_l - a_l) - (\omega_l - a_l)] - (\alpha + \beta \varepsilon_l) a_l \} \\ &= \sum_l \left\{ \omega_l \ln \frac{\omega_l}{\omega_l - a_l} - a_l \ln \frac{a_l}{\omega_l - a_l} - (\alpha + \beta \varepsilon_l) a_l \right\} \\ &= \sum_l [\omega_l \ln (1 + e^{-\alpha - \beta \varepsilon_l}) + a_l (\alpha + \beta \varepsilon_l) - a_l (\alpha + \beta \varepsilon_l)] = \sum_l \omega_l \ln (1 + e^{-\alpha - \beta \varepsilon_l})\end{aligned}\quad (5.5)$$

Among them, using $\frac{\omega_l}{\omega_l - a_l} = 1 + e^{-\alpha - \beta \varepsilon_l}$, $\frac{a_l}{\omega_l - a_l} = e^{-\alpha - \beta \varepsilon_l}$, we obtain the grand partition function

$$\Xi = \prod_l \Xi_l = \prod_l (1 + e^{-\alpha - \beta \varepsilon_l})^{\omega_l} \quad (5.6)$$

Thus, the grand partition function for Bose/Fermi systems can be uniformly written as (+ corresponds to Fermi, - corresponds to Bose)

$$\Xi = \prod_l \Xi_l = \prod_l (1 \mp e^{-\alpha - \beta \varepsilon_l})^{\mp \omega_l} = \prod_l (1 \mp e^{(\mu - \varepsilon_l)/k_B T})^{\mp \omega_l} \quad (5.7)$$

5.1.1 Grand Potential and Physical Quantities

Using the differential relation satisfied by the grand partition function

$$d \ln \Xi = -E d\beta - N d\alpha \quad (5.8)$$

we obtain the expression for internal energy in terms of the grand partition function

$$\begin{aligned}U &= \bar{E} = \sum_l a_l \varepsilon_l = \sum_l \frac{\omega_l \varepsilon_l}{e^{\beta \varepsilon_l + \alpha} \pm 1} = \sum_l \omega_l \varepsilon_l \frac{e^{-\alpha - \beta \varepsilon_l}}{1 \pm e^{-\alpha - \beta \varepsilon_l}} \\ &= \pm \sum_l \omega_l \left[(-) \frac{\partial}{\partial \beta} \ln (1 \pm e^{-\alpha - \beta \varepsilon_l}) \right]_{\alpha, V} \\ &= -\frac{\partial}{\partial \beta} \left[(\pm) \sum_l \omega_l \ln (1 \pm e^{-\alpha - \beta \varepsilon_l}) \right] = -\left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\alpha, V}\end{aligned}\quad (5.9)$$

we obtain the expression for the number of particles in terms of the grand partition function

$$\begin{aligned}N &= \sum_l a_l = \sum_l \frac{\omega_l}{e^{\alpha + \beta \varepsilon_l} \pm 1} = \sum_l \frac{\omega_l e^{-\alpha - \beta \varepsilon_l}}{1 \pm e^{-\alpha - \beta \varepsilon_l}} \\ &= (\pm) \sum_l \left[\omega_l (-) \frac{\partial}{\partial \alpha} (\ln 1 \pm e^{-\alpha - \beta \varepsilon_l})_{\beta, V} \right] \\ &= -\frac{\partial}{\partial \alpha} \left[\pm \sum_l \omega_l (\ln 1 \pm e^{-\alpha - \beta \varepsilon_l}) \right]_{\beta, V} = -\left(\frac{\partial \ln \Xi}{\partial \alpha} \right)_{\beta, V}\end{aligned}\quad (5.10)$$

According to the total differential expansion of internal energy

$$\begin{aligned}\delta U &= \sum_l \varepsilon_l \delta a_l + \sum_l a_l \delta \varepsilon_l = \sum_l \left(\varepsilon_l + \frac{\alpha}{\beta} \right) \delta a_l + \sum_l a_l \delta \varepsilon_l - \frac{\alpha}{\beta} \sum_l \delta a_l \\ &= \delta Q - \delta W + \mu \delta N\end{aligned}\quad (5.11)$$

The heat change term is written as

$$\begin{aligned}\beta Q &= \beta \sum_l \left(\varepsilon_l + \frac{\alpha}{\beta} \right) da_l = \sum_l (\beta \varepsilon_l + \alpha) da_l \\ &= \sum_l d[(\beta \varepsilon_l + \alpha) a_l] - \sum_l a_l d(\beta \varepsilon_l + \alpha) \\ &= d \left[\beta \sum_l a_l \varepsilon_l + \alpha \sum_l a_l \right] - \sum_l \frac{\omega_l}{e^{\beta \varepsilon_l + \alpha} \pm 1} d(\beta \varepsilon_l + \alpha) \\ &= d(\beta U + \alpha N) + \sum_l (\pm) \omega_l d \ln [1 \pm e^{-\beta \varepsilon_l - \alpha}] \\ &= d(\beta U + \alpha N) + d \ln \Xi = d(\beta U + \alpha N + \ln \Xi)\end{aligned}\quad (5.12)$$

The entropy expression can be given, which also satisfies $S = k_B \ln \Omega$

$$S = k_B (\ln \Xi + \alpha N + \beta U) = k_B \ln \Xi + \frac{U - \mu N}{T} \quad (5.13)$$

The pressure is obtained through the change in work

$$\begin{aligned}p &= \frac{\delta W}{\delta V} = - \sum_l a_l \left(\frac{\partial \varepsilon_l}{\partial V} \right) = - \sum_l \omega_l \left(\frac{\partial \varepsilon_l}{\partial V} \right) \frac{e^{-\alpha-\beta\varepsilon_l}}{1 \pm e^{-\alpha-\beta\varepsilon_l}} \\ &= \pm \sum_l \omega_l \left[\frac{\partial}{\beta \partial V} \ln (1 \pm e^{-\alpha-\beta\varepsilon_l}) \right]_{\alpha, \beta} \\ &= \frac{\partial}{\beta \partial V} \left[(\pm) \sum_l \omega_l \ln (1 \pm e^{-\alpha-\beta\varepsilon_l}) \right] = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial V} \right)_{\alpha \beta}\end{aligned}\quad (5.14)$$

From the grand potential $J = U - TS - N\mu$, we obtain the statistical expression of the grand thermodynamic potential

$$J(T, V, \mu) = -k_B T \ln \Xi(T, V, \mu) = k_B T \sum_l (\mp) \omega_l \ln (1 \mp e^{(\mu-\varepsilon_l)/k_B T}) \quad (5.15)$$

and the grand potential satisfies the total differential relation

$$dJ = -S dT - p dV - N d\mu \quad (5.16)$$

According to the Legendre transformation, the statistical expressions of the thermodynamic characteristic functions (F, U, H, G) can be obtained

$$F = J + N\mu = k_B T \left(-\ln \Xi + \mu \frac{\partial}{\partial \mu} \ln \Xi \right) \quad (5.17a)$$

$$U = J + TS + N\mu = k_B T \left(\mu \frac{\partial}{\partial \mu} \ln \Xi + T \frac{\partial}{\partial T} \ln \Xi \right) \quad (5.17b)$$

$$H = J + TS + pV + N\mu = k_B T \left(\mu \frac{\partial}{\partial \mu} \ln \Xi + T \frac{\partial}{\partial T} \ln \Xi + V \frac{\partial}{\partial V} \ln \Xi \right) \quad (5.17c)$$

$$G = J + pV + N\mu = k_B T \left(-\ln \Xi + \mu \frac{\partial}{\partial \mu} \ln \Xi + V \frac{\partial}{\partial V} \ln \Xi \right) \quad (5.17d)$$

Consider changing the parameters (β, α, V) to (T, μ, V) , let $\lambda = e^{-\alpha} = e^{\beta\mu}$, called fugacity, then the physical quantities are expressed as

$$N = - \left(\frac{\partial \ln \Xi}{\partial \alpha} \right)_{\beta V} = \lambda \left(\frac{\partial \ln \Xi}{\partial \lambda} \right)_{\beta V} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{\beta V} = k_B T \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{TV} \quad (5.18a)$$

$$\begin{aligned} U &= - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\alpha V} = - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\lambda V} = - \frac{\partial (\ln \Xi, \alpha)}{\partial (\beta, \alpha)} = - \frac{\partial (\ln \Xi, \alpha)}{\partial (\beta, \mu)} \frac{\partial (\beta, \mu)}{\partial (\beta, \alpha)} \\ &= - \left[\left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\mu V} (-\beta) - \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{\beta V} \left(\frac{\partial \alpha}{\partial \beta} \right)_\mu \right] \frac{-1}{\beta} = - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\mu V} + N\mu = k_B T^2 \left(\frac{\partial \ln \Xi}{\partial T} \right)_{\mu V} + N\mu \end{aligned} \quad (5.18b)$$

$$p = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial V} \right)_{\beta \alpha} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial V} \right)_{\beta \lambda} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial V} \right)_{\beta, -\beta \mu} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial V} \right)_{\beta, \mu} = k_B T \left(\frac{\partial \ln \Xi}{\partial V} \right)_{T, \mu} \quad (5.18c)$$

5.1.2 Free Bose/Fermi Gas

For an ideal, free three-dimensional Bose gas, the number of quantum states within a certain space $dx, dy, dz, dp_x, dp_y, dp_z$ is

$$\omega_s \frac{\Delta \omega_l}{h^3} = \omega_s \frac{d^3x d^3p}{h^3} \quad (5.19)$$

ω_s is the spin degeneracy, for particles with non-zero mass generally $\omega_s = 2s + 1$, s is the spin quantum number; for photons (mass is 0), $s = 1, \omega_s = 2$.

First, discuss the free Bose gas, assuming the system temperature is much higher than the critical temperature for Bose-Einstein condensation, the contribution of the ground state occupation can be ignored, and the grand potential is rewritten in integral form:

$$J(T, V, \mu) = -k_B T \ln \Xi(T, V, \mu) = k_B T \int \omega_s \frac{V d^3p}{h^3} \ln (1 - e^{(\mu - \varepsilon)/k_B T}) = -p(T, \mu)V \quad (5.20)$$

From this, the thermodynamic parameters entropy, pressure, and particle number are obtained

Table 4: Relationship between Thermodynamic Characteristic Functions and Grand Partition Function

State Function	Statistical Mechanics Expression
U	$-\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\alpha V} = k_B T^2 \left(\frac{\partial \ln \Xi}{\partial T}\right)_{\mu V} + k_B T \mu \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{TV}$
J	$-k_B T \ln \Xi$
N	$-\left(\frac{\partial \ln \Xi}{\partial \alpha}\right)_{\beta V} = k_B T \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{TV}$
$F = J + N\mu$	$-k_B T \ln \Xi + k_B T \mu \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{TV}$
$S = -\left(\frac{\partial J}{\partial T}\right)_V = \frac{U - F}{T}$	$k_B \ln \Xi + k_B T \left(\frac{\partial \ln \Xi}{\partial T}\right)_{\mu V}$
$p = -\left(\frac{\partial J}{\partial V}\right)_T$	$\frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta \alpha} = k_B T \left(\frac{\partial \ln \Xi}{\partial V}\right)_{T, \mu}$
$H = U + pV$	$k_B T \left[\mu \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{TV} + T \left(\frac{\partial \ln \Xi}{\partial T}\right)_{\mu V} + V \left(\frac{\partial \ln \Xi}{\partial V}\right)_{T, \mu} \right]$
$G = F + pV = H - TS$	$k_B T \left[-\ln \Xi + \mu \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{TV} + V \left(\frac{\partial \ln \Xi}{\partial V}\right)_{T, \mu} \right]$
$C_V = \left(\frac{\partial U}{\partial T}\right)_V$	$k_B \left[2T \left(\frac{\partial \ln \Xi}{\partial T}\right)_{\mu V} + T^2 \left(\frac{\partial^2 \ln \Xi}{\partial T^2}\right)_{\mu V} + \mu \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{TV} \right]$

as

$$S = -k_B \int \omega_s \frac{V d^3 p}{h^3} \ln(1 - e^{(\mu - \varepsilon)/k_B T}) + k_B \int \omega_s \frac{V d^3 p}{h^3} f(\varepsilon, \mu) \left(\frac{\varepsilon - \mu}{k_B T}\right), \quad (5.21a)$$

$$p = -k_B T \int \omega_s \frac{d^3 p}{h^3} \ln(1 - e^{(\mu - \varepsilon)/k_B T}) \quad (5.21b)$$

$$N = \int \omega_s \frac{V d^3 p}{h^3} f(\varepsilon, \mu), \quad f(\varepsilon, \mu) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} - 1} \quad (5.21c)$$

For better discussion, physical quantities can be expressed using the distribution function $f(\varepsilon, \mu)$, for pressure

$$\begin{aligned} p &= -k_B T \int \omega_s \frac{d^3 p}{h^3} \ln(1 - e^{(\mu - \varepsilon)/k_B T}) \\ &= -k_B T \omega_s \frac{1}{h^3} \int d\Omega \int \frac{1}{3} dp^3 \ln(1 - e^{(\mu - \varepsilon)/k_B T}) \\ &= \omega_s \frac{1}{h^3} \int d\Omega \int \left(\frac{p^2 c^2}{3\varepsilon}\right) p^2 dp \frac{1}{e^{(\varepsilon - \mu)/k_B T} - 1} \\ &= \int \omega_s \frac{d^3 p}{h^3} \left(\frac{p^2 c^2}{3\varepsilon}\right) \frac{1}{e^{(\varepsilon - \mu)/k_B T} - 1} \\ &= \int \omega_s \frac{d^3 p}{h^3} f(\varepsilon, \mu) \left(\frac{p^2 c^2}{3\varepsilon}\right) \end{aligned} \quad (5.22)$$

The third step of the derivation uses integration by parts, and Einstein's mass-energy relation is adopted: $\varepsilon^2 = (pc)^2 + (mc^2)^2$, $\varepsilon d\varepsilon = c^2 pdp$

Therefore, the formula applies to both non-relativistic/relativistic Bose gases. The above equation also shows that the microscopic statistical quantity of pressure, i.e., the contribution of each particle to the total pressure is $p^2 c^2 / 3\varepsilon$. Discuss separately:

(1) Non-relativistic Bose gas, using $\varepsilon \simeq mc^2 + p^2/2m$, the internal energy and pressure per unit volume

$$u = \frac{U}{V} - nmc^2 \simeq \int \omega_s \frac{d^3 p}{h^3} f(\varepsilon, \mu) \frac{p^2}{2m} \quad (5.23a)$$

$$p \simeq \int \omega_s \frac{d^3 p}{h^3} f(\varepsilon, \mu) \frac{p^2}{3m} \quad (5.23b)$$

Thus, the relationship between internal energy and pressure per unit volume for a non-relativistic Bose gas is

$$p = \frac{2}{3}u \quad (5.24)$$

(2) Relativistic Bose gas, using $\varepsilon \simeq pc$, the internal energy and pressure per unit volume

$$u = \frac{U}{V} - nmc^2 \simeq \int \omega_s \frac{d^3 p}{h^3} f(\varepsilon, \mu) pc \quad (5.25a)$$

$$p \simeq \int \omega_s \frac{d^3 p}{h^3} f(\varepsilon, \mu) \frac{pc}{3} \quad (5.25b)$$

Thus, the relationship between internal energy and pressure per unit volume for a relativistic Bose gas is

$$p = \frac{1}{3}u \quad (5.26)$$

For detailed discussion, see Subsubsec. 5.2.3; discussing the grand potential of Fermi gas, the microscopic statistical quantity of pressure can also be obtained as $p^2 c^2 / 3\varepsilon$

5.2 Classical Bose Gas

Using fugacity $\lambda = e^{-\alpha} = e^{\beta\mu}$, the distribution function is rewritten

$$f_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} \pm 1} = \frac{1}{e^{\beta\varepsilon_s + \alpha} \pm 1} = \frac{1}{e^{\beta\varepsilon_s}/\lambda \pm 1} \quad (5.27)$$

If $\lambda \ll 1 (\mu\beta \gg 0)$, this is a weak degeneracy case, indistinguishability is not important

$$f_s \simeq \lambda e^{-\beta\varepsilon_s} = e^{-\beta\varepsilon_s - \alpha} \quad (5.28)$$

If $\lambda \sim 1$ or $\lambda \geq 1 (\mu\beta \leq 0)$, this is a strong degeneracy case, indistinguishability is important, for fermions $\lambda \geq 1$, we have

$$f_s = \frac{1}{e^{\varepsilon_s}/\lambda + 1} \simeq 1 \quad (5.29)$$

For bosons $\lambda \sim 1 (\lambda \leq 1)$, we have

$$f_s = \frac{1}{e^{\beta\varepsilon_s}/\lambda - 1} \simeq \begin{cases} \frac{\lambda}{1 - \lambda} & , \varepsilon_s = 0 \\ \frac{1}{e^{\beta\varepsilon_s} - 1} \simeq \frac{k_B T}{\varepsilon_s} & , \varepsilon_s > 0 \end{cases} \quad (5.30)$$

Discussing from the perspective of the grand partition function (+ corresponds to fermions, - corresponds to bosons)

$$\begin{aligned}\ln \Xi &= \pm \sum_s \omega_s \ln [1 \pm e^{-\beta(\varepsilon_s - \mu)}] = \pm \sum_s \omega_s \ln [1 \pm \lambda e^{-\beta\varepsilon_s}] \\ &= \pm \int_0^\infty g(\varepsilon) \ln [1 \pm \lambda e^{-\beta\varepsilon}] d\varepsilon \pm \omega_g \ln [1 \pm \lambda]\end{aligned}\quad (5.31)$$

Written as two terms, one for the excited state contribution and the other for the ground state contribution, which can be ignored in most cases (considered for strongly degenerate Bose gases).

5.2.1 Weakly Degenerate Ideal Gas

Using the series expansion of the logarithmic function

$$\ln(1 + x) = \sum_{k=1}^{\infty} \frac{(-1)^{n+1} x^n}{n} \quad (5.32)$$

According to the three-dimensional density of states Eq. 4.200, the grand partition function for a weakly degenerate gas is (after transformation, + corresponds to bosons, - corresponds to fermions)

$$\begin{aligned}\ln \Xi &= \pm \int_0^\infty g(\varepsilon) \ln [1 \pm e^{-\beta(\varepsilon - \mu)}] d\varepsilon = \pm \int_0^\infty g(\varepsilon) \ln [1 \pm \lambda e^{-\beta\varepsilon}] d\varepsilon \\ &= \pm \int_0^\infty g(\varepsilon) \sum_{n=1}^{\infty} \frac{(-)^{n+1} (\pm \lambda e^{-\beta\varepsilon})^n}{n} = \sum_{n=1}^{\infty} \frac{(\mp)^{n+1} \lambda^n}{n} \int_0^\infty g(\varepsilon) e^{-n\beta\varepsilon} d\varepsilon \\ &= 2\pi V \omega_s \left(\frac{2m}{h^2} \right)^{3/2} \sum_{n=1}^{\infty} \frac{(\mp)^{n+1} \lambda^n}{n} \int_0^\infty \sqrt{\varepsilon} e^{-n\beta\varepsilon} d\varepsilon \\ &= 2\pi V \omega_s \left(\frac{2mk_B T}{h^2} \right)^{3/2} \sum_{n=1}^{\infty} \frac{(\mp)^{n+1} \lambda^n}{n^{5/2}} \int_0^\infty e^{-t} t^{1/2} dt \\ &= V \omega_s \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \text{Li}_{5/2}^{(\mp)}(\lambda) = z(T, V) \text{Li}_{5/2}^{(\mp)}(\lambda)\end{aligned}\quad (5.33)$$

Here, $\text{Li}_s(z)$ is the Jonquière's polylogarithm function defined in the complex space, related to the Fermi-Dirac integral $F_j(x)$ as

$$\text{Li}_s(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^s} = \frac{1}{\Gamma(s)} \int_0^\infty \frac{t^{s-1}}{e^t/z - 1} dt \quad (5.34)$$

The definition of the Fermi-Dirac partial integral $F_j(x)$ is

$$F_j(x, b) = \frac{1}{\Gamma(j+1)} \int_b^\infty \frac{t^j}{\exp(t-x) + 1} dt \quad (5.35)$$

The derivative of the polylogarithm function satisfies

$$z \frac{\partial \text{Li}_s(z)}{\partial z} = \text{Li}_{s-1}(z), \quad \frac{\partial \text{Li}_s(e^\mu)}{\partial \mu} = \text{Li}_{s-1}(e^\mu) \quad (5.36)$$

Thus, the number of particles is

$$N = \lambda \left(\frac{\partial \ln \Xi}{\partial \lambda} \right)_{TV} = z(T, V) \text{Li}_{3/2}^{(\mp)}(\lambda) \quad (5.37)$$

$$\text{Let } y(T, n) = \frac{N}{z(T, V)} = \text{Li}_{3/2}^{(\mp)}(\lambda) = \lambda \mp \frac{\lambda^2}{2^{3/2}} + \frac{\lambda^3}{3^{3/2}} \mp \dots, y \ll 1$$

$$y = \frac{N}{z(T, V)} = \frac{N}{V\omega_S} \left(\frac{2\pi m k_B T}{h^2} \right)^{-\frac{3}{2}} \quad (5.38)$$

Using the method of undetermined coefficients $\lambda = a_0 + a_1 y + a_2 y^2 + a_3 y^3 + \dots$ to solve for λ for better calculation, we get

$$\lambda = y \pm \frac{1}{2^{3/2}} y^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}} \right) y^3 + \dots \quad (5.39)$$

Thus, the internal energy of the system is

$$\begin{aligned} U &= - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\lambda V} = k_B T^2 \left(\frac{\partial \ln \Xi}{\partial T} \right)_{\lambda V} = k_B T^2 \left(\frac{\partial z}{\partial T} \right)_V \text{Li}_{5/2}^{(\mp)}(\lambda) \\ &= \frac{3k_B T}{2} z \text{Li}_{5/2}^{(\mp)}(\lambda) = \frac{3k_B T}{2} z \text{Li}_{3/2}^{(\mp)}(\lambda) \frac{\text{Li}_{5/2}^{(\mp)}(\lambda)}{\text{Li}_{3/2}^{(\mp)}(\lambda)} = \frac{3Nk_B T}{2} \frac{\text{Li}_{5/2}^{(\mp)}(\lambda)}{\text{Li}_{3/2}^{(\mp)}(\lambda)} \\ &= \frac{3Nk_B T}{2y} \left(\lambda \mp \frac{1}{2^{5/2}} \lambda^2 + \frac{1}{3^{5/2}} \lambda^3 + \dots \right) \\ &= \frac{3Nk_B T}{2} \left[1 \pm \frac{y}{2^{5/2}} + \left(\frac{1}{8} - \frac{2}{3^{5/2}} \right) y^2 + \dots \right] \end{aligned} \quad (5.40)$$

The heat capacity is

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T} \right)_{NV} = \frac{3Nk_B}{2} \left[1 \pm \frac{y}{2^{5/2}} + \left(\frac{1}{8} - \frac{2}{3^{5/2}} \right) y^2 + \dots \right] \\ &\quad + \frac{3Nk_B T}{2} \left[\pm \frac{1}{2^{5/2}} \left(\frac{\partial y}{\partial T} \right)_{NV} + \left(\frac{1}{8} - \frac{2}{3^{5/2}} \right) \left(\frac{\partial y^2}{\partial T} \right)_{NV} + \dots \right] \\ &= \frac{3Nk_B}{2} \left\{ 1 \mp \frac{y}{2^{7/2}} - \left(\frac{1}{4} - \frac{4}{3^{5/2}} \right) y^2 + \dots \right\} \\ &= 3Nk_B / 2 \times (1 \mp 0.08839y + 0.0066y^2 + \dots) \end{aligned} \quad (5.41)$$

Using Eq. 5.14 or Eq. 5.24, the pressure is obtained

$$\begin{aligned} p &= \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial V} \right)_{T,V} = \frac{k_B T}{V} \ln \Xi = \frac{2U}{3V} \\ &= \frac{Nk_B T}{V} \left[1 \pm \frac{y}{2^{5/2}} + \left(\frac{1}{8} - \frac{2}{3^{5/2}} \right) y^2 + \dots \right] \end{aligned} \quad (5.42)$$

In a localized system where the number of particles can be distinguished, the entropy expression is different from that of a non-localized system where the number of particles cannot be distinguished Eq. 5.13, and is

$$S = Nk_B \ln z + U/T \quad (5.43)$$

Thus, the relationship between the microstate numbers of the two particle systems is

$$\Omega_{\text{nonlocal}} = \frac{1}{N!} \Omega_{\text{local}} \quad (5.44)$$

Another condition for weak degeneracy can also be given, i.e., $\lambda \simeq y \ll 1$, where Eq. 4.108 gives λ_T , and the average particle motion distance $a = \left(\frac{V}{N}\right)^{1/3}$

$$\lambda \simeq y = \frac{N}{\omega_S V} \left(\frac{\hbar}{\sqrt{2\pi m k_B T}} \right)^3 \sim \left(\frac{\lambda_T}{a} \right)^3 \quad (5.45)$$

This actually indicates that identical particles are indistinguishable, and the particle wave functions overlap, with a spatial extension range $\sim \lambda_T$

Next, discuss Gibbs paradox from the perspective of entropy

$$S_{\text{local}}(T, V, N) = Nk_B \ln z + U/T = Nk_B \ln \left[V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] + 3Nk_B/2 \quad (5.46a)$$

$$\begin{aligned} S_{\text{nonlocal}}(T, V, N) &= S_{\text{local}}(T, V, N) - k_B \ln N! = Nk_B \ln z + U/T - k_B \ln N! \\ &= Nk_B \ln \left[V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] + 3Nk_B/2 - k_B N \ln N + Nk_B \\ &= Nk_B \ln \left[\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] + 5Nk_B/2 \end{aligned} \quad (5.46b)$$

Eq. 5.46b is called the Sackur-Tetrode equation. If the number of particles and volume are both doubled, then

$$S_{\text{local}}(T, 2V, 2N) = 2S_{\text{local}}(T, V, N) + 2Nk_B \ln 2 \quad (5.47a)$$

$$S_{\text{nonlocal}}(T, 2V, 2N) = 2S_{\text{nonlocal}}(T, V, N) \quad (5.47b)$$

This indicates that for a localized system of non-identical particles, separating the same number of particles on both sides with a partition cannot return to the pre-mixing state, while a non-localized system considering identical particles can solve the extensive property of entropy, i.e., the Sackur-Tetrode equation.

5.2.2 Bose-Einstein Condensation

Bose-Einstein condensation (BEC) usually forms when a gas of bosons with very low density is cooled to temperatures very close to absolute zero (temperature reference Fig. 33). Under this condition, a large portion of the bosons occupy the lowest quantum state, where microscopic quantum mechanical phenomena, especially wave function interference, become apparent on a macroscopic scale. As the temperature decreases, the chemical potential μ continuously increases, $\mu \rightarrow 0^-$, and the number of particles in the ground state continuously increases. Using the eigenvalue equation of a two-level system Eq. 4.92,

(1) Under the Boltzmann distribution, the distribution numbers are obtained

$$a_0 = \frac{N}{1 + e^{-\beta\varepsilon}}, \quad a_1 = \frac{Ne^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}, \quad \frac{a_1}{a_0} = e^{-\beta\varepsilon} \quad (5.48)$$

Thus, we obtain

$$\text{Quantum limit: } \frac{\varepsilon}{k_B T} \gg 1, a_1 \ll a_0 \quad (5.49\text{a})$$

$$\text{Classical limit: } \frac{k_B T}{\varepsilon} \gg 1, a_1 \simeq a_0 \simeq \frac{N}{2} \sim O(N) \quad (5.49\text{b})$$

The microstate number of classical particles is given by $\Omega = \binom{N}{a_1} = \frac{N!}{a_0! a_1!}$, and the minimum free energy gives

$$\begin{aligned} F &= U - TS = a_1 \varepsilon - k_B T [N \ln N - (N - a_1) \ln (N - a_1) - a_1 \ln a_1] \\ 0 &= \left(\frac{\partial F}{\partial a_1} \right) = \varepsilon + k_B T [-\ln (N - a_1) + \ln a_1] \Rightarrow \frac{a_1}{a_0} = e^{-\varepsilon/(k_B T)} \end{aligned} \quad (5.50)$$

(2) Under the Bose-Einstein distribution, the distribution numbers are obtained

$$a_0 = \frac{1}{e^{-\beta \mu} - 1}, \quad a_1 = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1}, \quad a_0 + a_1 = N \quad (5.51)$$

Thus, we obtain

$$\text{Quantum limit: } \frac{\varepsilon}{k_B T} \gg 1, a_1 \ll a_0 \quad (5.52\text{a})$$

$$\text{Classical limit: } \frac{k_B T}{\varepsilon} \sim 10^{12} \gg 1, a_0 = N - a_1 \simeq N \sim 10^{23} \gg a_1 \quad (5.52\text{b})$$

Due to the indistinguishability of bosons, when the distribution is $\{a_0, a_1\}$, the number of microstates is $\Omega = 1$. The minimum free energy gives $F = U - TS = a_1 \varepsilon$, requiring

$$a_1 = 0, \quad a_0 = N \quad (5.53)$$

Next, discuss the BEC of a three-dimensional Bose gas. According to Eq. 5.30, the number of particles in the ground state and excited state N_g, N_{ex} is

$$N_g = \frac{1}{e^{-\beta \mu} - 1} = \frac{1}{1/\lambda - 1} = \frac{\lambda}{1 - \lambda}, \quad \lambda < 1 \quad (5.54\text{a})$$

$$N_{ex} = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \text{Li}_{3/2}^+(\lambda) \leq V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \text{Li}_{3/2}^+(1) = N_c \quad (5.54\text{b})$$

(1) From the perspective of particle number: It indicates that the number of particles in the excited state has an upper limit. Let's assume this scenario: keeping the temperature and volume constant, particles are added to the container one by one. Initially, $\lambda \ll 1$, the number of particles in the ground state is very small $N_g \sim \lambda \sim O(1)$, and particles are basically in the excited state, $N_{ex} = N$; as the number of particles N increases, λ increases, but when $N_g \sim \lambda \sim O(1)$, particles are still basically in the excited state, $N_{ex} = N$; when N increases to N_c , N_{ex} cannot continue to increase, and newly added particles can only be in the ground state.

(2) From the perspective of temperature change: At high temperatures, $\lambda \ll 1$, particles are mainly in the excited state. As the temperature decreases, λ increases until $N_{ex} = N_c(T_c)$, giving the phase transition temperature $T_C \propto n^{2/3}$

$$T_c = \frac{h^2}{2\pi m k_B} \left[\text{Li}_{3/2}^+(1) \right]^{-2/3} n^{2/3} \quad (5.55)$$

The number of ground state particles below the critical temperature $T < T_c$ is

$$N_g = N - N_{ex} = \left[1 - (T/T_c)^{3/2} \right] N \quad (5.56)$$

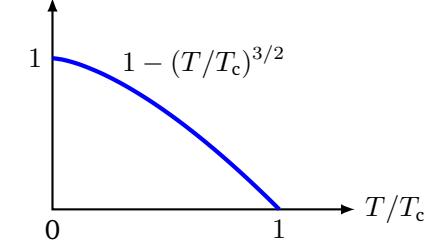


Fig. 45: Number of Ground State Particles Temperature Dependence

(3) From the perspective of volume change: When the temperature and number of particles remain constant, reducing the volume will also lead to an increase in particle density, resulting in BEC. The critical volume is given by Eq. 5.54b

$$V_c = N \lambda_T^3 \frac{1}{\text{Li}_{3/2}^+(1)} \quad (5.57)$$

Similarly, the number of particles in the ground state is obtained

$$N_g = N - N_{ex} = N \left(1 - \frac{V}{V_c} \right) \quad (5.58)$$

Next, discuss the physical quantities and state equations: Assuming the ground state energy is 0, the internal energy is given first for the case $T \geq T_c$

$$U = U_{ex} = \int_0^\infty \varepsilon g(\varepsilon) f(\varepsilon) d\varepsilon = \frac{3k_B T}{2} V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \text{Li}_{5/2}^+(\lambda) = \frac{3}{2} \frac{k_B T V}{\lambda_T^3} \text{Li}_{5/2}^+(\lambda) \quad (5.59)$$

The corresponding high-temperature heat capacity, with discontinuity in heat capacity as a special first-order phase transition

$$C_V = \frac{15Nk_B}{4} \frac{\text{Li}_{5/2}^+(\lambda)}{\text{Li}_{3/2}^+(\lambda)} - \frac{9Nk_B}{4} \frac{\text{Li}_{3/2}^+(\lambda)}{\text{Li}_{1/2}^+(\lambda)} \quad (5.60)$$

It is considered that at $T > T_c$, particles are mainly in the excited state, and the number of particles does not change with temperature. By differentiating Eq. 5.54b with respect to temperature, λ, μ satisfy

$$\frac{d \ln \lambda}{d \ln T} = -\frac{3\text{Li}_{3/2}(\lambda)}{2\text{Li}_{1/2}(\lambda)} \quad (5.61)$$

At high temperatures, $\lambda = \exp(\mu\beta) \rightarrow 1$, $\text{Li}_s(\lambda) \rightarrow \lambda$, $C_V \simeq 1.5Nk_B$

At $T \leq T_c$, when BEC occurs, the internal energy and heat capacity are rewritten as

$$U = U_{ex} = \frac{3k_B T}{2} V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \text{Li}_{5/2}^+ = \frac{3Nk_B T}{2} \left(\frac{T}{T_c} \right)^{3/2} \frac{\text{Li}_{5/2}^+(1)}{\text{Li}_{3/2}^+(1)} = 0.770Nk_B T \left(\frac{T}{T_c} \right)^{3/2} \quad (5.62a)$$

$$C_V = \frac{15Nk_B}{4} \left(\frac{T}{T_c} \right)^{3/2} \frac{\text{Li}_{5/2}^+(1)}{\text{Li}_{3/2}^+(1)} = 1.93Nk_B \left(\frac{T}{T_c} \right)^{3/2} \quad (5.62b)$$

Here, the relationship between the polylogarithm function and the Riemann ζ function is used:
 $\text{Li}_s(1) = \zeta(s)$, $(\text{Re}(s) > 1)$

$$\text{Li}_{3/2}(1) = \zeta(3/2) = 2.6114, \quad \text{Li}_{5/2}(1) = \zeta(5/2) = 1.3415 \quad (5.63)$$

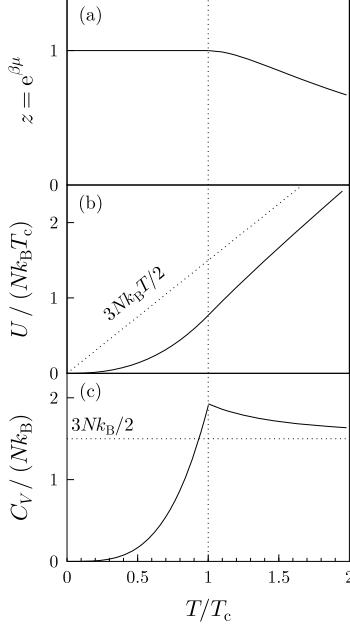


Fig. 46: Bose Gas Escape Velocity, Internal Energy, and Heat Capacity near BEC Temperature

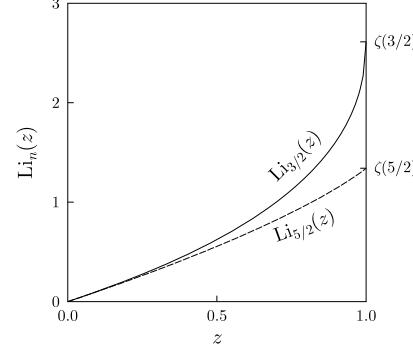
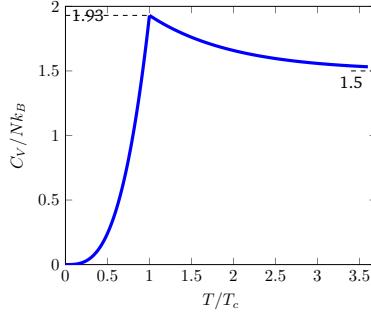


Fig. 47: Common Multi-Logarithmic Functions



According to the grand partition function of the Bose gas Eq. 5.31, Eq. 5.33 can be obtained (note the contributions of the ground state and excited state separately)

$$\ln \Xi = -\ln(1 - \lambda) + V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \text{Li}_{5/2}^+(\lambda) = -\ln(1 - \lambda) + \frac{V}{\lambda_T^3} \text{Li}_{5/2}^+(\lambda) \quad (5.64)$$

From the grand partition function, the physical quantities internal energy U , pressure p , and entropy S are obtained (using Eq. 5.54b)

(1) $T > T_c$, normal phase: $\lambda = e^{-\alpha} = e^{\beta\mu} < 1$

$$U = -\frac{\partial}{\partial \beta} \ln \Xi = \frac{3k_B T}{2} V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \text{Li}_{5/2}^+(\lambda) = \frac{3}{2} \frac{k_B T V}{\lambda_T^3} \text{Li}_{5/2}^+(\lambda) \quad (5.65a)$$

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln \Xi = \frac{k_B T}{\lambda_T(T)^3} \text{Li}_{5/2}^+(\lambda) = \frac{N k_B T}{V} \frac{\text{Li}_{5/2}^+(\lambda)}{\text{Li}_{3/2}^+(\lambda)} \quad (5.65b)$$

$$S = k_B \ln \Xi - \mu N/T + U/T = \frac{5}{2} \frac{k_B V}{\lambda_T^3} \text{Li}_{5/2}^+(\lambda) - \frac{V}{\lambda_T^3} \text{Li}_{3/2}^+(\lambda) k_B \ln \lambda \quad (5.65c)$$

(2) $T < T_c$, BEC condensed phase: $\lambda = e^{-\alpha} = e^{\beta\mu} = 1$, $\mu = 0$, $U_g = S_g = 0$, Using Eq. 5.57, Eq. 5.58

$$N_{ex} = \frac{V}{\lambda_T^3} \text{Li}_{3/2}^+(1) = N \left(\frac{T}{T_c} \right)^{3/2}, \quad N_g = N - N_{ex} \quad (5.66)$$

The physical quantities become

$$U = \frac{3}{2} \frac{k_B T V}{\lambda_T^3} \text{Li}_{5/2}^+(1) = 2.01 \frac{k_B T V}{\lambda_T^3} \quad (5.67a)$$

$$p = \frac{k_B T}{\lambda_T^3} \text{Li}_{5/2}^+(1) = \frac{N_{ex} k_B T}{V} \frac{\zeta(5/2)}{\zeta(3/2)} = 0.51 \frac{N_{ex} k_B T}{V} \quad (5.67b)$$

$$S = \frac{5k_B V}{2\lambda_T^3} \text{Li}_{5/2}^+(1) = \frac{5N_{ex} k_B}{2} \frac{\text{Li}_{5/2}^+(1)}{\text{Li}_{3/2}^+(1)} = 1.28 N_{ex} k_B \quad (5.67c)$$

By comparing the pressure of the BEC state and the normal state, it can be known that the pressure of the Bose gas in the BEC phase is independent of volume, and the compressibility is infinite. Considering the specific volume $v = V/N = 1/n$, since $n \propto T^{3/2}$, the phase transition curve $p \propto T^{5/2} \propto n^{5/3}$

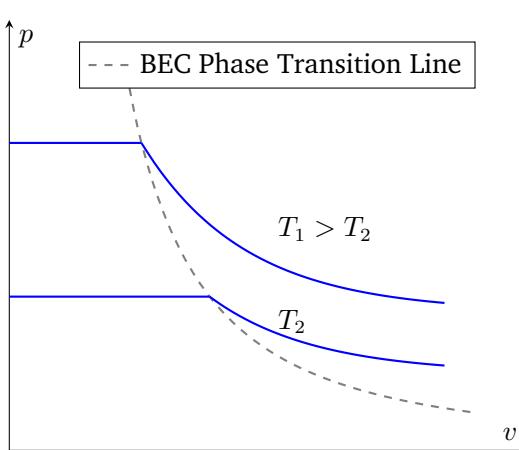


Fig. 48: Low Temperature Bose Gas $p - v$ Phase Diagram,
Below the dashed line is BEC State

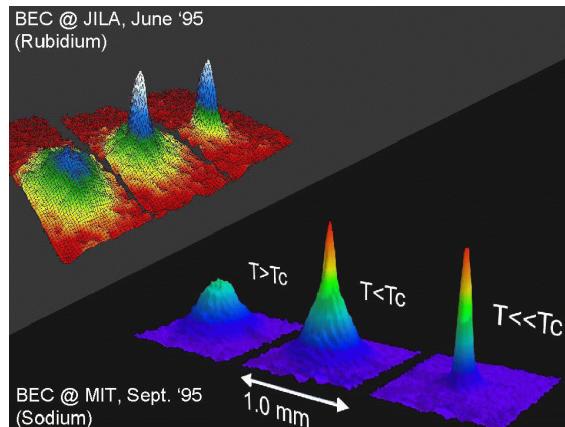


Fig. 49: Utilizing Laser Cooling and Magnet Trap Evaporation Methods to Cool Rubidium and Sodium Atoms, From Left to Right, Condensation Progressively Completes

Next, discuss the latent heat of the phase transition process

$$L = T \Delta S = \frac{5k_B T}{2} \frac{\text{Li}_{5/2}^+(1)}{\text{Li}_{3/2}^+(1)} \quad (5.68)$$

The BEC phase transition satisfies the Clapeyron equation Eq. 3.70

$$\frac{dp}{dT} = \frac{5p}{2T} = \frac{5k_B}{2\lambda_T^3(T)} \text{Li}_{5/2}^+(1) = \frac{L}{T \Delta v} \quad (5.69)$$

5.2.3 Revisiting Photon/Phonon Gas

According to the dispersion relation and energy relation of the photon gas

$$\mathbf{p} = \hbar \mathbf{k}, \quad \omega = c \mathbf{k}, \quad \varepsilon(\mathbf{p}) = \hbar \omega = cp \quad (5.70)$$

Based on the spin degree of freedom $\omega_s = 2$, its energy state density is obtained

$$\begin{aligned} g(\varepsilon) &= 2 \int \delta(\varepsilon - cp) \frac{d^3 p d^3 r}{h^3} \\ &= \frac{2V}{h^3} 4\pi \int_0^\infty \delta(\varepsilon - cp) p^2 dp = \frac{8\pi V}{h^3} \frac{p^2}{c} \Big|_{p=\varepsilon/c} = \frac{8\pi V \varepsilon^2}{h^3 c^3} \end{aligned} \quad (5.71)$$

And the state density

$$g(\omega) = g(\varepsilon) \frac{d\varepsilon}{d\omega} = \frac{8\pi V (\hbar\omega)^2}{c^3 h^3} \hbar d\omega = \frac{V \omega^2}{\pi^2 c^3} \quad (5.72)$$

Using the Planck distribution for photons Eq. 4.178, the Planck law (energy density per unit energy interval) is obtained

$$u(\omega, T) = \frac{U(\omega)}{V} = \varepsilon g(\omega) f(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} \quad (5.73)$$

In the high-frequency and low-frequency regions, the Wien displacement law and Rayleigh-Jeans law can be obtained $u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} = u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} =$

$$\text{Rayleigh-Jeans Law: } \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\beta\hbar\omega} = \frac{k_B T \omega^2}{\pi^2 c^3}, \quad \hbar\omega \ll k_B T \quad (5.74a)$$

$$\text{Wien Displacement Law: } \frac{\hbar\omega^3}{\pi^2 c^3} e^{-\hbar\omega/k_B T}, \quad \hbar\omega \gg k_B T \quad (5.74b)$$

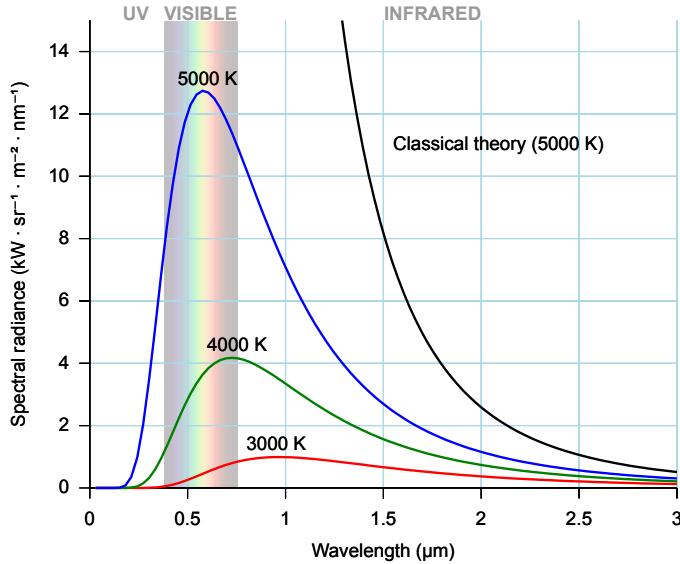


Fig. 50: Black Body Radiation Unit Energy Interval Energy Density and Wavelength Relationship

The energy density inside the cavity is

$$\begin{aligned} u(T) &= \int_0^\infty u(\omega, T) d\omega = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \\ &= \frac{\hbar}{\pi^2 c^3} (\beta\hbar)^{-4} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\hbar}{\pi^2 c^3} (\beta\hbar)^{-4} \sum_l \frac{3!}{l^4} = \frac{\pi^2 k_B^4 T^4}{15 c^3 \hbar^3} \end{aligned} \quad (5.75)$$

Here, using $\sum_l \frac{3!}{l^4} = \frac{6\pi^4}{90}$, the corresponding energy flux density returns to the Stefan-Boltzmann law Eq. 2.50

$$J(\omega, T) = \frac{c}{4} u(\omega, T) \Rightarrow J(T) = \frac{c}{4} u(T) = \frac{\pi^2 k_B^4 T^4}{60 c^3 \hbar^3} = \sigma T^4 \quad (5.76)$$

In the discussion of Eq. 5.75, an integral formula is given, which will also be used in the Debye model Eq. 4.206, and a proof is provided here

$$\begin{aligned} I_n &= \int_0^\infty \frac{x^n}{e^x - 1} dx = \int_0^\infty x^n \frac{e^{-x}}{1 - e^{-x}} dx \\ &= \int_0^\infty x^n e^{-x} \sum_{p=0}^\infty e^{-px} dx = \sum_{p=1}^\infty \int_0^\infty x^n e^{-px} dx \\ &= \sum_{p=1}^\infty \frac{1}{p^{n+1}} \int_0^\infty x^{n+1-p} e^{-x} dx = \zeta(n+1)\Gamma(n+1) = n! \zeta(n+1) \end{aligned} \quad (5.77)$$

The Debye function can be obtained, thus allowing for the discussion of solids, as detailed in Subsubsec. 4.5.2.

$$D\left(\frac{T}{\Theta_D}\right) = \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx = \begin{cases} \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} & T \ll \Theta_D \\ \int_0^{\Theta_D/T} \frac{x^3}{x} dx = \frac{1}{3} \left(\frac{\Theta_D}{T}\right)^3 & T \gg \Theta_D \end{cases} \quad (5.78)$$

The logarithm of the grand partition function of the photon gas $\ln \Xi$

$$\begin{aligned} \ln \Xi &= -\omega_s \int \frac{d^3 p d^3 r}{h^3} \ln(1 - e^{-\beta\varepsilon}) = -\frac{V}{\pi^2 \hbar^3} \int dp p^2 \ln\left(1 - e^{-\frac{pc}{k_B T}}\right) \\ &= -\frac{V}{\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3 \int dx x^2 \ln(1 - e^{-x}) \\ &= \frac{V \pi^2}{45} \left(\frac{k_B T}{\hbar c}\right)^3 = \frac{\beta U(T, V)}{3} = \frac{u(T)}{3k_B T} V \end{aligned} \quad (5.79)$$

Where the dimensionless momentum is defined as $x = \frac{pc}{k_B T}$, using the distribution integral $\int_a^b u(x)v'(x)dx = [u(x)v(x)]_a^b - \int_a^b u'(x)v(x)dx$ to obtain

$$\int_0^\infty dx x^2 \ln(1 - e^{-x}) = \frac{x^3}{3} \ln(1 - e^{-x}) \Big|_0^\infty - \frac{1}{3} \int_0^\infty \frac{x^3}{e^x - 1} dx = -\frac{\pi^4}{45} \quad (5.80)$$

The grand potential J of the photon gas is obtained in two ways

$$J = -k_B T \ln \Xi = -\frac{\pi^2}{45} \frac{k^4 T^4}{\hbar^3 c^3} V \quad (5.81a)$$

$$J = -pV = -V \frac{\omega_s}{h^3} \int d^3 p \left(\frac{p^2 c^2}{3\varepsilon}\right) \frac{1}{e^{\varepsilon/k_B T} - 1} \quad (5.81b)$$

For the photon gas, the chemical potential $\mu = 0$, thus $F = J$, according to $dJ = -SdT - pdV = dF$, the various physical quantities are

$$S = - \left(\frac{\partial J}{\partial T} \right)_V = \frac{4\pi^2}{45} \frac{k^4 T^3}{\hbar^3 c^3} V, \quad (5.82a)$$

$$p = - \left(\frac{\partial J}{\partial V} \right)_T = \frac{\pi^2}{45} \frac{k^4 T^4}{\hbar^3 c^3}, \quad (5.82b)$$

$$U = J + TS = \frac{\pi^2}{15} \frac{k^4 T^4}{\hbar^3 c^3} V \quad (5.82c)$$

It can be verified that the photon gas satisfies the relativistic equation of state Eq. 5.26, i.e., $p = \frac{1}{3}u$. Next, discuss the partition function of relativistic gases, the single-particle partition function can be written as

$$\begin{aligned} Z_1 &= \int d^3 k g(k) e^{-\beta \varepsilon} = \int_0^{+\infty} \frac{V \cdot 4\pi k^2 dk}{(2\pi)^3} e^{-\beta(\hbar ck)} \\ &= \frac{V}{2\pi^2} \left(\frac{1}{\beta \hbar c} \right)^3 \int_0^\infty e^{-x} x^2 dx = \frac{V}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 = \frac{V}{\Lambda^3} \end{aligned} \quad (5.83)$$

Thus defining the thermal wavelength Λ of massless particles or extremely relativistic gases

$$\Lambda = \frac{\hbar c \pi^{2/3}}{k_B T} = \frac{\hbar c}{2\pi^{1/3} k_B T} \quad (5.84)$$

The logarithm of the N-particle partition function is obtained

$$Z_N = \frac{Z_1^N}{N!}, \quad \ln Z_N = N \ln V + 3N \ln T + \text{const.} \quad (5.85)$$

Thus obtaining the internal energy

$$U = - \frac{\partial \ln Z_N}{\partial \beta} = 3Nk_B T \quad (5.86)$$

Free energy

$$F = -k_B T \ln Z_N = -k_B T N \ln V - 3Nk_B T \ln T - k_B T \times \text{const.} \quad (5.87)$$

Thus obtaining the pressure

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{Nk_B T}{V} = nk_B T \quad (5.88)$$

The expression for enthalpy is

$$H = U + pV = 4Nk_B T \quad (5.89)$$

In cases where the number of particles is large, using Stirling's approximation to obtain the partition function

$$\ln Z_N = N \ln V - 3N \ln \Lambda - N \ln N + N = N \ln \left(\frac{1}{n\Lambda^3} \right) + N \quad (5.90a)$$

Table 5: Thermodynamic Characteristic Functions and Grand Partition Function Relationship

State Function	Non-Relativistic Expression	Extremely Relativistic Expression
State Function	Non-Relativistic Expression	Extremely Relativistic Expression
Z_1	$\frac{V}{\lambda_T^3}, \quad \lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$	$\frac{V}{\Lambda^3}, \quad \Lambda = \frac{\hbar c \pi^{2/3}}{k_B T}$
U	$\frac{3}{2} N k_B T$	$3 N k_B T$
H	$\frac{5}{2} N k_B T$	$4 N k_B T$
p	$\frac{2}{3} u$	$\frac{1}{3} u$
F	$N k_B T [\ln(n\lambda_T^3) - 1]$	$N k_B T [\ln(n\Lambda^3) - 1]$
S	$N k_B \left[\frac{5}{2} - \ln(n\lambda_T^3) \right]$	$N k_B \left[\frac{5}{2} - \ln(n\Lambda^3) \right]$
G	$N k_B T \ln(n\lambda_T^3)$	$N k_B T \ln(n\Lambda^3)$
Adiabatic Process	$p V^{\frac{5}{3}} = \text{const.}$	$p V^{\frac{4}{3}} = \text{const.}$

The wave function of the Fermi system can be given by Eq. 4.21, according to the Pauli exclusion principle, fermions will occupy energy levels one by one until all fermions are occupied, and the equal energy surface is a sphere. In momentum reciprocal space, the ground state of the system is a Fermi sphere, whose surface is an equal energy surface, called the Fermi surface, corresponding to the Fermi energy. The Fermi surface is the boundary between occupied and unoccupied states. For a low-energy excited state, a particle jumps from inside the Fermi sphere to the outside, leaving a hole inside the Fermi sphere, called a particle-hole excitation. The energy of the system's excited state is expressed as the sum of the energy of particle-type excitations and hole-type excitations. The physical quantities related to the Fermi surface are: Fermi temperature, Fermi energy, Fermi momentum, Fermi wave vector, Fermi velocity

$$k_B T_F = \varepsilon_F, \quad p_F = \sqrt{2m\varepsilon_F}, \quad k_F = p_F/\hbar, \quad v_F = p_F/m \quad (5.91)$$

5.3.1 Strongly Degenerate Fermi Gas

According to the discussion in Subsec. 5.2, the condition for strong degeneracy satisfies the fugacity

$$\lambda = e^{\beta\mu} \gg 1 \Leftrightarrow \mu \gg k_B T \quad (5.92)$$

Thus, it is known that strong degeneracy requires the system to be in conditions of low mass, low temperature, and high density. Examples include electrons in metals, neutron stars, and liquid ^3He .

When $T = 0$ K, the low energy states are completely occupied, and the distribution function becomes a step function

$$f(\varepsilon_s, T = 0) = \begin{cases} 1 & , \varepsilon_s < \mu \\ 0 & , \varepsilon_s > \mu \end{cases} = \Theta(\mu - \varepsilon_s) \quad (5.93)$$

The chemical potential at zero temperature is equal to the degenerate Fermi energy

$$\mu(T = 0 \text{ K}) = \varepsilon_F \quad (5.94)$$

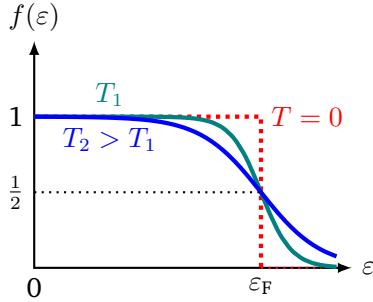


Fig. 51: Distribution function of the Fermi system

When $T \neq 0$ K, for $\varepsilon < \mu$, $f(\varepsilon) < 1$, some particles are excited out, reducing the number of

particles below the Fermi surface. The number of hole-type excitations is $f_h = 1 - f(\varepsilon)$; for $\varepsilon > \mu$, $f(\varepsilon) > 0$, some particles are excited out, and the number of particle-type excitations is $f(\varepsilon)$.

The form of the grand partition function for the Fermi system is given by

$$\ln \Xi = \sum_l \omega_l \ln [1 + e^{(\mu-\varepsilon)/k_B T}] = \omega_s \int \frac{V d^3 p}{h^3} \ln [1 + e^{(\mu-\varepsilon)/k_B T}] \quad (5.95)$$

Thus, the grand potential is obtained

$$J = -pV = -k_B T \ln \Xi = -V k_B T \int \frac{V d^3 p}{h^3} \ln [1 + e^{(\mu-\varepsilon)/k_B T}] \quad (5.96)$$

According to Eq. 5.21c, Eq. 5.21b, and considering the electron spin degeneracy of 2, the particle number density, energy density, and pressure (degenerate pressure) are obtained

$$n = \int \omega_s \frac{d^3 p}{h^3} f(\varepsilon, \mu) = \frac{8\pi}{h^3} \int_0^{p_F} p^2 dp = \frac{8\pi}{3h^3} p_F^3 \quad (5.97a)$$

$$u = \int \omega_s \frac{d^3 p}{h^3} f(\varepsilon, \mu) \varepsilon = \frac{8\pi}{h^3} \int_0^{p_F} \varepsilon(p) p^2 dp \quad (5.97b)$$

$$p = \int \omega_s \frac{d^3 p}{h^3} f(\varepsilon, \mu) \left(\frac{p^2 c^2}{3\varepsilon} \right) = \frac{8\pi}{h^3} \int_0^{p_F} \frac{p^2 c^2}{3\varepsilon(p)} p^2 dp \quad (5.97c)$$

Here, Eq. 5.97a gives the relationship between Fermi momentum and particle number density, $p_F \sim n^{1/3}$

$$p_F = \left(\frac{3}{8\pi} \right)^{1/3} h n^{1/3} \sim n^{1/3} \quad (5.98)$$

Special relativity gives the energy

$$\varepsilon^2(p) = m^2 c^4 + p^2 c^2 \quad (5.99)$$

The following discusses three cases: non-relativistic, extreme relativistic, and general relativistic.

(1) In the non-relativistic case ($p_F c \ll \varepsilon_F$), the energy-momentum relationship is

$$\varepsilon(p) \simeq mc^2 + \frac{p^2}{2m} \quad (5.100)$$

The non-relativistic energy density and pressure, applying Eq. 5.98

$$u = nmc^2 + \frac{4\pi}{5h^3} \frac{p_F^5}{m} = \frac{3^{5/3}}{40\pi^{2/3}} \frac{h^2}{m} n^{5/3} \sim n^{5/3} \quad (5.101a)$$

$$p = \frac{8\pi}{15h^3} \frac{p_F^5}{m} = \frac{3^{2/3}}{20\pi^{2/3}} \frac{h^2}{m} n^{5/3} = \frac{2}{3} u \sim n^{5/3} \quad (5.101b)$$

(2) In the extreme relativistic case, where the electron density is high and the Fermi energy is much greater than the electron rest energy, i.e., $p_F c \gg \varepsilon_F$, the energy-momentum relationship is

$$\varepsilon(p) \simeq pc \quad (5.102)$$

The extreme relativistic energy density and pressure, applying Eq. 5.98

$$u = \frac{2\pi c}{h^3} p_F^4 = \frac{3^{4/3}}{8\pi^{1/3}} hc n^{4/3} \sim n^{4/3} \quad (5.103a)$$

$$p = \frac{1}{3} u = \frac{3^{1/3}}{8\pi^{1/3}} hc n^{4/3} \sim n^{4/3} \quad (5.103b)$$

(3) In the general relativistic case, the energy density integral needs to be considered

$$u_e = \frac{8\pi}{h^3} \int_0^{p_F} \sqrt{m_e^2 c^4 + p^2 c^2} p^2 \, dp = \frac{8\pi}{h^3} m_e^4 c^5 \int_0^{\xi_F} \sqrt{1 + \tilde{p}_F^2} \tilde{p}_F^2 d\tilde{p}_F \quad (5.104)$$

Here, using the dimensionless transformation $\tilde{p} = p/m_e c = \sinh \frac{\xi}{4}$, $\xi_F = 4 \sinh^{-1} \frac{p_F}{m_e c}$, and using the electron Compton wavelength $\lambda_e = \frac{h}{m_e c}$, the general relativistic energy density integral becomes

$$\begin{aligned} u_e &= \frac{8\pi}{h^3} m_e^4 c^5 \int_0^{\xi_F} \sqrt{1 + \sinh^2(\xi/4)} \sinh^2(\xi/4) d\sinh(\xi/4) = \frac{8\pi}{h^3} m_e^4 c^5 \int_0^{\xi_F} \frac{1}{16} \sinh^2(\xi/2) d\xi \\ &= \frac{8\pi}{h^3} m_e^4 c^5 \frac{1}{64} (e^\xi - e^{-\xi} - 2\xi) \Big|_0^{\xi_F} = \frac{8\pi}{h^3} m_e^4 c^5 \frac{1}{32} (\sinh \xi_F - \xi_F) = \frac{1}{2^5 \pi^2} \frac{m_e c^2}{\lambda_e^3} (\sinh \xi_F - \xi_F) \end{aligned} \quad (5.105)$$

The general relativistic pressure is

$$\begin{aligned} p_e &= \frac{8\pi}{h^3} m_e^4 c^5 \int_0^{p_F} \frac{p^2 c^2}{3\sqrt{m_e^2 c^4 + p^2 c^2}} p^2 \, dp = \frac{2\pi}{3h^3} m_e^4 c^5 \int_0^{\xi_F} \sinh^4(\xi/4) d\xi \\ &= \frac{\pi}{24h^3} m_e^4 c^5 (e^\xi - e^{-\xi} - 8e^{\xi/2} + 8e^{-\xi/2} + 6\xi) \Big|_0^{\xi_F} = \frac{1}{2^5 \cdot 3\pi^2} \frac{m_e c^2}{\lambda_e^3} [\sinh \xi_F - 8 \sinh(\xi_F/2) + 3\xi_F] \end{aligned} \quad (5.106)$$

And the general relativistic electron number density is

$$n_e = \frac{1}{3\pi^2} \frac{1}{\lambda_c^3} \sinh^3(\xi_F/4) \quad (5.107)$$

When $\xi_F \ll 1$, in the non-relativistic case, the electron number density, energy density, and pressure are

$$n_e \simeq \frac{1}{2^6 \cdot 3\pi^2} \frac{1}{\lambda_c^3} \xi_F^3 \quad (5.108a)$$

$$u_e \simeq \frac{1}{2^6 \cdot 3\pi^2} \frac{m_e c^2}{\lambda_c^3} \xi_F^3 \sim n \quad (5.108b)$$

$$p_e \simeq \frac{1}{2^{10} \cdot 15\pi^2} \frac{m_e c^2}{\lambda_c^3} \xi_F^5 \sim n^{5/3} \quad (5.108c)$$

When $\xi_F \gg 1$, in the extreme relativistic case, the electron number density, energy density, and pressure are

$$n_e \simeq \frac{1}{2^3 \cdot 3\pi^2} \frac{1}{\lambda_e^3} e^{\frac{3\xi_F}{4}} \quad (5.109a)$$

$$u_e \simeq \frac{1}{2^6 \pi^2} \frac{m_e c^2}{\lambda_e^3} e^{\xi_F} \sim n^{4/3} \quad (5.109b)$$

$$p_e \simeq \frac{1}{2^6 \cdot 3\pi^2} \frac{m_e c^2}{\lambda_e^3} e^{\xi_F} \sim n^{4/3} \quad (5.109c)$$

5.3.2 Electrons in Metals

The electron number density can be estimated as follows

$$n_e = N_A \frac{Z\rho}{A} \quad (5.110)$$

where Z is the atomic number, ρ is the mass density of the metal, and A is the atomic mass. For example, for copper, $\rho_{\text{Cu}} = 8.9 \text{ g cm}^{-3}$, atomic mass $A = 63$, the electron number density is: $n_e = 8.5 \times 10^{22} \text{ cm}^{-3}$. According to Eq. 5.98, the Fermi momentum is $p_F = 2.7 \text{ keV}$. Since $p_F \ll m_e$, the electrons in metals are non-relativistic. The Fermi energy is $E_F = 7.1 \text{ eV} = 8.2 \times 10^4 \text{ K}$, which is much higher than room temperature, so the electrons in metals are strongly degenerate (using the relationship between electron volts and temperature $1 \text{ eV} = 1.16 \times 10^4 \text{ K}$).

Considering the distribution of strongly degenerate gases, the particle number distribution

$$N = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon = \int_0^\varepsilon g(\varepsilon) d\varepsilon \Rightarrow N'(\varepsilon) = g(\varepsilon) \quad (5.111)$$

The form of the partition function and particle number distribution is obtained

$$\begin{aligned} \ln \Xi &= \int_0^\infty \ln [1 + e^{-\beta(\varepsilon-\mu)}] g(\varepsilon) d\varepsilon = \int_0^\infty \ln [1 + e^{-\beta(\varepsilon-\mu)}] dN(\varepsilon) \\ &= N(\varepsilon) \ln [1 + e^{-\beta(\varepsilon-\mu)}] \Big|_0^\infty - \int_0^\infty N(\varepsilon) d\ln [1 + e^{-\beta(\varepsilon-\mu)}] = \beta \int_0^\infty \frac{N(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1} d\varepsilon = \beta \int_0^\infty N(\varepsilon) f(\varepsilon) d\varepsilon \end{aligned} \quad (5.112)$$

We can perform some physical quantity integral operations by calculating the following integral

$$\begin{aligned} I &= \int_0^\infty I(\varepsilon) f(\varepsilon) d\varepsilon = \int_0^\infty I(\varepsilon) [f(\varepsilon) - \Theta(\varepsilon - \mu) + \Theta(\varepsilon - \mu)] d\varepsilon \\ &= \int_0^\mu I(\varepsilon) d\varepsilon + \int_\mu^\infty I(\varepsilon) f(\varepsilon) d\varepsilon - \int_0^\mu I(\varepsilon) [1 - f(\varepsilon)] d\varepsilon \end{aligned} \quad (5.113)$$

These three terms correspond to three contributions: Fermi sphere contribution + particle-type excitation contribution + hole-type excitation contribution. Continue to simplify the integral

$$\begin{aligned} I &= I_0 + \int_\mu^\infty \frac{I(\varepsilon)}{e^{(\varepsilon-\mu)/k_B T} + 1} d\varepsilon - \int_0^\mu \frac{I(\varepsilon)}{e^{(\mu-\varepsilon)/k_B T} + 1} d\varepsilon = I_0 + \int_0^\infty \frac{I(\mu + \varepsilon) - I(\mu - \varepsilon)}{e^{\varepsilon/k_B T} + 1} d\varepsilon + \int_\mu^\infty \frac{I(\mu - \varepsilon)}{e^{\varepsilon/k_B T} + 1} d\varepsilon (\sim e^{-\mu/k_B T}) \\ &= I_0 + 2I'(\mu) \int_0^\infty \frac{\varepsilon}{e^{\varepsilon/k_B T} + 1} d\varepsilon + 2 \frac{I^{(3)}(\mu)}{3!} \int_0^\infty \frac{\varepsilon^3}{e^{\varepsilon/k_B T} + 1} d\varepsilon + \dots = I_0 + 2I' (k_B T)^2 \int_0^\infty \frac{x}{e^x + 1} dx + 2 \frac{I^{(3)} (k_B T)^4}{3!} \end{aligned} \quad (5.114)$$

Here, using the Sommerfeld expansion, there is an integral expression

$$C_n = n! \left[\left(1 - \frac{1}{2^{n+1}} \right) \zeta(n+1) - \frac{1}{2^{n+1}} \zeta(n+1) \right] = n! \left(1 - \frac{1}{2^n} \right) \zeta(n+1) \quad (5.115)$$

The integral expression finally becomes the Sommerfeld expansion formula

$$\begin{aligned} I &= \int_0^\infty I(\varepsilon) f(\varepsilon) d\varepsilon = I_0 + 2 \sum_{l=0}^{\infty} \frac{I^{(2l+1)} (k_B T)^{2l+2}}{(2l+1)!} C_{2l+1} \\ &= I_0(\mu) + 2 \sum_{l=0}^{\infty} I^{(2l+1)}(\mu) (k_B T)^{2l+2} \left[1 - \frac{1}{2^{2l+1}} \right] \zeta(2l+2) \\ &= \int_0^\mu I(\varepsilon) d\varepsilon + \frac{\pi^2 (k_B T)^2}{6} I'(\mu) + \frac{7\pi^4 (k_B T)^4}{360} I^{(3)}(\mu) + \dots \end{aligned} \quad (5.116)$$

Expansion of the particle number

$$\begin{aligned} N &= \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon = \int_0^\mu g(\varepsilon) f(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + \dots \\ &= \int_0^{\varepsilon_F} g(\varepsilon) + \int_{\varepsilon_F}^\mu g(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + \dots \\ &\simeq N + g(\varepsilon_F)(\mu - \varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \end{aligned} \quad (5.117)$$

Change in chemical potential

$$\begin{aligned} \Delta\mu &= \mu - \varepsilon_F \simeq -\frac{\pi^2}{6} (k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)} \\ &= -\frac{\pi^2}{6} (k_B T)^2 [\ln g(\varepsilon_F)]' = -\frac{\pi^2}{12} \frac{(k_B T)^2}{\varepsilon_F} \end{aligned} \quad (5.118)$$

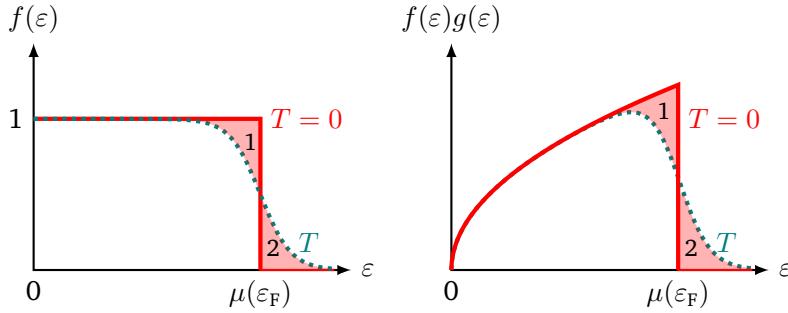


Fig. 52: Distribution function, particle number distribution function, where the density of states $g(\varepsilon) \propto \varepsilon^{\frac{1}{2}}$

It can be concluded that thermal excitation is symmetrically distributed along the energy, $f(\mu + \Delta\varepsilon) = 1 - f(\mu - \Delta\varepsilon)$, with areas 1 and 2 being equal; however, the density of states for the total number of particles is asymmetric. To maintain the total number of particles constant, the chemical potential must change with temperature, influenced by the derivative of the density of states, resulting in different trends of the chemical potential μ with temperature.

$$\Delta\mu \simeq -\frac{\pi^2}{6} \frac{g'(\varepsilon_F)}{g(\varepsilon_F)} (k_B T)^2 \quad (5.119)$$

Next, calculate the internal energy $U = U_0 + \Delta U$

$$\begin{aligned} U &\simeq \int_0^\mu g(\varepsilon) \varepsilon d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 [g(\mu)\mu]' \simeq \int_0^{\varepsilon_F} g(\varepsilon) \varepsilon d\varepsilon + [g(\varepsilon_F) \varepsilon_F] \Delta\mu + \frac{\pi^2}{6} (k_B T)^2 [g(\varepsilon_F) \varepsilon_F]' \\ &= U_0 + g(\varepsilon_F) \varepsilon_F \left[-\frac{\pi^2}{6} (k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)} \right] + \frac{\pi^2}{6} (k_B T)^2 [g'(\varepsilon_F) \varepsilon_F + g(\varepsilon_F)] = U_0 + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) \end{aligned} \quad (5.120)$$

The heat capacity of free electrons is obtained

$$C_e = \frac{\partial \Delta U}{\partial T} = \frac{\pi^2}{3} g(\varepsilon_F) k_B^2 T = \frac{\pi^2}{2} \frac{N}{\varepsilon_F} k_B^2 T = \frac{\pi^2}{2} N k_B \frac{T}{T_F} \quad (5.121)$$

Considering strongly degenerate electrons, the energy range of electrons that can be thermally excited is approximately: $\varepsilon_F - k_B T < \varepsilon \leq \varepsilon_F$, i.e., the proportion of electrons that can be effectively

thermally excited: $k_{\text{B}}T/\mu$, each thermally excited electron contributes to the specific heat: $3k_{\text{B}}/2$, therefore, the contribution of strongly degenerate electron gas to the specific heat is:

$$C_V = \frac{3}{2} n_e k_{\text{B}} \frac{k_{\text{B}} T}{\mu} \quad (5.122)$$

Considering that electrons in metals are non-relativistic particles, the pressure of the electron gas is:

$$p_e = \frac{8\pi}{h^3} \int_0^\infty \left(\frac{p^2}{3m} \right) \frac{p^2 \, dp}{e^{\frac{\varepsilon - \mu}{k_{\text{B}}T}} + 1} = \frac{16\sqrt{2}\pi}{3h^3} m^{3/2} \int_0^\infty \frac{\varepsilon^{3/2} \, d\varepsilon}{e^{\frac{\varepsilon - \mu}{k_{\text{B}}T}} + 1} = \frac{16\sqrt{2}\pi}{3h^3} m^{3/2} \mu^{5/2} \int_0^\infty \frac{\tilde{\varepsilon}^{3/2} \, d\tilde{\varepsilon}}{e^{\frac{\tilde{\varepsilon}-1}{\tilde{T}}} + 1} \quad (5.123)$$

Here, the dimensionless electron energy and temperature are $\tilde{\varepsilon} = \varepsilon/\mu$, $\tilde{T} = k_{\text{B}}T/\mu$, and the integral expression is:

$$\begin{aligned} I &\equiv \int_0^\infty \frac{\tilde{\varepsilon}^{3/2} \, d\tilde{\varepsilon}}{e^{\frac{\tilde{\varepsilon}-1}{\tilde{T}}} + 1} = \tilde{T} \left(\int_{-1/\tilde{T}}^0 + \int_0^\infty \right) \frac{(1 + \tilde{T}x)^{3/2} \, dx}{e^x + 1} \\ &= \tilde{T} \int_0^{1/\tilde{T}} \frac{(1 - \tilde{T}x)^{3/2} \, dx}{e^{-x} + 1} + \tilde{T} \int_0^\infty \frac{(1 + \tilde{T}x)^{3/2} \, dx}{e^x + 1} \\ &= \tilde{T} \int_0^{1/\tilde{T}} (1 - \tilde{T}x)^{3/2} \left(1 - \frac{1}{e^x + 1} \right) dx + \tilde{T} \int_0^\infty \frac{(1 + \tilde{T}x)^{3/2} \, dx}{e^x + 1} \\ &= \tilde{T} \int_0^{1/\tilde{T}} (1 - \tilde{T}x)^{3/2} \, dx + \tilde{T} \int_0^\infty \frac{(1 + \tilde{T}x)^{3/2} - (1 - \tilde{T}x)^{3/2}}{e^x + 1} \, dx \\ &= \int_0^1 y^{3/2} \, dy + 3\tilde{T}^2 \int_0^\infty \frac{x \, dx}{e^x + 1} = \frac{2}{5} \left(1 + \frac{5\pi^2}{8} \tilde{T}^2 \right) \end{aligned} \quad (5.124)$$

Thus, the pressure of strongly degenerate electron gas is obtained

$$p_e = \frac{32\sqrt{2}\pi}{15h^3} m_c^{3/2} \mu^{5/2} \left[1 + \frac{5\pi^2}{8} \left(\frac{k_{\text{B}}T}{\mu} \right)^2 \right] \equiv C \mu^{5/2} \left[1 + \frac{5\pi^2}{8} \left(\frac{k_{\text{B}}T}{\mu} \right)^2 \right] \quad (5.125)$$

From the grand potential expression, the expressions for particle number, entropy, and internal energy are obtained (ignoring higher-order terms of \tilde{T})

$$N_e = - \left(\frac{\partial J}{\partial \mu} \right)_{T,V} = V \left(\frac{\partial p}{\partial \mu} \right)_T = \frac{5}{2} C \mu^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{k_{\text{B}}T}{\mu} \right)^2 \right] V \quad (5.126a)$$

$$S_e = - \left(\frac{\partial J}{\partial T} \right)_{\mu,V} = V \left(\frac{\partial p}{\partial T} \right)_\mu = \frac{5\pi^2}{4} C k \mu^{3/2} \left(\frac{k_{\text{B}}T}{\mu} \right) V \quad (5.126b)$$

$$U = -p_e V + n_e \mu + TS_e = \frac{3}{2} C \mu^{5/2} \left[1 + \frac{5\pi^2}{8} \left(\frac{k_{\text{B}}T}{\mu} \right)^2 \right] V \quad (5.126c)$$

5.3.3 White Dwarfs/Neutron Stars

White dwarfs are a special type of celestial body, "white" refers to their surface temperature being higher than the Sun, "dwarf" refers to their luminosity being smaller than the Sun. The radius and density of Sirius B can be estimated. The luminosity of Sirius B is 1/18 of the Sun's luminosity, i.e., $L_{\text{WD}} = 0.026L_{\odot}$, with a temperature of $T = 2.5 \times 10^4 \text{ K} = 4.3T_{\odot}$, and the Sun's temperature is $T_{\odot} = 5772 \text{ K}$. According to the Stefan-Boltzmann law Eq. 2.73, the luminosity of a white dwarf is

$$L_{\text{WD}} = 4\pi R_{\text{WD}}^2 \sigma T_{\text{WD}}^4 \quad (5.127)$$

The ratio of the radius of Sirius B to the Sun's radius

$$\frac{R_{\text{WD}}}{R_{\odot}} = \left(\frac{L_{\text{WD}}}{L_{\odot}} \right)^{1/2} \left(\frac{T_{\odot}}{T_{\text{WD}}} \right)^2 \simeq 0.0084 \quad (5.128)$$

Thus, based on the Sun's radius $R_{\odot} = 7 \times 10^8 \text{ m}$, the radius of Sirius B is approximately $R_{\text{WD}} = 6 \times 10^6 \text{ m}$. According to Kepler's law, the mass of Sirius B is calculated to be $M_{\text{WD}} = 1.0M_{\odot}$, and the density can be estimated as

$$\frac{\rho_{\text{WD}}}{\rho_{\odot}} = \left(\frac{M_{\text{WD}}}{M_{\odot}} \right) \left(\frac{R_{\odot}}{R_{\text{WD}}} \right)^3 \simeq 1.7 \times 10^6 \quad (5.129)$$

White dwarfs and neutron stars can be collectively referred to as Fermi stars, as their internal pressure comes from the degeneracy pressure of Fermi gas. However, although these two types of stars have comparable masses, neutron stars have a radius 1800 times smaller and are denser than white dwarfs. The interior of a white dwarf is balanced by degeneracy pressure and gravity. Considering the effects of special relativity, as the density of a white dwarf increases, the Fermi energy of electrons increases and becomes extremely relativistic particles, reaching the mass limit, known as the Chandrasekhar limit.

Below, the Chandrasekhar limit is discussed using a helium white dwarf (or applicable to carbon-oxygen white dwarfs) as an example. First, under the zero-temperature approximation, the equation of state of white dwarf matter is obtained: $p = p(\rho)$ (not zero temperature is $p = p(\rho, T)$). It is assumed that the interior of a helium white dwarf is composed of helium ions and free electrons. To maintain the overall electrical neutrality of the star, one helium atom corresponds to two free electrons. The pressure of the white dwarf is provided by electrons, while the mass is provided by helium nuclei. The mass of helium nuclei can be evenly distributed to electrons, introducing the average molecular weight of electrons:

$$\mu_e = \frac{n_B}{n_c} = 2 \quad (5.130)$$

where n_B is the baryon helium nucleus number density, and n_c is the electron number density. The mass density of the matter is

$$\rho = n_B m_B = n_e \mu_e m_B = \frac{1}{3\pi^2} \left(\frac{p_{FC}}{\hbar c} \right)^3 \mu_e m_B \quad (5.131)$$

The Fermi momentum of electrons is solved

$$p_F = (3\pi^2)^{1/3} \hbar \mu_e^{-1/3} m_B^{-1/3} \rho^{1/3} \quad (5.132)$$

First, estimate the critical density ρ_c when electrons start to become relativistic. When electrons start to become relativistic, $p_F \sim mec$, the electron number density at this time is:

$$n_e = \frac{8\pi}{3h^3} p_F^3 = \frac{1}{3\pi^2} \left(\frac{m_e c}{\hbar} \right)^3 = \frac{1}{3\pi^2} \lambda_c^{-3} \simeq 5.87 \times 10^{35} \text{ m}^{-3} \quad (5.133)$$

In the above equation, $\lambda_d = \pi/m_ec = 3.86 \times 10^{-13}$ m is the Compton wavelength of electrons. The corresponding critical mass density is:

$$\rho_c = n_e \mu_e m_B = \frac{1}{3\pi^2} \frac{\mu_e m_B}{\lambda_c^3} = 9.80 \times 10^8 \mu_e \text{kgm}^{-3} \quad (5.134)$$

where $m_B = 1.67 \times 10^{-27}$ kg is the nucleon mass. Substituting $p_F = mec$ into Eq. 5.140b, the critical pressure inside the white dwarf when $\rho = \rho_c$ can be estimated as:

$$p_e \simeq \frac{0.77}{15\pi^2} \frac{m_e c^2}{\lambda_c^3} \simeq 7.37 \times 10^{17} \text{ Pa} \quad (5.135)$$

(1) When $\rho \ll \rho_c$, electrons are non-relativistic particles, and the pressure of dense matter is mainly electron degeneracy pressure (ignoring the contribution of atomic nuclei to the system pressure):

$$p = \frac{1}{15\pi^2} \frac{p_F^5}{\hbar^3 m_c} = \frac{(3\pi^2)^{2/3}}{5m_c} \frac{\hbar^2}{(\mu_e m_B)^{5/3}} \rho^{5/3} \equiv K \rho^{5/3} \quad (5.136)$$

In the core region where the mass density is low, the electrons in the core region are non-relativistic particles, and the electron degeneracy pressure has a constant exponential relationship with the mass density with an exponent of 5/3.

(2) When $\rho \gg \rho_c$, electrons are extremely relativistic particles, and the pressure of dense matter is mainly electron degeneracy pressure:

$$p = \frac{1}{12\pi^2} \frac{p_F^4 c}{\hbar^3} = \frac{(3\pi^2)^{1/3}}{4} \frac{\hbar c}{(\mu_e m_B)^{4/3}} \rho^{4/3} \equiv K \rho^{4/3} \quad (5.137)$$

In summary, under the two extreme conditions of low density ($\rho \ll \rho_c$) and high density ($\rho \gg \rho_c$), the equation of state of a white dwarf can be approximated as the following polytropic process form:

$$p = K \rho^\gamma \quad (5.138)$$

where K is a constant, and γ is the exponent, changing from $\frac{5}{3}$ to $\frac{4}{3}$, affecting the maximum mass of the white dwarf.

At any density, introduce the parameter

$$\xi_F \equiv 4 \sinh^{-1} \left(\frac{p_F}{me c} \right) = 4 \ln \left\{ \frac{p_F}{me c} + \left[1 + \left(\frac{p_F}{me c} \right)^2 \right]^{1/2} \right\} \quad (5.139)$$

According to Eq. 5.105, Eq. 5.106, the internal mass density and pressure of a white dwarf are obtained:

$$\rho = \frac{1}{3\pi^2} \frac{1}{\lambda_e^3} \mu_e m_B \sinh^3 \left(\frac{\xi_F}{4} \right) \quad (5.140a)$$

$$p = \frac{1}{2^5 \cdot 3\pi^2} \frac{m_e c^2}{\lambda_e^3} \left(\sinh \xi_F - 8 \sinh \frac{1}{2} \xi_F + 3 \xi_F \right) \quad (5.140b)$$

Next, we discuss the internal structure of a white dwarf: assuming perfect spherical symmetry, the internal pressure and gravity of the star reach hydrostatic equilibrium. Consider a thin shell with a radius of $(r - r + dr)$, the total mass of this shell is $dm(r)$:

$$dm(r) = \rho(r) 4\pi r^2 dr \quad (5.141)$$

The total pressure difference on the shell is:

$$dF_p = [p(r) - p(r + dr)] \cdot 4\pi r^2 \simeq -\frac{dp(r)}{dr} \cdot 4\pi r^2 dr \quad (5.142)$$

Additionally, the shell is subjected to the gravitational force of the total mass $m(r)$ within a sphere of radius r , which is:

$$dF_{\text{grav}} = -\frac{Gm(r)dm(r)}{r^2} \quad (5.143)$$

When the star's interior reaches hydrostatic equilibrium, $dF_p + dF_{\text{grav}} = 0$, thus obtaining the hydrostatic equilibrium equation:

$$\frac{dp(r)}{dr} = -\frac{Gm(r)\rho(r)}{r^2} \Rightarrow \frac{r^2}{\rho(r)} \frac{dp(r)}{dr} = -Gm(r) = -G \int_0^r 4\pi r^2 \rho(r) dr \quad (5.144)$$

Differentiating both sides of the equation with respect to radius r , we obtain the complete differential form of the hydrostatic equilibrium equation:

$$\frac{d}{dr} \left(\frac{r^2}{\rho(r)} \frac{dp(r)}{dr} \right) = -G \cdot 4\pi r^2 \rho(r) \quad (5.145)$$

The boundary conditions for this second-order differential equation are:

$$\rho(r=0) = \rho_0, \quad \frac{dp}{dr}(r=0) = 0 \quad (5.146)$$

This means that the mass density at the center of the star ρ_0 must be provided, and the total mass at the center of the star is zero, leading to a pressure gradient of zero at the center.

Assuming the equation of state inside the star is a unified polytropic equation $p = K\rho^\gamma$, substituting this polytropic equation into the hydrostatic equilibrium equation to solve the structure of the star, this problem is the famous polytropic sphere theory. First, the equation is non-dimensionalized.

$$\frac{\rho}{\rho_c} \equiv \theta^{\frac{1}{\gamma-1}} \quad (5.147)$$

The radius is non-dimensionalized using the parameter α , i.e.: $\frac{r}{\alpha} \equiv \xi$, where the constant

$$\alpha \equiv \left[\frac{K}{4\pi G} \left(\frac{\gamma}{\gamma-1} \right) \right]^{1/2} \rho_c^{(\gamma-2)/2} \quad (5.148)$$

The non-dimensionalized hydrostatic equilibrium equation (Lane-Emden equation, $n \equiv \frac{1}{\gamma - 1}$) is:

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left[\xi^2 \frac{d\theta}{d\xi} \right] = -\theta^n \quad (5.149)$$

The boundary conditions for the equation are: at $\xi = 0$, $\theta(\xi = 0) = 1$, and $\frac{d\theta}{d\xi}(\xi = 0) = 0$. The numerical solution of the equation requires continuous integration of the Lane-Emden equation from the center of the star $\xi = 0$ outward. For $n < 5$, the solution $\theta(\xi)$ decreases continuously with increasing radius ξ , and at a certain finite value $\xi = \xi^*$, $\theta(\xi^*) = 0$, which corresponds to reaching the surface of the star, and the radius of the star is:

$$R = \alpha \xi_n^* \quad (5.150)$$

The total mass of the star is:

$$M = \int_0^R 4\pi r^2 \rho(r) dr = 4\pi \rho_0 \alpha^3 \int_0^{\xi^*} \xi^2 \theta^n d\xi = 4\pi \rho_0^{\frac{(3\gamma-4)}{2}} \left(\frac{K\gamma}{4\pi G(\gamma-1)} \right)^{3/2} M_n^* \quad (5.151)$$

where M_n^* is the non-dimensional numerical integral:

$$M_n^* \equiv \int_0^{\xi^*} \xi^2 \theta^n d\xi = -\xi^2 \frac{d\theta}{d\xi} \Big|_{\xi=\xi_n^*} \quad (5.152)$$

According to Eq. 5.149, Eq. 5.152, eliminating ρ_0 , we obtain:

$$\left(\frac{GM}{M_n^*} \right)^{n-1} \left(\frac{R}{\xi_n^*} \right)^{3-n} = \frac{[(n+1)K]^n}{4\pi G} \quad (5.153)$$

Considering the polytropic index of the white dwarf's equation of state, at low density, electrons are non-relativistic with $\gamma = 5/3$, corresponding to $n = 1.5$. In this case, the scaling relationship between the mass and radius of the white dwarf and the central mass density is:

$$M \propto \rho_0^{1/2}, \quad R \propto \rho_0^{-1/6} \quad (5.154)$$

As the central density increases, the mass of the white dwarf continues to increase, but the radius continues to decrease, making the white dwarf denser. When the central mass density far exceeds the critical density ρ_c , electrons become extremely relativistic, and the polytropic index of the white dwarf's equation of state is $\gamma = 4/3$, corresponding to $n = 3$. In this case, the scaling relationship between the mass and radius of the white dwarf and the central mass density is as follows:

$$M \propto \rho_0^0 = \text{const.}, \quad R \propto \rho_0^{-1/3} \quad (5.155)$$

If the mass of the white dwarf reaches a maximum value, it no longer increases with the increase in central mass density. Since the mass of the white dwarf remains constant, it is not difficult to understand that the radius of the white dwarf continues to decrease with the density's $1/3$, making the white dwarf denser, and the star becomes unstable and continues to collapse. At this time, the maximum mass of the star is:

$$M_{\max} = M_3^* 4\pi \left(\frac{K}{\pi G} \right)^{3/2}, \quad K = \frac{(3\pi^2)^{1/3}}{4} \frac{\hbar c}{(\mu_c m_B)^{4/3}} \quad (5.156)$$

Thus, the Chandrasekhar mass is obtained:

$$M_{\text{Ch}} = \frac{\sqrt{3\pi}}{2} M_3^* \frac{m_{\text{pl}}^3}{(\mu_e m_B)^2} = 5.83 \mu_e^{-2} M_\odot \quad (5.157)$$

where $m_{\text{pl}} = \sqrt{\hbar c/G} = 2.18 \times 10^{-8}$ kg is the Planck mass. For helium white dwarfs and carbon-oxygen white dwarfs, $\mu_e = 2$, the Chandrasekhar mass is $M_{\text{Ch}} = 1.46 M_\odot$; for iron white dwarfs $\mu_e = 56/26 = 2.15$, the Chandrasekhar mass is $M_{\text{Ch}} = 1.26 M_\odot$. When the white dwarf reaches its maximum mass, the internal electrons become relativistic, and the average density has exceeded the critical density, the radius of the white dwarf does not exceed:

$$R_{\text{WD}} \leq \left(\frac{3M_{\text{Ch}}}{4\pi\rho_c} \right)^{1/3} = 2.3 \frac{m_{\text{pl}}}{\mu_e m_B} \frac{1}{\lambda_e} \simeq 1.2 \times 10^4 \mu_e^{-1} \text{ km} \quad (5.158)$$

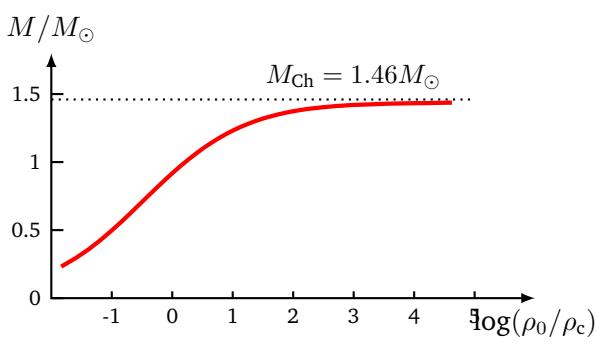


Fig. 53: The Relationship Between the Mass of Carbon-Oxygen White Dwarfs and the Central Density of the Star

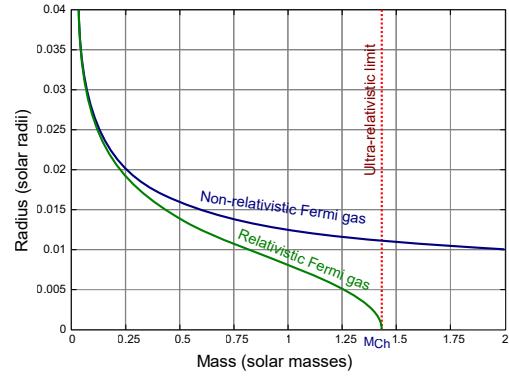


Fig. 54: The Relationship Between the Mass of Carbon-Oxygen White Dwarfs and the Radius of the Star

For neutron stars, Oppenheimer proposed a simple model assuming that neutron stars are composed of a pure ideal gas of free neutrons. The internal pressure of neutron stars is provided by neutron degeneracy pressure, and all their mass is also provided by neutrons. Similarly, the maximum mass of a neutron star should be:

$$M_{\text{NS}} \sim \frac{\sqrt{3\pi}}{2} M_3 \frac{m_{p1}^3}{m_n^2} \sim 5.83 M_\odot \quad (5.159)$$

The radius of a neutron star satisfies:

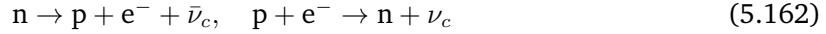
$$R_{\text{NS}} \leq 2.3 \frac{m_{\text{pl}}}{m_n} \frac{\hbar}{m_n c} \simeq 6.3 \text{ km} \quad (5.160)$$

The neutrons inside a neutron star are relativistic, and the mass-energy density of the neutron star's core needs to include the contribution of the neutron star's internal energy, rather than simply being the rest energy of neutrons ($\rho \neq n_n m_n$), i.e.:

$$\rho = \frac{u_n}{c^2} = \frac{1}{2^5 \pi^2} \frac{m_n^4 c^3}{\hbar^3} (\sinh \xi_F - \xi_F) \quad (5.161)$$

where $\xi_F = 4 \sinh^{-1} (p_F/m_n c)$ is the dimensionless Fermi momentum parameter for neutrons. Neutron stars are already very dense, close to collapsing into black holes, and Newtonian mechanics is no longer applicable. The structure of neutron stars needs to be solved using the hydrostatic equilibrium equations under general relativity. Oppenheimer numerically solved the structure of neutron stars in 1939, obtaining a maximum mass of about $0.7M_\odot$, known as the Oppenheimer limit.

Neutron stars are not composed purely of neutrons because the mass of protons is smaller than that of neutrons, and free neutrons undergo β decay to protons and electrons. Inside neutron stars, due to the high density of the core region, only about ten percent of neutrons undergo inverse β decay to equal amounts of protons and electrons, causing the Fermi energy of electrons E_F^e to reach the mass difference between neutrons and protons. At this point, β decay and inverse β decay reach equilibrium (known as β equilibrium), resulting in:



The system reaches β equilibrium, meaning chemical equilibrium, where the chemical potential of neutrons equals the sum of the chemical potentials of protons and electrons:

$$\mu_n = \mu_p + \mu_e \quad (5.163)$$

The above equation only applies when the system's temperature is approximately zero, and fermions are in a strongly degenerate state. At a system temperature of $T \simeq 0$ K, the influence of neutrinos can be ignored because the energy of emitted neutrinos $\varepsilon_\nu \sim T \sim 0$ K. For high-temperature systems of protons, neutrons, and electron-positron pairs, the influence of neutrinos cannot be ignored, and we obtain a new, analytical β equilibrium condition:

$$\mu_n = \mu_p + 2\mu_e \quad (5.164)$$

Therefore, the interior of a neutron star is not composed of 100 neutrons but consists of mostly neutrons, a small number of protons, and an equal number of electrons as protons. Given the baryon number density n_B in the core region, the ratio of proton number density to neutron number density can be calculated based on baryon number conservation ($n_B = n_n + n_p$), charge conservation ($n_p = n_e$), and β -equilibrium. The internal composition is still under study, and neutrons, protons, and electrons represent one of the simplest models.

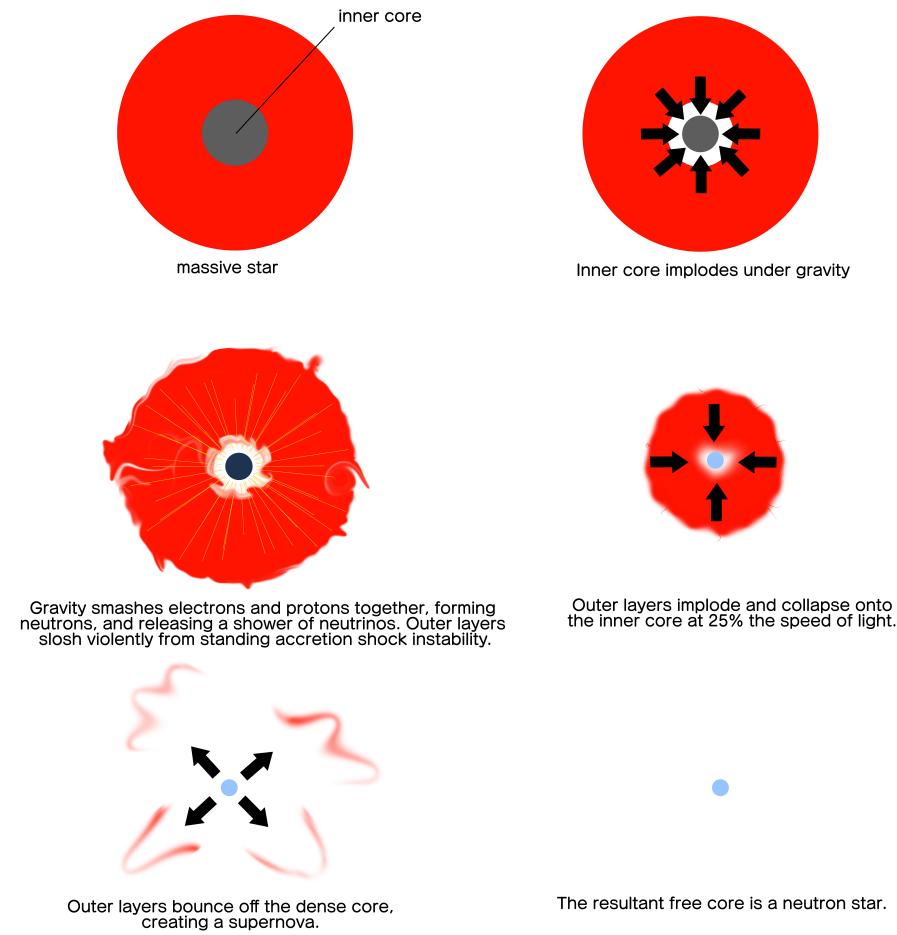


Fig. 55: The Formation Process of Neutron Stars

Chapter 6 Ensemble Theory

The idea of **ensemble** theory is that under given macroscopic conditions, a system can exist in a large number of possible microscopic states. Although at any given moment, the system can only be in one possible microscopic state, during actual measurements, it always experiences a macroscopically short but microscopically long time Δt . During the time Δt , the system traverses all possible microscopic states. The measurement obtained is actually the time average of a certain physical quantity within the time Δt , known as the ensemble average (also known as the thermodynamic quantity). In many cases, we cannot accurately predict the microscopic state of the system, but the ensemble reflects the nature of changes in macroscopic physical quantities, independent of time.

The macroscopic state can be described by $(E, N, V), (T, N, V), (T, \mu, V) \dots$; the microscopic state can be the system state $|\psi(t)\rangle$ in quantum mechanics or a point in the system's phase space Γ in classical mechanics, $\mathbf{q}_1, \mathbf{p}_1, \mathbf{q}_2, \mathbf{p}_2 \dots = \{\mathbf{q}_i, \mathbf{p}_i\}$. The most important points of ensemble theory are: the description of phase space, the distribution of microscopic particles, and the statistical average of macroscopic physical quantities (ensemble average).

6.1 Classical Ensemble Theory

Consider N particles moving in d -dimensional space, a microscopic state corresponds to a point in the Γ space (phase space), called the representative point, denoted as \mathbf{q}, \mathbf{p} . To describe the state evolution of the system over time, consider the canonical equations

$$\dot{q}_i = \nabla_{p_i} H, \quad \dot{p}_i = -\nabla_{q_i} H \quad (6.1)$$

The evolution of the system state over time means the trajectory of the representative point moving in the Γ space. For the average value of a physical quantity $O = O(t) = O(\mathbf{q}(t), \mathbf{p}(t))$, it can be written in the form of a Poisson bracket

$$\begin{aligned} \dot{O} &= \frac{dO}{dt} = \sum_i \frac{\partial O}{\partial q_i} \dot{q}_i + \frac{\partial O}{\partial p_i} \dot{p}_i \\ &= \sum_i \frac{\partial O}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial O}{\partial p_i} \frac{\partial H}{\partial q_i} = \{O, H\} \end{aligned} \quad (6.2)$$

Conserved quantities satisfy $\dot{O} = 0$, for example: energy H in a conservative system, number of particles, etc.

Assume there are \mathcal{N} systems in the ensemble, at time t , the state of the l -th system is $\mathbf{q}^l, \mathbf{p}^l$. The ensemble average gives the statistical average of the physical quantity O , where $\Delta n(\mathbf{q}, \mathbf{p}, t)$ is the number of systems between $\mathbf{q} - \Delta \mathbf{q}, \mathbf{p} - \Delta \mathbf{p}$

$$O = \frac{1}{\mathcal{N}} \sum_{l=1}^{\mathcal{N}} O [\mathbf{q}^l(t), \mathbf{p}^l(t)] = \sum_{\mathbf{q}, \mathbf{p}} \Delta \mathbf{q} \Delta \mathbf{p} \frac{\Delta n(\mathbf{q}, \mathbf{p}, t)}{\mathcal{N} \Delta \mathbf{q} \Delta \mathbf{p}} O(\mathbf{q}, \mathbf{p}) = \int d\mathbf{q} d\mathbf{p} \rho(\mathbf{q}, \mathbf{p}, t) O(\mathbf{q}, \mathbf{p}) \quad (6.3)$$

Thus, the probability density in phase space is obtained: $\rho(\mathbf{q}, \mathbf{p}, t)$

$$\rho(\mathbf{q}, \mathbf{p}, t) \Delta \mathbf{q} \Delta \mathbf{p} = \frac{1}{\mathcal{N}} \Delta n(\mathbf{q}, \mathbf{p}, t) = \frac{1}{\mathcal{N}} \sum_{\{l | \mathbf{q} < \mathbf{q}^l(t) < \mathbf{q} + \Delta \mathbf{q}, \mathbf{p} < \mathbf{p}^l(t) < \mathbf{p} + \Delta \mathbf{p}\}} 1 \quad (6.4)$$

The probability that the system is at $\mathbf{q} \rightarrow \mathbf{q} + \Delta \mathbf{q}, \mathbf{p} \rightarrow \mathbf{p} + \Delta \mathbf{p}$ at time t is: $\rho(\mathbf{q}, \mathbf{p}, t) \Delta \mathbf{q} \Delta \mathbf{p}$, satisfying positivity and normalization

$$\rho(\mathbf{q}, \mathbf{p}, t) \geq 0, \quad \int \rho d\mathbf{q} d\mathbf{p} = \frac{1}{\mathcal{N}} \int d\mathbf{q} d\mathbf{p} \sum_{\{l | \mathbf{q} < \mathbf{q}^l(t) < \mathbf{q} + d\mathbf{q}, \mathbf{p} < \mathbf{p}^l(t) < \mathbf{p} + d\mathbf{p}\}} 1 = \frac{\mathcal{N}}{\mathcal{N}} = 1 \quad (6.5)$$

If the number of systems \mathcal{N} in the ensemble is large enough, i.e., the systems in the Γ space are dense enough, and the state density function of the system is smooth enough, the ensemble can be regarded as a fluid in phase space. Define the velocity and gradient operator in phase space \mathbf{v}_q and ∇_q as:

$$\mathbf{v}_\Gamma \equiv (\dot{q}_1, \dot{q}_2, \dots, \dot{q}_f, \dot{p}_1, \dot{p}_2, \dots, \dot{p}_f) \quad (6.6a)$$

$$\nabla_\Gamma \equiv \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \dots, \frac{\partial}{\partial q_f}, \frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \dots, \frac{\partial}{\partial p_f} \right) \quad (6.6b)$$

During the evolution of the system, they all satisfy Hamilton's canonical equations Eq. 6.1, thus:

$$\nabla_\Gamma \cdot \mathbf{v}_r \equiv \sum_{\alpha=1}^f \left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right) = \sum_{\alpha=1}^f \left(\frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha} - \frac{\partial^2 H}{\partial p_\alpha \partial q_\alpha} \right) = 0 \quad (6.7)$$

Rewriting as the conservation equation of the number of systems:

$$\iiint_{\Delta\Omega} \left[\frac{\partial \rho}{\partial t} + \nabla_\Gamma \cdot (\rho \mathbf{v}_\Gamma) \right] d\Omega = 0 \quad (6.8)$$

The physical meaning of the above equation is that if the ensemble is regarded as a fluid in phase space, then this fluid is an incompressible fluid. This equation is similar to the mass conservation equation in fluid mechanics. Take any fixed volume element $\Delta\Omega$ in phase space, then the number of systems in this volume element is $\mathcal{N} = \iiint_{\Delta\Omega} \rho d\Omega$, the change in the number of systems in this volume element is $\frac{d\mathcal{N}}{dt} = \iiint_{\Delta\Omega} \frac{\partial \rho}{\partial t} d\Omega$, then $\frac{d\mathcal{N}}{dt} > 0$ or < 0 , indicating an increase/decrease in the number of systems in the volume $\Delta\Omega$. Since the number of systems is conserved, the increase in the number of systems in the volume $\Delta\Omega$ should equal the number of systems flowing out from the total surface S of the volume element $\Delta\Omega$, i.e., the integral expression of the conservation of the number of systems

$$\frac{d\mathcal{N}}{dt} = \iiint_{\Delta\Omega} \frac{\partial \rho}{\partial t} d\Omega = - \iint_{\Omega} \rho \mathbf{v}_\Gamma \cdot d\mathbf{s} = - \iint_{\Delta\Omega} \nabla_\Gamma \cdot (\rho \mathbf{v}_\Gamma) d\Omega \Rightarrow \iiint_{\Delta\Omega} \left[\frac{\partial \rho}{\partial t} + \nabla_\Gamma \cdot (\rho \mathbf{v}_\Gamma) \right] d\Omega = 0 \quad (6.9)$$

Substituting Eq. 6.7 into Eq. 6.8, we obtain Liouville's theorem

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \nabla_\Gamma \cdot (\rho \mathbf{v}_\Gamma) = \frac{\partial \rho}{\partial t} + \mathbf{v}_\Gamma \cdot \nabla_\Gamma \rho = 0 \quad (6.10)$$

Liouville's theorem states that in the process of following any system in phase space, the surrounding system state density ρ always remains constant, and the surrounding systems neither converge nor diverge. In the evolution in phase space, the system is constrained by the canonical equations, and the volume occupied by the representative point remains unchanged.

6.1.1 Liouville's Theorem

Substituting the canonical equations into Liouville's theorem, we can obtain the form of Liouville's theorem expressed in Poisson brackets:

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{\alpha=1}^J \left[\frac{\partial\rho}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial\rho}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right] = \frac{\partial\rho}{\partial t} + [\rho, H] = 0 \quad (6.11)$$

From this, it can be seen that the microscopic dynamic equations of the system have time-reversal symmetry, i.e., if $p(q_1, q_2, \dots, q_f; p_1, p_2, \dots, p_f, t)$ satisfies Liouville's theorem, then $\rho(q_1, q_2, \dots, q_f; -p_1, -p_2, \dots, -p_f, t)$ also satisfies it.

The Liouville operator is given by

$$i\hat{L} = \sum_{i=1}^n \left[\frac{\partial H}{\partial p_i} \frac{\partial}{\partial q^i} - \frac{\partial H}{\partial q^i} \frac{\partial}{\partial p_i} \right] = \{\bullet, H\} \quad (6.12)$$

Liouville's theorem is written as

$$\frac{\partial\rho}{\partial t} = -\{\rho, H\}, \quad \frac{\partial\rho}{\partial t} + i\hat{L}\rho = 0 \quad (6.13)$$

Below, we derive another corollary of Liouville's theorem, i.e., the physical quantity B is a function of the system state, and $\langle B \rangle$ represents the expectation value of B

$$\frac{d\langle B \rangle}{dt} = \langle [B, H] \rangle \quad (6.14)$$

where the state function: $B = B(q_1, q_2, \dots, q_f; p_1, p_2, \dots, p_f)$. According to the definition of ensemble average and Liouville's theorem, we have:

$$\begin{aligned} \frac{d\langle B \rangle}{dt} &= \int d\Omega \frac{\partial\rho}{\partial t} B(\Omega) = \int d\Omega B(\Omega) \sum_{\alpha=1}^f \left(\frac{\partial\rho}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} - \frac{\partial\rho}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} \right) \\ &= - \sum_{\alpha=1}^f \int d\Omega \rho \left(\frac{\partial B}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} - \frac{\partial B}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} \right) = - \int d\Omega \rho [H, B] = \langle [B, H] \rangle \end{aligned} \quad (6.15)$$

where integration by parts assumes that any meaningful physical quantity approaches zero at infinity in Γ -space. For equilibrium states, $\frac{d\langle B \rangle}{dt} = 0$, requiring the equilibrium state density ρ_{eq} to satisfy: $\frac{\partial\rho_{eq}}{\partial t} = 0$, substituting into Liouville's theorem, satisfying $[\rho_{eq}, H] = 0$, i.e., ρ_{eq} commutes with the Hamiltonian H of the system, and is a conserved quantity of the system. If $\rho = \rho(H)$, we have: $\frac{\partial\rho}{\partial t} = 0$, indicating that the equilibrium state density is a function of the Hamiltonian.

$$\text{Microcanonical Ensemble: } \rho(\mathbf{q}, \mathbf{p}) = \frac{1}{\Omega} \delta(E - H(\mathbf{q}, \mathbf{p})) \quad (6.16a)$$

$$\text{Canonical Ensemble: } \rho(\mathbf{q}, \mathbf{p}) = \frac{1}{Z} e^{-\beta H(\mathbf{q}, \mathbf{p})} \quad (6.16b)$$

$$\text{Grand Canonical Ensemble: } \rho(\mathbf{q}_N, \mathbf{p}_N) = \frac{1}{\Xi} e^{-\beta [H(\mathbf{q}_N, \mathbf{p}_N)_N - \mu N]} \quad (6.16c)$$

6.2 Quantum Ensemble Theory

In quantum ensemble theory, the ensemble density $\rho(\mathbf{q}, \mathbf{p})$ in classical theory is written as the ensemble density operator $\hat{\rho}$, and the quantum state is described by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \quad (6.17)$$

Assume $|m\rangle, m = 1, 2, \dots$ is a complete set of orthonormal eigenstates of a certain linear Hermitian operator, satisfying $\langle m | m' \rangle = \delta_{mm'}$; $\sum_m |m\rangle \langle m| = 1$, choose them as the basis, and expand the wave function

$$|\psi\rangle = \sum_m |m\rangle \langle m | \psi \rangle = \sum_m a_m |m\rangle \quad (6.18)$$

where the ensemble density operator is defined as

$$\hat{\rho} \equiv \frac{1}{N} \sum_i^N |(i)\rangle \langle (i)| \quad (6.19)$$

satisfying Hermitian conjugation equal to itself

$$\hat{\rho}^\dagger(t) = |\psi(t)\rangle \langle \psi(t)| = \hat{\rho}(t) \quad (6.20)$$

The matrix elements of the ensemble density operator

$$\rho_{nm} = \frac{1}{N} \sum_i^N \langle n | (i) \rangle \langle (i) | m \rangle = \frac{1}{N} \sum_i^N a_n^{(i)} a_m^{(i)*} \quad (6.21)$$

Substituting the above equation back into the definition of the ensemble density operator 6.19, we obtain

$$\hat{\rho} = \frac{1}{N} \sum_i^N \sum_n \sum_m a_n^{(i)} a_m^{(i)*} |n\rangle \langle m| \quad (6.22)$$

The trace of the density matrix is 1, because

$$\text{Tr}(\hat{\rho}) = \sum_n \hat{\rho}_{nn} = \frac{1}{N} \sum_i^N \sum_n |a_n^{(i)}|^2 = \frac{1}{N} \sum_i^N 1 = 1 \quad (6.23)$$

The density matrix $\hat{\rho}$ is the classical probability sum of each state in the ensemble, reflecting the distribution of systems in the ensemble, corresponding to the density ρ in the classical ensemble, and can also be used to find the ensemble average of any physical quantity. For a mechanical quantity \hat{A} , represented as a matrix:

$$\hat{A} = \sum_{mn} B_{mn} |m\rangle \langle n| \quad (6.24)$$

The ensemble average of A is:

$$\begin{aligned} \langle \hat{A} \rangle &\equiv \frac{1}{N} \sum_i^N \langle (i) | \hat{A} | (i) \rangle = \frac{1}{N} \sum_i^N \sum_m \sum_n \langle (i) | m \rangle \langle m | \hat{A} | n \rangle \langle n | (i) \rangle \\ &= \frac{1}{N} \sum_i^N \sum_m \sum_n a_m^{(i)*} a_n^{(i)} \hat{A}_{mn} = \sum_m \sum_n \hat{\rho}_{nm} \hat{A}_{mn} = \text{Tr}(\hat{\rho} \hat{A}), \end{aligned} \quad (6.25)$$

That is, the ensemble average of the mechanical quantity \hat{A} is the trace after multiplying it with the density matrix, corresponding to the classical ensemble average $\langle \hat{A} \rangle = \int \rho A d\Omega$.

Next, we consider the dynamic evolution of the density $\hat{\rho}$. According to the Schrödinger equation, we know:

$$i\hbar \frac{d\hat{\rho}}{dt} = i\hbar \frac{1}{N} \sum_i^N \left\{ \frac{d}{dt} |(i)\rangle\langle(i)| + |(i)\rangle \frac{d}{dt} \langle(i)| \right\} = \frac{1}{N} \sum_i^N \{ \hat{H} |(i)\rangle\langle(i)| - |(i)\rangle\langle(i)| \hat{H} \} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H} = [\hat{H}, \hat{\rho}] \quad (6.26)$$

The dynamic evolution equation of the density operator $\hat{\rho}$ (quantum Liouville theorem) is derived as:

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}] \quad (6.27)$$

When the system is in equilibrium, the ensemble is stable, i.e., requiring $[\hat{H}, \hat{\rho}] = 0$, equivalent to requiring $\hat{\rho}$ to be a conserved quantity, which is the stable ensemble in classical theory.

The density matrix is divided into pure state/mixed state density matrices. A pure state density matrix means that all particles in the ensemble are in the same state, written as

$$\rho_p^2 = |\psi\rangle\langle\psi| \quad (6.28)$$

The matrix eigenvalue is one 1 and the rest are 0, for example

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \Rightarrow \hat{\rho}_p = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad (6.29)$$

A mixed state density matrix means that the particles in the ensemble are in multiple states, with matrix eigenvalues between 0 and 1, written as

$$\rho_m = \frac{1}{N} \sum_i |\psi_i\rangle\langle\psi_i|, \quad \rho_m^2 = \frac{1}{N^2} \sum_{ii'} (\langle\psi_i|\psi_{i'}\rangle) |\psi_i\rangle\langle\psi_{i'}| \neq \rho_m \quad (6.30)$$

For example

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \quad |\psi_2\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) \Rightarrow \hat{\rho}_m = \frac{1}{4} \left[\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} + \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \right] = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (6.31)$$

Generally, the energy eigenstates of the system are chosen as the basis, and in general, the energy eigenstates are degenerate. Introduce the quantum number s to remove the degeneracy, where s is the eigenvalue of the operator \hat{S} . It is required that the operator \hat{S} commutes with \hat{H} and $\hat{\rho}$. Therefore, we have:

$$\hat{S}|ns\rangle = s|ns\rangle \quad (6.32)$$

Since $\hat{\rho}$ commutes with \hat{H} , $|ns\rangle$ is also an eigenstate of $\hat{\rho}$, so the matrix elements of $\hat{\rho}$ are diagonal, i.e., we have:

$$\hat{\rho} = \sum_{n,s} \hat{\rho}_{ns} |ns\rangle\langle ns| \quad (6.33a)$$

$$\hat{\rho}_{ns} = \frac{1}{N} \sum_i \langle ns | (i)\rangle\langle(i) | ns \rangle = \frac{1}{N} \sum_i |a_{ns}^{(i)}|^2 = \frac{\mathcal{N}_{ns}}{N} \quad (6.33b)$$

where $\mathcal{N}_{ns} = \sum_i |a_{ns}^{(i)}|^2$ is the number of systems in the ensemble in the quantum state $|ns\rangle$.

The physical meaning of $\hat{\rho}_{ns}$ is the probability that the systems in the ensemble are in the energy eigenstate $|ns\rangle$. From this, we can obtain the density matrix expressions for several major ensembles:

For the microcanonical ensemble, where Ω is the total number of quantum states in the range $E \leq E_n \leq E + \Delta E$.

$$\hat{\rho}_{ns} = \begin{cases} \frac{1}{\Omega}, & E \leq E_n \leq E + \Delta E, \\ 0, & \text{others,} \end{cases} \quad (6.34)$$

For the quantum canonical ensemble, the corresponding canonical partition function is, considering the degeneracy of energy levels, summing over the quantum number s , we get:

$$Z = \text{Tr}(\hat{\rho}) = \sum_{ns} e^{-\beta E_n} = \sum_n \Omega_n e^{-\beta E_n} \quad (6.35)$$

The density matrix for the canonical ensemble is:

$$\hat{\rho} = e^{-\beta \hat{H}} = e^{-\beta \hat{H}} \sum_{ns} |ns\rangle \left\langle ns \right| = \sum_{ns} e^{-\beta E_n} \left| ns \right\rangle \langle ns | \quad (6.36)$$

Grand canonical ensemble The grand partition function is:

$$\Xi = \text{Tr} \left(e^{\beta(\mu \hat{N} - \hat{H})} \right) = \sum_{N=0}^{\infty} (e^{\beta \mu})^N \sum_{ns} e^{-\beta E_n} = \sum_{N=0}^{\infty} z^N Z \quad (6.37)$$

The corresponding density operator is:

$$\hat{\rho} = \frac{1}{\Xi} e^{-\beta(H - \mu \hat{N})} \quad (6.38)$$

Summarized in the following expression, corresponding to Eq. 6.16a, Eq. 6.16b, Eq. 6.16c.

$$\text{Microcanonical Ensemble: } \hat{\rho} = \frac{1}{\Omega} \delta(E - \hat{H}) \quad (6.39a)$$

$$\text{Canonical Ensemble: } \hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}} \quad (6.39b)$$

$$\text{Grand Canonical Ensemble: } \hat{\rho} = \frac{1}{\Xi} e^{-\beta(H - \mu \hat{N})} \quad (6.39c)$$

Ensemble	Density $\rho(\mathbf{q}, \mathbf{p})$	Density Matrix $\hat{\rho}$
Microcanonical Ensemble	$\frac{1}{\Omega} \delta(E - H(\mathbf{q}, \mathbf{p}))$	$\frac{1}{\Omega} \delta(E - \hat{H})$
Canonical Ensemble	$\frac{1}{Z} e^{-\beta H(\mathbf{q}, \mathbf{p})}$	$\frac{1}{Z} e^{-\beta \hat{H}}$
Grand Canonical Ensemble	$\frac{1}{\Xi} e^{-\beta [H(\mathbf{q}_N, \mathbf{p}_N)_N - \mu N]}$	$\frac{1}{\Xi} e^{-\beta(H - \mu \hat{N})}$

Table 6: Density in Classical and Quantum Ensembles

6.3 Microcanonical Ensemble

The microcanonical ensemble, also known as the NVE ensemble, is an ensemble composed of isolated systems.

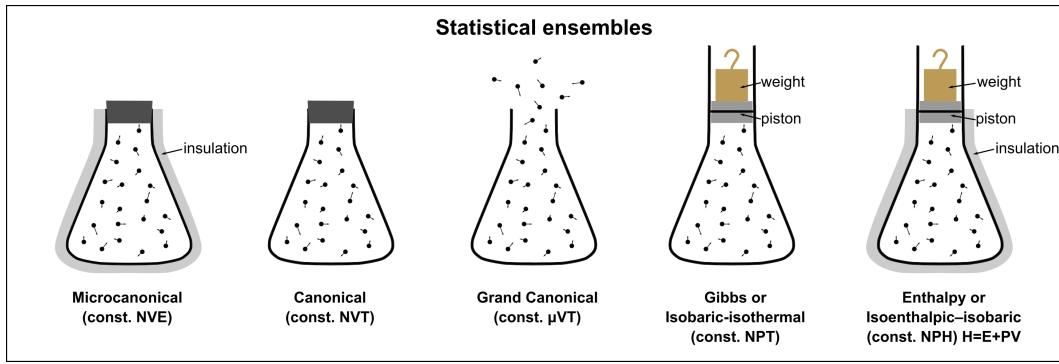


Fig. 56: Various Statistical Ensembles

The characteristic of the microcanonical ensemble is that all systems have the same energy, number of particles, and volume, but the temperature can vary. The microcanonical ensemble satisfies the **equal probability assumption**, that is, the systems in the ensemble composed of isolated systems have the same probability of being in different microscopic states.

6.3.1 Thermodynamic Characteristic Function: Entropy

The state density function of the microcanonical ensemble ρ_{mc} is:

$$\rho_{mc}(q_i, p_i) = \frac{1}{\sigma(E)} \delta(H(q_i, p_i) - E) \quad (6.40)$$

The energy of an isolated system is conserved, and all systems are located on the energy surface in phase space

$$H(q_1, q_2, \dots, q_f; p_1, p_2, \dots, p_f) = E \quad (6.41)$$

where $\sigma(E)$ is the total area of the energy surface $H(q_i, p_i) = E$, and the factor $1/\sigma(E)$ ensures the normalization of ρ_{mc} :

$$\int \rho_{mc} d\Omega = \frac{1}{\sigma(E)} \int \delta(H(q_i, p_i) - E) d\Omega = \frac{1}{\sigma(E)} \int d\sigma = 1 \quad (6.42)$$

Handling the δ function is inconvenient, and in most cases, E is not strictly single-valued. It is generally assumed that the system energy range is $E \leq H(q_i, p_i) \leq E + \Delta E$, where $\Delta E \ll E$, and it is assumed that ρ_{mc} is constant

$$\rho_{mc} = \begin{cases} \frac{1}{\Omega}, & E \leq H(q_i, p_i) \leq E + \Delta E \\ 0, & \text{others,} \end{cases} \quad (6.43)$$

where Ω is the total volume of the microcanonical ensemble in phase space:

$$\Omega = \int_{E \leq H(q_i, p_i) \leq E + \Delta E} d\Omega \quad (6.44)$$

Below, we prove that the constant distribution of ρ_{mc} represented by Eq. 6.43 is the most probable distribution of the system. Divide the energy surface into a large number of equal-area surface

elements σ_i , assuming that each surface element contains n_i systems. For a given distribution $\{n_i\}$, the total number of ways $W\{\{n_i\}\}$ is: $\frac{\mathcal{N}!}{\prod_i n_i!}$, further assuming that ω_i is the probability of a system appearing in σ_i , then the probability of n_i subsystems appearing in $\Delta\sigma_i$ is $\omega_i^{n_i}$. Finally, the probability of the distribution $\{n_i\}$ is $W_{\text{tot}}\{\{n_i\}\}$ (similar to the Boltzmann distribution of microstates)

$$W_{\text{tot}}\{\{n_i\}\} = \mathcal{N}! \prod_i \frac{\omega_i^{n_i}}{n_i!} \quad (6.45)$$

To find the extremum (using approximate conditions), consider the constraint of conservation of the number of systems

$$d \ln W_{\text{tot}} = - \sum_i (\ln n_i - \ln \omega_i) dn_i, \quad d\mathcal{N} = \sum_i dn_i = 0 \quad (6.46)$$

The most probable distribution satisfies

$$\ln n_i = \alpha + \ln \omega_i \Leftrightarrow n_i = \omega_i e^\alpha \propto \omega_i \propto \Delta\sigma_i \quad (6.47)$$

Therefore, the number of systems per unit area of the microcanonical ensemble on the energy surface is constant, i.e., ρ_{mc} is constant.

According to the definition of Gibbs entropy Eq. 4.82, $S = \langle k_B \ln \Omega \rangle = \langle -k_B \ln \rho \rangle$, the entropy of the microcanonical system is

$$S(N, V, E) = \langle -k_B \ln \rho_{\text{mc}} \rangle = \int \rho_{\text{mc}} (-k_B \ln \rho_{\text{mc}}) d\Omega = k_B \ln \Omega(N, V, E) \quad (6.48)$$

From the thermodynamic characteristic function - entropy, we can obtain the expression of physical quantities. Due to the differential relationship $dS = \frac{p}{T} dV + \frac{1}{T} dE - \frac{\mu}{T} dN$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V} = k_B \left(\frac{\partial \ln \Omega}{\partial E} \right)_{N,V} \quad (6.49a)$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{N,E} = k_B \left(\frac{\partial \ln \Omega}{\partial V} \right)_{N,E} \quad (6.49b)$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N} \right)_{V,E} = k_B \left(\frac{\partial \ln \Omega}{\partial N} \right)_{V,E} \quad (6.49c)$$

6.3.2 Ideal Gas

Using the microcanonical ensemble theory to derive the thermodynamic parameters of a three-dimensional monoatomic ideal gas. Assume the gas contains N molecules, and its Hamiltonian (ignoring potential energy) is:

$$H = \sum_i^{3N} \frac{p_i^2}{2m} \quad (6.50)$$

Considering the complete identity of particles, the volume of the ensemble in phase space with energy in the range $E \leq H(q_i, p_i) \leq E + \Delta E$ is:

$$\Omega(E) = \frac{1}{N! h^{3N}} \int_{E \leq H(q_i, p_i) \leq E + \Delta E} dq_1 dq_2 \cdots dq_{3N} dp_1 dp_2 \cdots dp_{3N} \quad (6.51)$$

First, calculate the volume of the energy sphere $\Sigma(E)$ with $H \leq E$:

$$\begin{aligned}\Sigma(E) &= \frac{1}{N!h^{3N}} \int_{H(q_i, p_i) \leq E} dq_1 dq_2 \cdots dq_{3N} dp_1 dp_2 \cdots dp_{3N} \\ &= \frac{V^N}{N!h^{3N}} \int_{H(q_i, p_i) \leq E} dp_1 dp_2 \cdots dp_{3N} \\ &= \frac{V^N}{N!h^{3N}} (2mE)^{\frac{3N}{2}} \int \cdots \int_{\sum_i x_i^2 \leq 1} dx_1 \cdots dx_{3N}\end{aligned}\quad (6.52)$$

The $3N$ -dimensional integral in the above equation represents the volume of a $3N$ -dimensional sphere with radius 1, and its value is:

$$V_{3N}(1) = \int \cdots \int_{\sum_i x_i^2 \leq 1} dx_1 \cdots dx_{3N} = C_{3N} = \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} \quad (6.53)$$

This formula can be simply calculated and proved. Due to dimensional analysis, the volume of an n -dimensional sphere with radius R is $V_n = C_n R^n$, and the corresponding surface area of the n -dimensional sphere is $S_n = dV_n/dR = nC_n R^{n-1}$, where C_n is the integral constant, and n is the dimension. According to Euler's integral formula, we have

$$\begin{aligned}\pi^{n/2} &= \int \cdots \int_{-\infty}^{\infty} e^{-\sum_{i=1}^n x_i^2} dx_1 \cdots dx_n \\ &= \int_0^{\infty} e^{-R^2} dV_n = \int_0^{\infty} e^{-R^2} nC_n R^{n-1} dR \\ &= nC_n \frac{1}{2} \Gamma\left(\frac{n}{2}\right) = \left(\frac{n}{2}\right)! C_n\end{aligned}\quad (6.54)$$

The volume of the energy sphere

$$\Sigma(E) = \frac{V^N}{N!h^{3N}} (2mE)^{\frac{3N}{2}} \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} = \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{\frac{3N}{2}}}{N! \left(\frac{3N}{2}\right)!} \quad (6.55)$$

The number of microstates of the system with energy in the range $E \leq H(q_i, p_i) \leq E + \Delta E$ is:

$$\Omega(E) = \frac{\partial \Sigma}{\partial E} \Delta E = \frac{3N}{2} \frac{\Delta E}{E} \Sigma(E) \quad (6.56)$$

The entropy of the ideal gas is:

$$S = k_B \ln \Omega = N k_B \ln \left[\frac{V}{h^3 N} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{5}{2} N k_B + k_B \left[\ln \left(\frac{3N}{2} \right) + \left(\frac{\Delta E}{E} \right) \right] \quad (6.57)$$

Using Stirling's formula. When N is very large, $\ln N \ll N$, in the thermodynamic limit, the last term can be ignored, and the entropy of an ideal gas with many gas molecules is

$$S = N k_B \ln \left[\frac{V}{h^3 N} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{5}{2} N k_B + O(\ln N) \quad (6.58)$$

This indicates that the width of the energy shell ΔE has no significant impact on the value of entropy, but if ΔE is allowed to approach zero, it will lead to the non-physical conclusion of entropy approaching negative infinity. This indicates that a strictly isolated system with a definite

energy does not exist physically.

From the above Eq. 6.58, the expression for internal energy can be inversely solved as:

$$U(S, V, N) = E = \frac{3h^2 N^{5/3}}{4\pi m V^{2/3}} \exp\left(\frac{3S}{3Nk_B} - \frac{5}{3}\right) \quad (6.59)$$

Using the total differential of internal energy $dU = T dS - p dV + \mu dN$, the temperature is obtained as:

$$T = \left(\frac{\partial U}{\partial S}\right)_{N,V} = \frac{2}{3Nk_B} U, \quad U = \frac{3}{2} N k_B T \quad (6.60)$$

The pressure is:

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,V} = \frac{2}{3V} U, \quad pV = Nk_B T \quad (6.61)$$

The chemical potential per particle is:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{N,S} = \frac{5}{3} \frac{U}{N} - \frac{2}{3} \frac{U}{N} \frac{S}{Nk_B} = k_B T \ln \left[\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right] \quad (6.62)$$

6.3.3 Harmonic Oscillator System

The Hamiltonian of the harmonic oscillator system is:

$$H(q_i, p_i) = \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 q_i^2 \right) \quad (6.63)$$

Similar to the discussion in the previous section, first calculate the volume $\Sigma(E, V, N)$ in phase space with $H(q_i, p_i) \leq E$:

$$\begin{aligned} \Sigma(E, V, N) &= \frac{1}{h^N} \int_{H(q_i, p_i) \leq E} dq_1 dq_2 \cdots dq_N dp_1 dp_2 \cdots dp_N \\ &= \frac{1}{h^N} \left(\frac{2E}{\omega} \right)^N \int_{\sum_{i=1}^{2N} x_i^2 \leq 1} d^{2N} x_i = \frac{1}{N!} \left(\frac{E}{\hbar \omega} \right)^N \end{aligned} \quad (6.64)$$

where the volume of the unit sphere in $2N$ -dimensional space is: $C_{2N} = \pi^N / N!$, and the generalized coordinates are obtained by dimensionless transformation of (q_i, p_i)

$$\begin{aligned} x_i &\equiv \frac{q_i}{\sqrt{2E/m\omega^2}}, \quad i = 1, 2, \dots, N \\ x_i &\equiv \frac{p_i}{\sqrt{2mE}}, \quad i = N+1, N+2, \dots, 2N. \end{aligned} \quad (6.65)$$

In the above calculation, we have used the fact that Therefore, the number of microstates of the system with energy in the range $E \leq H(q_i, p_i) \leq E + \Delta E$ is:

$$\Omega(E) = \frac{\partial \Sigma}{\partial E} \Delta E = \frac{1}{(N-1)!} \frac{E^{N-1}}{(\hbar\omega)^N} \Delta E \quad (6.66)$$

The entropy of the harmonic oscillator system is

$$S = k_B \ln \Omega = N k_B \left[1 + \ln \left(\frac{E}{N \hbar \omega} \right) + \frac{1}{N} \ln \left(\frac{\Delta E}{E} \right) \right] \quad (6.67)$$

Generally, $\ln(\Delta E/E)$ is a finite value, so the last term can be ignored. Finally, the entropy of the harmonic oscillator system is:

$$S = k_B \ln \Omega = Nk_B \left[1 + \ln \left(\frac{E}{N\hbar\omega} \right) \right] \quad (6.68)$$

According to the total differential relationship: $dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN$, the temperature, energy, and heat capacity are Nk_B

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = Nk_B \frac{1}{E}, \quad E = Nk_B T \quad (6.69)$$

The pressure is (since the harmonic oscillator is fixed in space, there is no free movement to generate pressure, and the thermodynamic quantities are independent of volume):

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = 0, \quad p = 0 \quad (6.70)$$

The chemical potential of the system is:

$$\frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{E,N} = k_B \ln \left(\frac{E}{N\hbar\omega} \right) \quad (6.71)$$

6.3.4 Paramagnetic System

In a magnetic field H , N non-interacting spin $\frac{1}{2}$ particles, where g is the Landé g-factor, and the vacuum permeability μ_0 is normalized

$$H = - \sum_i g\mu_B H \hat{s}_{iz} \quad (6.72)$$

According to the partition function of the two-level system discussed Eq. 4.226, using the probability method to calculate

$$z = \sum_s e^{-\beta\varepsilon_s} = e^{\beta g\mu_B H} + e^{-\beta g\mu_B H} \quad (6.73)$$

Thus, the internal energy of the system is

$$U = -N \left(\frac{\partial \ln z}{\partial \beta} \right) = -Ng\mu_B H \frac{e^{\beta g\mu_B H} - e^{-\beta g\mu_B H}}{e^{\beta g\mu_B H} + e^{-\beta g\mu_B H}} = -Ng\mu_B H \tanh \beta g\mu_B H \quad (6.74)$$

In the microcanonical system, the system has 2^N possible states

$$|s\rangle = \{| \uparrow\downarrow\dots \rangle, | \downarrow\uparrow\dots \rangle, | \uparrow\downarrow\dots \rangle, | \downarrow\downarrow\dots \rangle, \dots \} \quad (6.75)$$

List the eigenvalue equation of the system

$$\hat{H} | \uparrow\downarrow\dots \rangle = [-g\mu_B H + g\mu_B H + \dots] | \uparrow\downarrow\dots \rangle = -g\mu_B H (N_\uparrow - N_\downarrow) | \uparrow\downarrow\dots \rangle \quad (6.76)$$

Thus, the number of particles with spin up is

$$E_S = -g\mu_B H (N_\uparrow - N_\downarrow) = (N - 2N_\uparrow) g\mu_B H \Rightarrow N_\uparrow = \frac{N}{2} - \frac{E_S}{2g\mu_B H} \quad (6.77)$$

Accordingly, the number of microstates and entropy

$$\Omega(E, N) = C_N^{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \quad (6.78a)$$

$$S = k_B \ln \Omega = k_B [\ln N! - \ln N_\uparrow! - \ln N_\downarrow!] \quad (6.78b)$$

$$\simeq k_B \left[N \ln N - \left(\frac{N}{2} - \frac{E}{2g\mu_B H} \right) \ln \left(\frac{N}{2} - \frac{E}{2g\mu_B H} \right) - \left(\frac{N}{2} + \frac{E}{2g\mu_B H} \right) \left(\frac{N}{2} + \frac{E}{2g\mu_B H} \right) \right]$$

According to the coldness, we get

$$\begin{aligned} \beta &= \frac{1}{k_B T} = \left(\frac{\partial S/k_B}{\partial E} \right)_N = \frac{1}{2g\mu_B H} \ln \left(\frac{N}{2} - \frac{E}{2g\mu_B H} \right) - \frac{1}{2g\mu_B H} \ln \left(\frac{N}{2} + \frac{E}{2g\mu_B H} \right) \\ &= \frac{1}{2g\mu_B H} \ln \frac{N - E/(g\mu_B H)}{N + E/(g\mu_B H)} \Rightarrow \frac{N - E/(g\mu_B H)}{N + E/(g\mu_B H)} = e^{2\beta g\mu_B H} \end{aligned} \quad (6.79)$$

The same energy result as Eq. 6.74 can be obtained

$$E = N g \mu_B H \frac{1 - e^{2\beta g\mu_B H}}{1 + e^{2\beta g\mu_B H}} = -N g \mu_B H \tanh \beta g \mu_B H \quad (6.80)$$

Chemical potential

$$\frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{E,N} = -k_B \ln N + \frac{1}{2} \ln \frac{N - E/(g\mu_B H)}{N + E/(g\mu_B H)} - 1 \quad (6.81)$$

6.4 Canonical Ensemble

The canonical ensemble, also known as the *NVT* ensemble, is an ensemble composed of systems in thermal contact with a large heat source.

The characteristic of the canonical ensemble is that all systems have the same temperature, number of particles, and volume, but the energy can vary and exchange.

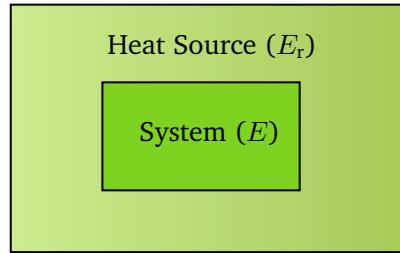


Fig. 57: The system in the canonical ensemble is in a large heat source, with energy exchange with the source

To use the conclusions of the microcanonical ensemble, consider the ensemble and the heat source together as a larger isolated system, with the total energy of this system being the energy of the heat source (E_r) plus the energy of the system E , and it is constant:

$$E_r + E = E_t = \text{const.} \quad (6.82)$$

6.4.1 Thermodynamic Characteristic Function: Free Energy

There is energy exchange between the system and the heat source. When the system is in a certain microstate with energy E_s , the heat source is in any possible microstate with energy $E_t - E_s$. According to the principle of equal probability, the probability ρ_s of the system being in state s is proportional to the number of microstates of the heat source with energy $E_t - E_s$, i.e.,

$$\rho_{c,s} \propto \Omega_r(E_t - E_s) \quad (6.83)$$

Since the value of $\Omega_r(E_t - E_s)$ is too large, we take the logarithm and expand Ω_r as a power series of E_s and approximate, using $S_r = k_B \ln \Omega_r$

$$\ln \Omega_r(E_t - E_s) \simeq \ln \Omega_r(E_t) - \left(\frac{\partial \ln \Omega_r}{\partial E_r} \right)_{E_r=E_t} E_s = \ln \Omega_r(E_t) - \beta E_s, \quad \left(\frac{\partial \ln \Omega_r}{\partial E_r} \right)_{N_r, V_r} = \frac{1}{k_B} \left(\frac{\partial S_r}{\partial E_r} \right)_{N_r, V_r} = \frac{1}{k_B T} = \beta \quad (6.84)$$

From the above two equations, we obtain the state density function of the canonical ensemble (the normalization factor Z is the canonical partition function)

$$\rho_{c,s} = \frac{1}{Z} e^{-\beta E_s}, \quad Z = \sum_s e^{-\beta E_s} \quad (6.85)$$

The summation is over all microstates of the system with given particle number, volume, and temperature. For energy level E_l , its degeneracy is Ω_l , i.e., the energy level corresponds to Ω_1 microstates of the system, so the probability of the system being at energy level E_l is (rewriting the partition function)

$$\rho_{c,l} = \frac{1}{Z} \Omega_l e^{-\beta E_l}, \quad Z = \sum_l \Omega_l e^{-\beta E_l} \quad (6.86)$$

The above discussion is about the case where the system energy levels are discrete. For classical physical systems with continuous phase space, the phase space is divided into phase space cells with volume h^{Nd} , where d is the degree of freedom of the system. Each phase space cell corresponds to a physical state, and the state distribution function of the canonical ensemble is

$$\rho_c(q_i, p_i) = \frac{1}{N! h^{Nd}} \frac{e^{-\beta E(q_i, p_i)}}{Z}, \quad Z = \frac{1}{N! h^{Nd}} \int e^{-\beta E(q_i, p_i)} d\Omega \quad (6.87)$$

Similarly, it can be proven that for the i -th phase space cell, with n_i systems, according to the principle of equal probability, the probability of finding the system in the i -th phase space cell (corresponding to system energy E_i) is:

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad (6.88)$$

In equilibrium, the internal energy of the system is the average value of energy:

$$U = \langle E_i \rangle = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad (6.89)$$

The entropy is the ensemble average of the system's Gibbs entropy:

$$\begin{aligned} S &= \langle -k_B \ln \rho \rangle = \int \rho_c (-k_B \ln \rho_c) d\Omega \\ &= \int \rho_c [k_B \beta H(q_i, p_i) + k_B \ln Z] = k_B \beta \langle H \rangle + k_B \ln Z = k_B \beta U + k_B \ln Z \end{aligned} \quad (6.90)$$

It can also be proven that the coldness

$$\frac{1}{T} = \frac{\partial S}{\partial U} = k_B U \frac{\partial \beta}{\partial U} + k_B \beta + \frac{\partial}{\partial U} (k_B \ln Z) = k_B \beta \quad (6.91)$$

The Helmholtz free energy in the canonical ensemble theory is obtained:

$$F(N, V, T) = U - TS = -k_B T \ln Z(N, V, T) \quad (6.92)$$

According to the total differential of free energy F : $dF = -S dT - p dV + \mu dN$, the thermodynamic quantities are obtained:

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N} \quad (6.93a)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial T} \right)_{V,N} \quad (6.93b)$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -\frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial N} \right)_{T,V} \quad (6.93c)$$

6.4.2 Ideal Gas

The canonical partition function for an ideal gas is:

$$Z(N, V, T) = \frac{1}{N! h^{3N}} \int d^3N q d^{3N} p e^{-\beta H(q_i, p_i)} = \frac{1}{N! h^{3N}} V^N \prod_{i=1}^{3N} \int_{-\infty}^{\infty} e^{-\beta \frac{p_i^2}{2m}} dp_i, H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \quad (6.94)$$

Where the integral uses Gaussian integration and dimensionless p_i : $x_i = \frac{p_i}{\sqrt{2m/\beta}}$, De Broglie wavelength, obtaining the canonical partition function

$$Z(N, V, T) = \frac{V^N}{N! h^{3N}} \left(\frac{2m\pi}{\beta} \right)^{3N/2} = \frac{V^N}{N! \lambda_T^{3N}} \quad (6.95)$$

From this, the free energy is obtained:

$$F(N, V, T) = -k_B T \ln Z = -Nk_B T \left\{ 1 + \ln \left[\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \right\} \quad (6.96)$$

According to the total differential of free energy F : $dF = -S dT - p dV + \mu dN$, the following is obtained:

$$p = - \left(\frac{\partial F}{\partial V} \right)_{N,T} = \frac{Nk_B T}{V}, \quad pV = Nk_B T \quad (6.97a)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{N,V} = Nk_B \left\{ \frac{5}{2} + \ln \left[\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \right\} \quad (6.97b)$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T} = -k_B T \ln \left[\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \quad (6.97c)$$

Using the Legendre transformation, the internal energy of the system is obtained

$$U = F + TS = \frac{3}{2} Nk_B T \quad (6.98)$$

Rewriting the expression for the system's entropy using internal energy instead of temperature, we get:

$$S(N, V, U) = Nk_B \left\{ \frac{5}{2} + \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3h^2 N} \right)^{3/2} \right] \right\} \quad (6.99)$$

The above results are almost consistent with those obtained from the microcanonical ensemble theory, except that in the microcanonical ensemble, the system's energy E is constant, while here the system's energy fluctuates, but the average value of the system's energy $U = \langle E \rangle$ is equal to the energy value in the microcanonical ensemble.

6.4.3 Real Gas: Two-Body Approximation

For a real gas, consider the potential energy V_{ij} between two molecules (i, j) , then the Hamiltonian of the system is:

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i < j} V_{ij} (|\mathbf{r}_i - \mathbf{r}_j|) \quad (6.100)$$

Assume V_{ij} only depends on the distance between molecules $|\mathbf{r}_i - \mathbf{r}_j|$. The canonical partition function of the system is:

$$\begin{aligned} Z(N, V, T) &= \frac{1}{N! h^{3N}} \int d^{3N} p \exp \left(-\frac{1}{2mk_B T} \sum_{i=1}^N p_i^2 \right) \int d^{3N} r \exp \left(-\frac{1}{k_B T} \sum_{i < j}^N V_{ij} \right) \\ &= \frac{1}{N!} \left(\frac{2\pi mk_B T}{h^2} \right)^{3N/2} \int d^{3N} r \prod_{i < j} e^{-\beta V_{ij}} \end{aligned} \quad (6.101)$$

The key to the calculation is the interaction factor $Q_N(V, T)$, if $V_{ij} = 0$, then $Q_N = V^N$, returning to the ideal gas result

$$Q_N(V, T) \equiv \int d^{3N} r \prod_{i < j} e^{-\beta V_{ij}} \quad (6.102)$$

The characteristics of molecular interactions are long-range attraction and short-range repulsion. There is a minimum potential energy $-V_0$ at $r = r_0$, which is less than 0, indicating attraction between molecules at $r = r_0$. The Lennard-Jones potential, which fits well with experiments, is:

$$V(r) = V_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right] \quad (6.103)$$

When the distance between two molecules $r \rightarrow \infty$, $V \rightarrow 0$, i.e., when the gas density is relatively low, the average distance between molecules is much greater than r_0 , and the real gas tends to be an ideal gas. Additionally, when $k_B T \gg V_0$, i.e., at high temperatures, the interaction between particles can be ignored, and the real gas also tends to be an ideal gas. Next, approximate the partition function Z to the first-order term of βV_0 , a small first-order quantity f_{ij} , the interaction

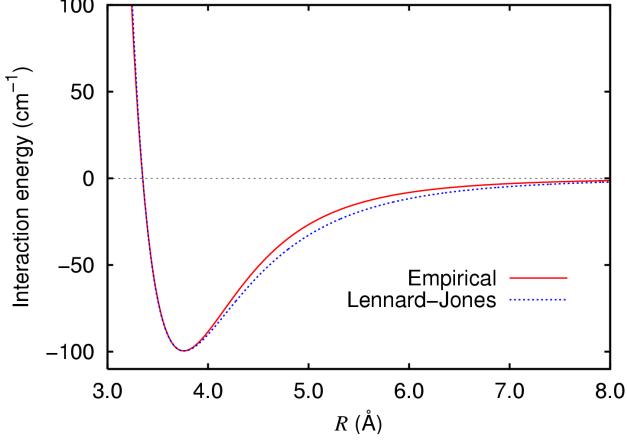


Fig. 58: Argon atom experiment and Lennard-Jones potential

factor Q is:

$$\begin{aligned}
 Q_N(V, T) &= \int d^{3N}r \prod_{i < j} (1 + f_{ij}), \quad f_{ij} = e^{-3v_{ij}} - 1 \ll 1 \\
 &= \int d^{3N}r \left(1 + \sum_{i < j} f_{ij} + \dots \right) \\
 &= V^N + V^{N-2} \sum_{i < j} \int d^3r_i d^3r_j (e^{-\beta V_{ij}} - 1) \\
 &\simeq V^N + V^{N-1} \frac{N(N-1)}{2} \int d^3r (e^{-\beta V_{ij}} - 1)
 \end{aligned} \tag{6.104}$$

The first term is the zero-order approximation, consistent with the expected ideal gas. The second term is the first-order correction brought by V_{ij} . Introduce the center of mass coordinates of molecules i, j : $\mathbf{R} = (\mathbf{r}_i + \mathbf{r}_j)/2$ and the relative coordinates $\mathbf{r} = \mathbf{r}_i - \mathbf{r}_j$. For $i < j$, there are $\binom{N}{2} = N(N-1)/2$ pairs of molecules giving the same contribution

Introduce the integral coefficient $a(T)$, which only depends on temperature:

$$a(T) = \int d^3r (e^{-\beta V_{ij}} - 1) = 4\pi \int_0^\infty r^2 dr (e^{-\beta V_i} - 1) \tag{6.105}$$

Substitute into the expression of the canonical partition function, take the approximation: $N(N-1)/2 \simeq N^2/2$, and obtain:

$$Z(N, V, T) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \left[V^N + V^{N-1} \frac{N^2}{2} a(T) + \dots \right] = \frac{1}{N!} \frac{V^N}{\lambda_T^{3N}} \left[1 + \frac{N^2}{2V} a(T) + \dots \right] \tag{6.106}$$

According to the total differential relationship of free energy F , the equation of state for real gases is obtained:

$$p(N, V, T) = - \left(\frac{\partial F}{\partial V} \right)_{N, T} = \frac{N k_B T}{V} - k_B T \frac{\frac{aN^2}{2V^2}}{1 + \frac{aN^2}{2V}} \simeq \frac{N k_B T}{V} \left(1 - \frac{a}{2} \frac{N}{V} \right) \tag{6.107}$$

Consider a more simplified Sutherland model, treating molecules as rigid spheres with mutual attraction, the potential energy of interaction between molecules is:

$$V(r) = \begin{cases} +\infty, & r < r_0 \\ -V_0 \left(\frac{r_0}{r}\right)^6, & r \gg r_0. \end{cases} \quad (6.108)$$

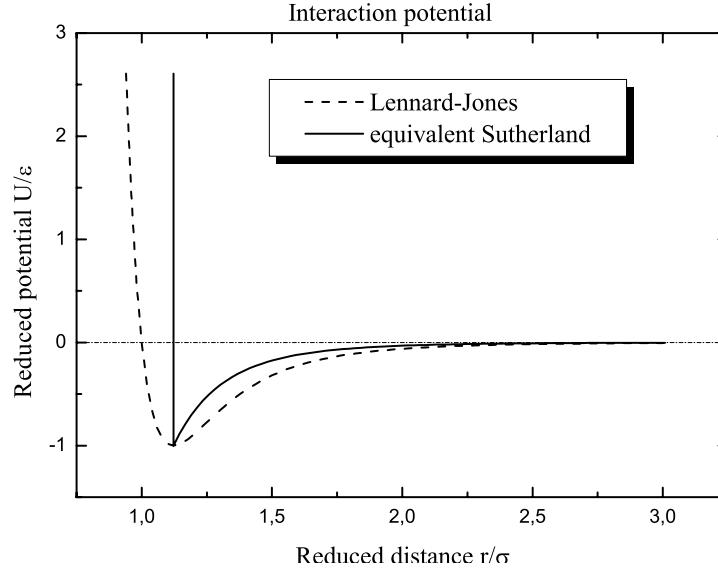


Fig. 59: Sutherland potential and Lennard-Jones potential

The shortest distance between two molecules is r_0 , and the radius of the molecule is $r_0/2$. Substitute the Sutherland potential into the expression for $a(T)$ Eq. 6.105, and obtain:

$$\begin{aligned} a(T) &= 4\pi \int_0^{r_0} r^2 dr (-1) + 4\pi \int_{r_0}^{\infty} r^2 dr \left(e^{3V_0(r_0/r)^6} - 1 \right) \\ &\simeq -\frac{4\pi}{3} r_0^3 + 4\pi \beta V_0 \int_{r_0}^{\infty} r^2 dr \left(\frac{r_0}{r} \right)^6 \simeq -\frac{4\pi}{3} r_0^3 (1 - \beta V_0) \end{aligned} \quad (6.109)$$

The equation of state for real gases is obtained:

$$p = \frac{Nk_B T}{V} \left[1 + \frac{2\pi r_0^3 N}{3V} \left(1 - \frac{V_0}{k_B T} \right) \right] \quad (6.110)$$

Based on the specific volume per particle $v = V/N$, and the approximation for low gas density $4\pi r_0^3/3 \ll v$, meaning the volume of the atom is much smaller than the average volume it occupies in the container. Define: $a = \frac{2\pi}{3} r_0^3 V_0$, $b = \frac{2\pi}{3} r_0^3$, returning to the Van der Waals equation Eq. 2.14

$$\begin{aligned} p + \frac{2\pi r_0^3 V_0}{3v^2} &= \frac{k_B T}{v} \left(1 + \frac{2\pi r_0^3}{3v} \right) \simeq \frac{k_B T}{v} \left(1 - \frac{2\pi r_0^3}{3v} \right)^{-1} \\ &\Rightarrow \left(p + \frac{a}{v^2} \right) (v - b) = k_B T \end{aligned} \quad (6.111)$$

6.4.4 Harmonic Oscillator System

The canonical partition function of the system:

$$\begin{aligned} Z(N, V, T) &= \frac{1}{h^N} \int d^N q d^N p e^{-\beta H(q_i, p_i)}, \quad H(q_i, p_i) = \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 q_i^2 \right) \\ &= \frac{1}{h^N} \prod_{i=1}^N \left[\int_{-\infty}^{\infty} dq_i e^{-\beta \frac{1}{2} m \omega^2 q_i^2} \int_{-\infty}^{\infty} dp_i e^{-\beta \frac{p_i^2}{2m}} \right] \\ &= \frac{1}{h^N} \left[\left(\frac{2\pi}{\beta m \omega^2} \right)^{1/2} \left(\frac{2m\pi}{\beta} \right)^{1/2} \right]^N = \left(\frac{k_B T}{\hbar \omega} \right)^N \end{aligned} \quad (6.112)$$

The free energy F of the system is obtained:

$$F(N, V, T) = -k_B T \ln Z(N, V, T) = -N k_B T \ln \left(\frac{k_B T}{\hbar \omega} \right) \quad (6.113)$$

According to the total differential of free energy F : $dF = -S dT - p dV + \mu dN$, we get:

$$p = - \left(\frac{\partial F}{\partial V} \right)_{N, T} = 0, \quad (6.114a)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{N, V} = N k_B \left[1 + \ln \left(\frac{k_B T}{\hbar \omega} \right) \right], \quad (6.114b)$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V, T} = -k_B T \ln \left(\frac{k_B T}{\hbar \omega} \right) \quad (6.114c)$$

After the Legendre transformation, the internal energy of the system is obtained:

$$U = F + TS = N k_B T \quad (6.115)$$

Rewrite the entropy $S(N, V, T)$ of the system as a function of $S(N, V, U)$, obtaining:

$$S(N, V, U) = N k_B \left[1 + \ln \left(\frac{U}{N \hbar \omega} \right) \right] \quad (6.116)$$

Ignoring the fluctuations of the system, this result is completely consistent with the result obtained using the microcanonical system theory.

6.4.5 Canonical System Fluctuations: Energy Fluctuations

The energy distribution of the canonical ensemble system has a peak state density with a maximum value, because the state density $D(E) \propto E^N$, and the Boltzmann factor decreases exponentially

$$\rho_c = \frac{1}{Z} D(E) e^{-\beta E}, \quad Z(N, V, T) = \int dE D(E) e^{-\beta E} \quad (6.117)$$

To solve for the energy value E^* at the maximum value. Differentiate $\rho_c(E)$ and set it to zero:

$$\frac{\partial \rho_c}{\partial E} = \frac{1}{Z} \left(\frac{\partial D}{\partial E} - D \beta \right) e^{-\beta E} = 0 \quad \Rightarrow \quad \frac{1}{D} \left(\frac{\partial D}{\partial E} \right)_{E^*} = \left(\frac{\partial \ln D}{\partial E} \right)_{E^*} = \frac{1}{k_B T} \quad (6.118)$$

Define the variance of E , ΔE^2 :

$$\Delta E^2 = \overline{E^2} - \bar{E}^2 \quad (6.119)$$

According to the derivative of internal energy with respect to coldness

$$\frac{\partial U}{\partial \beta} = -\frac{1}{Z} \int_0^\infty dED(E)E^2e^{-\beta E} + \frac{1}{Z^2} \left(\int_0^\infty dED(E)Ee^{-\beta E} \right)^2 = -\left(\overline{E^2} - \bar{E}^2 \right) \quad (6.120)$$

Thus, the energy variance is obtained

$$\Delta E^2 = -\frac{\partial U}{\partial \beta} = k_B T^2 \left(\frac{\partial U}{\partial T} \right)_{N,V} = k_B T^2 C_V \quad (6.121)$$

The relative ratio of variance ΔE to energy E :

$$\frac{\Delta E}{\langle E \rangle} = \frac{1}{U} \sqrt{k_B T^2 C_V} \sim \frac{1}{\sqrt{N}} \rightarrow 0, (N \rightarrow \infty) \quad (6.122)$$

where $U, C_V \propto N$ is used. The result shows that in the thermodynamic limit, $N \rightarrow \infty$, the canonical distribution approaches the microcanonical distribution. Therefore, the thermodynamic properties of the system at equilibrium obtained using the canonical ensemble theory and the microcanonical ensemble theory are consistent.

Next, expand $\ln \rho_c(E) \propto \ln [D(E)e^{-\beta E}]$ around $E^* = U$, and approximate to the second-order term of $(E - E^*)$

$$\ln [D(E)e^{-\beta E}] \simeq \ln [De^{-\beta E}] \Big|_{E^*} + \frac{1}{2} \frac{\partial^2}{\partial E^2} \ln [De^{-\beta E}] \Big|_{E^*} (E - E^*)^2 + \dots = -\beta(U - TS) - \frac{1}{2k_B T^2 C_V} (E - U)^2 + \dots \quad (6.123)$$

where the first derivative of $\ln [D(E)e^{-\beta E}]$ at $E = E^*$ is zero. Also, at $E = E^*$

$$\ln [De^{-\beta E}] \Big|_{E^*} = \ln [De^{-\beta E}] \Big|_{E_0} = -\beta F = -\beta(U - TS) \quad (6.124)$$

The second-order term satisfies

$$\ln D \Big|_{E^*} \simeq \ln(D\Delta E) \Big|_{E^*} \simeq \ln \Omega \Big|_{E^*} \simeq \frac{S}{k_B} \Big|_{E^*}, \quad \frac{\partial^2}{\partial E^2} \ln (De^{-\beta E}) \Big|_{E^*} \simeq \frac{1}{k_B} \frac{\partial^2 S}{\partial E^2} \Big|_{E^*} \quad (6.125)$$

where the derivative of entropy with respect to energy is

$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T}, \quad \frac{\partial^2 S}{\partial E^2} \Big|_{E^*} = -\frac{1}{T^2} \frac{1}{C_V} \quad (6.126)$$

Finally, the shape of $\rho_c(E)$ near the average value $\langle E \rangle = U$ is approximately a Gaussian function:

$$\rho_c(E) = \frac{1}{Z} D(E)e^{-\beta E} \simeq \frac{1}{Z} e^{-\beta(U - TS)} e^{-\frac{(E-U)^2}{2k_B T^2 C_V}} \quad (6.127)$$

6.4.6 Ferromagnetic-Paramagnetic Phase Transition: Ising Model

Heisenberg proposed that ferromagnetism in a lattice is generated by spin-spin interactions, summing only over adjacent atoms, denoted as $\langle ij \rangle$, the interaction Hamiltonian of a ferromagnet is:

$$H = - \sum_{(ij)} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (6.128)$$

In a ferromagnet, there are many magnetic domains where atomic spins are parallel, resulting in spontaneous magnetization. However, a ferromagnet does not have rotational invariance because the direction of spontaneous magnetization is random. Once spontaneous magnetization occurs, a specific direction is chosen, known as spontaneous symmetry breaking. When the system temperature is above the critical temperature ($T > T_c$), spontaneous magnetization disappears, and a phase transition from ferromagnet to paramagnet occurs.

One-Dimensional Ising Model

A uniaxial isotropic ferromagnetic crystal can first be discussed using the simplest one-dimensional Ising model, where N atoms are located on periodic lattice points, and the atomic magnetic moment can only take two directions: parallel or antiparallel to the crystal axis, represented by the quantum number σ_i : $\sigma_i = \pm 1$. The magnitude of the atomic magnetic moment is the Bohr magneton $\mu_B = e\hbar/2m$. Unlike paramagnets, ferromagnets have short-range interactions between two atoms, with interaction energy $-J/ + J$ for parallel/antiparallel spins, known as exchange interaction. If $J > 0$, the atomic spin interaction tends to align the atomic spins in the same direction. In the absence of an external magnetic field, considering only the nearest neighbor interactions, the Hamiltonian of the ferromagnet is:

$$H(\sigma_1, \sigma_2, \dots, \sigma_N) = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j, \quad \sigma_i, \sigma_j = \pm 1 \quad (6.129)$$

If an external magnetic field with magnetic induction intensity B is applied in the direction of the crystal axis, the potential energy of the magnetic moment μ_i in the external field is $-\mu_i \cdot \mathbf{B} = \mp \mu_B B \sigma_i$, so the Hamiltonian of the system is:

$$H = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - \mu_B B \sum_{i=1}^N \sigma_i \quad (6.130)$$

where $\sigma = +1$ indicates that the atomic spin is aligned with the magnetic field. Using periodic boundary conditions: $s_{N+1} = s_1$, the Hamiltonian is expanded into a symmetric form

$$H = -J \sum_{i=1}^N \sigma_i \sigma_{i+1} - \frac{1}{2} \mu_B B \sum_{i=1}^N (\sigma_i + \sigma_{i+1}) \quad (6.131)$$

The canonical partition function is:

$$Z(N, B, T) = \sum_{\sigma_1=\pm 1} \dots \sum_{\sigma_N=\pm 1} \exp \left\{ \beta \sum_{i=1}^N \left[J \sigma_i \sigma_{i+1} + \frac{1}{2} \mu_B B (\sigma_i + \sigma_{i+1}) \right] \right\} \quad (6.132)$$

Ising used combinatorial methods to calculate the above expression, while Kramers and Wannier used the matrix method, taking two bases in the one-dimensional spin space:

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (6.133)$$

Introduce the operator \hat{p} , with matrix elements:

$$\langle \sigma_i | \hat{p} | \sigma_{i+1} \rangle = \exp \left\{ \beta \sum_{i=1}^N \left[J \sigma_i \sigma_{i+1} + \frac{1}{2} \mu_B B (\sigma_i + \sigma_{i+1}) \right] \right\} \quad (6.134)$$

The matrix of the operator \hat{p} is:

$$\hat{p} = \sum_{i,j=1}^2 \hat{p}_{ij} |\sigma_i\rangle \langle \sigma_j| = \begin{pmatrix} \exp [\beta (J + \mu_B B)] & \exp (-\beta J) \\ \exp (-\beta J) & \exp [\beta (J - \mu_B B)] \end{pmatrix} \quad (6.135)$$

The canonical partition function is rewritten as:

$$Z(N, B, T) = \sum_{\sigma_1=\pm 1} \dots \sum_{\sigma_N=\pm 1} \langle \sigma_1 | \hat{p} | \sigma_2 \rangle \langle \sigma_2 | \hat{p} | \sigma_3 \rangle \dots \langle \sigma_N | \hat{p} | \sigma_1 \rangle = \sum_{\sigma_1=\pm 1} \langle \sigma_1 | \hat{p}^N | \sigma_1 \rangle = \text{Tr} (\hat{p}^N) \quad (6.136)$$

where the completeness condition of the basis is used: $\sum_{\sigma=\pm 1} |\sigma\rangle \langle \sigma| = I$ identity matrix. If the \hat{p} matrix is diagonalized, its trace is the sum of its diagonal elements, i.e., the sum of the two eigenvalues of the \hat{p} matrix. Therefore, first find the two eigenvalues of the \hat{p} matrix. The eigenvalue equation of the \hat{p} matrix is:

$$0 = \begin{vmatrix} \exp [\beta (J + \mu_B B)] - \lambda & \exp (-\beta J) \\ \exp (-\beta J) & \exp [\beta (J - \mu_B B)] - \lambda \end{vmatrix} \Rightarrow \lambda^2 - 2\lambda \exp(\beta J) \cosh(\beta \mu_B B) + 2 \sinh(2\beta J) = 0 \quad (6.137)$$

The two eigenvalues $\lambda_{1,2}$ are:

$$\lambda_{1,2} = \exp(\beta J) \cosh(\beta \mu_B B) \pm \left[\exp(-2\beta J) + \exp(2\beta J) \sinh^2(\beta \mu_B B) \right]^{1/2} \quad (6.138)$$

From this, the canonical partition function of the system is obtained:

$$Z(N, B, T) = \text{Tr}(\hat{p}^N) = \lambda_1^N + \lambda_2^N \quad (6.139)$$

The free energy F of the system is:

$$F = -k_B T \ln Z(N, B, T) = -k_B T \ln (\lambda_1^N + \lambda_2^N) \quad (6.140)$$

According to the total differential expression of F , the magnetization M of the system can be obtained:

$$M = - \left(\frac{\partial F}{\partial B} \right)_{N,T} = N \mu_B \frac{\sinh(\beta \mu_B B)}{\left[e^{-4\beta J} + \sinh^2(\beta \mu_B B) \right]^{1/2}} \cdot \frac{\lambda_1^N - \lambda_2^N}{\lambda_1^N + \lambda_2^N} \quad (6.141)$$

If there is no interaction between spins, i.e., $J = 0$, the two eigenvalues are:

$$\lambda_{1,2} = \cosh(\beta \mu_B B) \pm \left[1 + \sinh^2(\beta \mu_B B) \right]^{1/2} = \begin{cases} 2 \cosh(\beta \mu_B B) \\ 0 \end{cases} \quad (6.142)$$

At this time, the magnetization is:

$$M(J=0) = N \mu_B \tanh(\beta \mu_B B) \quad (6.143)$$

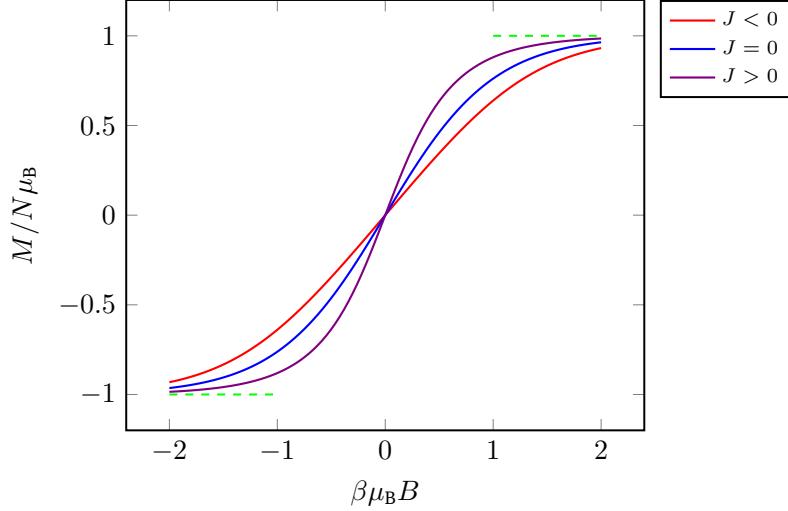


Fig. 60: Relationship between magnetization M and external magnetic induction intensity B in the one-dimensional Ising model

Returning to the formula for the magnetization of a paramagnet.

If the interaction energy is much greater than the energy of thermal motion, i.e., $\beta J \gg 1$, the two eigenvalues are approximately:

$$\lambda_{1,2} \simeq e^{\beta J} [\cosh(\beta\mu_B B) \pm \sinh(\beta\mu_B B)] = e^{\beta J \pm \beta\mu_B B} \quad (6.144)$$

The magnetization of the ferromagnet is:

$$M(\beta J \gg 1) = N\mu_B \frac{e^{N\beta\mu_B B} - e^{-N\beta\mu_B B}}{e^{N\beta\mu_B B} + e^{-N\beta\mu_B B}} = N\mu_B \tanh(N\beta\mu_B B) \quad (6.145)$$

It can be concluded that when $B = 0$, $M = 0$, even if the spin interaction is strong, the one-dimensional Ising model does not undergo spontaneous magnetization. This result is inconsistent with expectations, as strong spin interactions should tend to align atomic spins, producing ferromagnetism.

To explain why the one-dimensional Ising model does not undergo a ferromagnetic phase transition, it is necessary to calculate the average number of spins up and down (long program), as well as the number of parallel and antiparallel pairs of nearest neighbors (short program), to study the correlation between spins from a microscopic perspective. Assume that among N spins, N_+ spins are up ($\sigma = +1$), and N_- spins are down ($\sigma = -1$). Assume that among the nearest neighbor spin pairs, there are N_{++} pairs where both spins are $\sigma = +1$, N_{--} pairs where both spins are $\sigma = -1$, and N_{+-} pairs where one spin is up and the other is down. Consider a more general situation: each atom interacts with γ neighboring atoms. For all atoms with $\sigma = +1$, connect the atoms interacting with them with γ lines, then the N_+ atoms with spins up have a

total of γN_+ lines, and there is only one line between atoms, so:

$$\gamma N_+ = 2N_{++} + N_{+-} \quad (6.146a)$$

$$\gamma N_- = 2N_{--} + N_{+-} \quad (6.146b)$$

$$N = N_+ + N_- \quad (6.146c)$$

There are three constraints in total. The average value of spin-spin interaction is:

$$\left\langle \sum_{i,j} \sigma_i \sigma_j \right\rangle = N_{++} + N_{--} - N_{+-} \quad (6.147)$$

That is, spins in the same direction take positive values, and spins in opposite directions take negative values. To study spin correlation, use the constraint relationships to express the spin correlation quantities N_{++}, N_{--}, N_{+-} as much as possible in terms of $N_+, N_-,$ and $\left\langle \sum_{ij} \sigma_i \sigma_j \right\rangle.$

For the Ising model, $\gamma = 2$, so:

$$\frac{N_{+-}}{N} = \frac{1}{2} \left(1 - \frac{1}{N} \left\langle \sum_i \sigma_i \sigma_{i+1} \right\rangle \right) \quad (6.148a)$$

$$\frac{N_{++}}{N} = \frac{N_+}{N} - \frac{1}{2} \frac{N_{+-}}{N} \quad (6.148b)$$

$$\frac{N_{--}}{N} = \frac{N_-}{N} - \frac{1}{2} \frac{N_{+-}}{N} \quad (6.148c)$$

Due to lattice translational invariance, the average value $\left\langle \sum_i \sigma_i \sigma_{i+1} \right\rangle$ is independent of the subscript, so:

$$\left\langle \sum_{i=1}^N \sigma_i \sigma_{i+1} \right\rangle = N \langle \sigma_i \sigma_{i+1} \rangle \quad (6.149)$$

According to the calculation formula of statistical average value, directly calculate the average value of the spin interaction term:

$$\left\langle \sum_i \sigma_i \sigma_{i+1} \right\rangle = \frac{\sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} (\sum_i \sigma_i \sigma_{i+1}) \exp \left\{ \beta \sum_{i=1}^N [\sigma_i \sigma_{i+1} + \frac{1}{2} \mu_B B (\sigma_i + \sigma_{i+1})] \right\}}{\sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \exp \left\{ \beta \sum_{i=1}^N [\sigma_i \sigma_{i+1} + \frac{1}{2} \mu_B B (\sigma_i + \sigma_{i+1})] \right\}} \quad (6.150)$$

This average value can be directly obtained by differentiating the canonical partition function with respect to βJ , because in the exponential function of the partition function, the coefficient in front of $\sigma_i \sigma_{i+1}$ is βJ_0 , obtaining

$$\begin{aligned} \left\langle \sum_i \sigma_i \sigma_{i+1} \right\rangle &= \frac{1}{\beta} \frac{\partial}{\partial J} \ln Z = \frac{1}{\beta} \frac{\partial}{\partial J} \ln (\lambda_1^N + \lambda_2^N) \\ &= N \left(1 - \frac{2e^{-2\beta J}}{\left[e^{-2\beta J} + e^{2\beta J} \sinh^2(\beta \mu_B B) \right]^{1/2}} \cdot \frac{\lambda_1^{N-1} - \lambda_2^{N-1}}{\lambda_1^N + \lambda_2^N} \right) \end{aligned} \quad (6.151)$$

Substitute the above equation into Eq. 6.148a, obtaining:

$$\frac{N_{+-}}{N} = \frac{e^{-3\beta J}}{\left[e^{-4\beta J} + \sinh^2(\beta\mu_B B) \right]^{1/2}} \cdot \frac{\lambda_1^{N-1} - \lambda_2^{N-1}}{\lambda_1^N + \lambda_2^N} \quad (6.152)$$

If $J = 0$, i.e., there is no spin interaction, the above equation becomes:

$$\frac{N_{+-}}{N}(J=0) = \frac{1}{2} \cosh^{-1}(\beta\mu_B B) \quad (6.153)$$

For $B = 0$, we have $N_+ = N_- = \frac{N}{2}$, and from Eq. 6.148b, we get $N_{++} = N_{--} = \frac{N}{4}$, meaning half of the pairs are antiparallel, a quarter are parallel upwards, and a quarter are parallel downwards. If we consider the case where the spin interaction is very strong ($\beta J \gg 1$),

$$\frac{N_{+-}}{N} \simeq e^{-4\beta J} \frac{\sinh(N-1)(\beta\mu_B B)}{\sinh(\beta\mu_B B) \cosh(N\beta\mu_B B)} \quad (6.154)$$

The number of antiparallel pairs decreases exponentially with increasing interaction, meaning many "magnetic domains" form in the spin chain, where N_{++} and N_{--} values are quite large. Each domain has spins aligned in the same direction, but the upward and downward domains cancel each other out, i.e., $N_{++} = N_{--}$, resulting in a total magnetization of 0, so the one-dimensional Ising model does not exhibit ferromagnetism. If the spin interaction is very strong, neighboring spins align, showing local magnetization, i.e., short-range order, but on a larger scale, the magnetic moments of locally magnetized atoms cancel each other out, i.e., long-range disorder.

Two-Dimensional Ising Model—Mean Field Approximation

The two-dimensional Ising model exhibits ferromagnetism. Two approximation methods can be considered: mean field approximation and Bragg-Williams approximation.

In a system of N spins under an external magnetic field, the microscopic magnetic moments align along the field, producing a macroscopic magnetic moment. Each magnetic moment in the system also interacts with its neighboring magnetic moments. The total effect of the other γ magnetic moments around any magnetic moment is equivalent to a local magnetic field, known as the molecular field or internal field. This approximation method is the mean field approximation. It can be compared to the internal pressure in the Van der Waals equation, which is also obtained through the mean field approximation. Suppose the spin interaction energy between two magnetic moments is $-J\sigma_i\sigma_j$, and write the magnetic moment expression

$$E = -J\sigma_i\sigma_j = -\frac{J}{\mu_B^2} \mu_i \mu_j \equiv -\mu_i B_j^{eq} \quad (6.155)$$

where the effective magnetic field $B_j^{eq} = J\mu_j/\mu_B^2$ represents the effect of μ_j on μ_i . Assume the magnetization of the ferromagnet under the external field is m , then the contribution averaged over each magnetic moment is $\bar{\mu} = m/n$. Assume each magnetic moment interacts with its γ neighboring magnetic moments, then the γ neighboring magnetic moments produce an effective

magnetic induction intensity $\gamma J \bar{\mu} / \mu_B^2$. The energy of the i -th magnetic moment under the combined effect of the external and internal fields is

$$\varepsilon_i = -\sigma_i \mu_B B^{\text{eff}} = -\sigma_i \mu_B (B + B^{eq}) = -\sigma_i \mu_B \left(B + \frac{\gamma J}{n \mu_B^2} M \right) \quad (6.156)$$

Write the effective Hamiltonian

$$H^{\text{eff}} = H + \gamma J \bar{\sigma} / (g \mu_B), \quad \bar{\sigma} = M / (n \mu_B) \quad (6.157)$$

The magnetization of the system is:

$$M = n \bar{\mu} = n \mu_B \frac{e^{\beta \mu_B B^{\text{eff}}} - e^{-\beta \mu_B B^{\text{eff}}}}{e^{\beta \mu_B B^{\text{eff}}} + e^{-\beta \mu_B B^{\text{eff}}}} \quad (6.158)$$

When $B = 0$, the equation satisfied by the spontaneous magnetization M of the system is:

$$M = n \mu_B \tanh \left(\frac{\gamma J}{k_B T} \cdot \frac{M}{n \mu_B} \right) \quad (6.159)$$

Introduce the critical temperature, i.e., Curie temperature T_c (ferromagnetic phase transition temperature)

$$T_c \equiv \frac{\gamma J}{k_B} \quad (6.160)$$

Dimensionless the temperature, i.e., $\theta = T/T_c$, and introduce the dimensionless magnetic moment $\tilde{L} = M/n\mu_B$, then the magnetic moment equation is

$$\tilde{L} = \tanh(\tilde{L}/\theta) \quad (6.161)$$

The above equation is a transcendental equation, and its solution is

$$\tilde{L} = \begin{cases} 0, & T > T_c, \\ 0, \pm L_0, & T < T_c, \end{cases} \quad (6.162)$$

When $T > T_c$, $M = 0$, the system is in a paramagnetic state. When $T < T_c$, the system can be in the state of $M = 0$, but it is unstable and will transition to one of the two states $M = \pm L_0 n \mu_B$, resulting in spontaneous magnetization. After spontaneous magnetization occurs, the system may transition to either of the two stable states. After the phase transition, the system can only be in one of the two possible stable states, i.e., spontaneous symmetry breaking occurs.

Write the self-consistent mean field according to the effective Hamiltonian

$$\bar{\sigma} = \tanh \{ \beta g \mu_B [H + \gamma J \bar{\sigma} / (g \mu_B)] \} = \tanh (\beta g \mu_B H + \beta \gamma J \bar{\sigma}) \quad (6.163)$$

When $T > T_c \Rightarrow \bar{\sigma} = 0$ corresponds to no spontaneous magnetization, i.e., paramagnetic phase; when $T < T_c \Rightarrow \bar{\sigma} = \pm L_0$ corresponds to spontaneous magnetization, i.e., ferromagnetic phase.

For an external magnetic field $B = 0$, $T \leq T_c$, $M = N \mu_B \bar{\sigma} \propto |T - T_c|^\beta$, calculate the critical exponent

$$\begin{aligned} \bar{\sigma} &= \frac{\gamma J}{k_B T} \bar{\sigma} - \left(\frac{\gamma J}{k_B T} \right)^3 \bar{\sigma}^3 + \dots = \frac{T_c}{T} \bar{\sigma} - \left(\frac{T_c}{T} \right)^3 \bar{\sigma}^3 + \dots \\ \bar{\sigma}^2 &\simeq (T_c/T - 1) \Rightarrow \bar{\sigma} \propto |T_c/T - 1|^{1/2} \Rightarrow \beta = 1/2 \end{aligned} \quad (6.164)$$

When $T > T_c$, $H \rightarrow 0$, $M = \chi(T)H$, $\chi(T) \propto |T - T_c|^{-\gamma}$, calculate the critical exponent

$$\begin{aligned}\bar{\sigma} &\simeq \frac{g\mu_B H}{k_B T} + \frac{\gamma J \bar{\sigma}}{k_B T} = \frac{g\mu_B H}{k_B T} + \frac{T_c}{T} \bar{\sigma}, \quad \bar{\sigma} = \frac{g\mu_B H / (k_B T)}{1 - T_C/T} = \frac{g\mu_B / k_B}{T - T_C} H \\ M &= N\mu_B \bar{\sigma} = \frac{Ng\mu_B^2 / k_B}{T - T_C} H \Rightarrow \chi(T) = \frac{Ng\mu_B^2 / k_B}{T - T_C} \Rightarrow \gamma = 1\end{aligned}\quad (6.165)$$

According to the internal energy

$$U = -N\gamma J \bar{\sigma}^2 / 2 = \begin{cases} -N\gamma J (T_c/T - 1)/2 & T < T_c \\ 0 & T > T_c \end{cases} \quad (6.166)$$

Obtain the isothermal magnetic heat capacity

$$C_H = \left(\frac{\partial U}{\partial T} \right)_{H=0} = \begin{cases} \frac{N\gamma JT_c}{2T^2} = \frac{Nk_B T_c^2}{2T^2} \simeq \frac{Nk_B}{2}, & T < T_c \\ 0, & T > T_c \end{cases} \quad (6.167)$$

Thus, the critical exponent $\alpha = 0$. Finally, when $T = T_c$, $H \rightarrow 0$, $M \propto H^{1/\delta}$

$$\begin{aligned}\bar{\sigma} &= \tanh(\beta_c g\mu_B H + \bar{\sigma}) = \beta_c g\mu_B H + \bar{\sigma} - (\beta_c g\mu_B H + \bar{\sigma})^3 / 3 + \dots \\ &\Rightarrow 0 \simeq \beta_c g\mu_B H - \bar{\sigma}^3 / 3 \Rightarrow \delta = 3\end{aligned}\quad (6.168)$$

Two-Dimensional Ising Model—Bragg-Williams Approximation

Spin interactions are short-range, and the two-dimensional Ising model may exhibit short-range and long-range order, introducing short-range order parameter σ and long-range order parameter L

$$\frac{N_+}{N} = \frac{1}{2}(L+1) \quad (-1 \leq L \leq 1), \quad (6.169a)$$

$$\frac{N_{++}}{\frac{1}{2}\gamma N} = \frac{1}{2}(\sigma+1) \quad (-1 \leq \sigma \leq 1). \quad (6.169b)$$

Eq. 6.169a gives the probability of all N lattice points in the system having spins pointing up, determining the overall magnetic moment of the crystal $M = \mu_B(N_+ - N_-) = \mu_B NL$; Eq. 6.169b gives the proportion of pairs of neighboring lattice points with both spins pointing up, reflecting the correlation of neighboring spins, hence σ is called short-range order. The system energy is rewritten as:

$$E(N, L, \sigma) = -\frac{1}{2}NI\gamma(2\sigma - 2L + 1) - N\mu_B BL \quad (6.170)$$

For independent parameters of long-range and short-range order, the Bragg-Williams approximation assumes their relationship

$$\frac{N_{++}}{\frac{1}{2}\gamma N} \simeq \left(\frac{N_+}{N} \right)^2 \Rightarrow \sigma = \frac{1}{2}(L+1)^2 - 1 \quad (6.171)$$

That is, short-range and long-range order are approximately related, so the final magnetic moment of the crystal is only related to the degree of long-range order of the lattice spins, which is essentially a mean field approximation. Under this approximation, the system energy only depends on

N, L , specifically:

$$E(N, L) = -\frac{1}{2}N\gamma IL^2 - N\mu_B BL \quad (6.172)$$

Given L , i.e., given N_+ , the degeneracy of the system in the same energy state is (using $N_{\pm} = N(1 \pm L)/2$)

$$g(L) = \binom{N}{N_+} = \frac{N!}{[\frac{1}{2}N(1+L)]! [\frac{1}{2}N(1-L)]!} \quad (6.173)$$

Obtain the canonical partition function of the system:

$$\begin{aligned} Z &= \sum_{\{\sigma_0\}} e^{-\theta E(\sigma_0)} \simeq \sum_{L=-1}^L g(L) e^{\beta(\frac{1}{2}>1L^2+\mu_0 BL)} \\ &= \sum_{L=-1}^L \frac{N!}{[\frac{1}{2}N(1+L)]! [\frac{1}{2}N(1-L)]!} e^{\beta(\frac{1}{2}\gamma IL^2+\mu_0 BL)} \\ Z(B, T) &\simeq Z(B, T; \bar{L}) = g(\bar{L}) e^{\beta(\frac{1}{2}\gamma I\bar{L}^2+\mu_0 B\bar{L})} \end{aligned} \quad (6.174)$$

In the last step, the most probable \bar{L} corresponding to $Z(\bar{L})$ is used to replace Z in the above equation, where \bar{L} is the parameter of the partition function. In the thermodynamic limit $N \rightarrow \infty$, $Z(B, T; \bar{L})$ is large, and its natural logarithm is taken

$$\begin{aligned} \ln Z(B, T; \bar{L}) &= \ln \left\{ C_N^{N_+} \exp \left[\beta N \left(\frac{1}{2} \gamma I \bar{L}^2 + I \bar{L} \right) \right] \right\} \\ &= N \left[\beta \left(\frac{1}{2} \gamma I \bar{L}^2 + \mu_B B \bar{L} \right) - \frac{1+L}{2} \ln \frac{1+L}{2} - \frac{1-L}{2} \ln \frac{1-L}{2} \right] \end{aligned} \quad (6.175)$$

$\partial \ln Z / \partial L|_L = 0$, obtain the equation satisfied by \bar{L} :

$$\beta (\gamma I \bar{L} + \mu_B B) = \frac{1}{2} \ln \frac{1+\bar{L}}{1-\bar{L}} \Rightarrow \bar{L} = \tanh(\beta \mu_B B + \beta \gamma I \bar{L}) \quad (6.176)$$

Rewrite the natural logarithm of the canonical partition function of the system as:

$$\ln Z = N \left[\beta \left(\frac{1}{2} \gamma I \bar{L}^2 + \mu_B B \bar{L} \right) - \frac{1+\bar{L}}{2} \ln \frac{1+\bar{L}}{2} - \frac{1-\bar{L}}{2} \ln \frac{1-\bar{L}}{2} \right] = \frac{1}{2} N \gamma I \bar{L}^2 + \frac{1}{2} N k_B T \ln \frac{1-\bar{L}^2}{4} \quad (6.177)$$

Consider spontaneous magnetization, where $B = 0$. In Eq. 6.176, take $B = 0$, \bar{L} satisfies the equation:

$$\bar{L} = \tanh(\bar{L}/\theta) \quad (6.178)$$

Returning to Eq. 6.161, this shows that the Bragg-Williams approximation is equivalent to the mean field approximation.

According to Eq. 6.177, the free energy of the system is

$$F(T) = -k_B T \ln Z = \begin{cases} -N k_B T \ln 2, & T > T_c, \\ \frac{1}{2} N \gamma I \bar{L}_0^2 + \frac{1}{2} N k_B T \ln \frac{1-\bar{L}_0^2}{4}, & T < T_c \end{cases} \quad (6.179)$$

The internal energy of the system is:

$$U(T) = F + TS = -\frac{\partial \ln Z}{\partial \beta} = \begin{cases} 0, & T > T_c \\ -\frac{1}{N} \gamma I \bar{L}_0^2, & T < T_c \end{cases} \quad (6.180)$$

Thus, the heat capacity of the system is obtained

$$C(T) = \frac{dU}{dT} = \begin{cases} 0, & T > T_c, \\ -\frac{1}{2}N\gamma I \frac{dL_0^2}{dT}, & T < T_c. \end{cases} \quad (6.181)$$

When $T < T_c$, all thermodynamic quantities of the system depend on L_0 , and from Eq. 6.178, L_0 can be analyzed as a function of temperature $L_0(T)$. As $T \rightarrow 0$,

$$L_0 \simeq 1 - 2e^{-2/\theta} = 1 - 2e^{-2T_c/T} \quad (6.182)$$

Near the critical temperature T_c :

$$L_0 \simeq \sqrt{3} \left(1 - \frac{1}{\theta}\right)^{1/2} = \sqrt{3} \left(1 - \frac{T_c}{T}\right)^{1/2} \quad (6.183)$$

From Eq. 6.181, it can be seen that as the temperature $T \rightarrow T_c^-$, the heat capacity $C = \frac{3}{2}Nk_B$; while for $T > T_c$, the heat capacity of the magnetic moment $C = 0$. At the phase transition point $T = T_c$, $L_0 = 0$, the internal energy of the ferromagnet is continuous, but the heat capacity is discontinuous. Therefore, the ferromagnetic-paramagnetic phase transition is a second-order phase transition.

6.5 Grand Canonical Ensemble

The grand canonical ensemble, also known as the μVT ensemble, is composed of systems in contact with a large heat source and a particle source with constant chemical potential.

The characteristic of the grand canonical ensemble is that all systems have the same temperature, volume, and chemical potential, and the number of particles can vary.

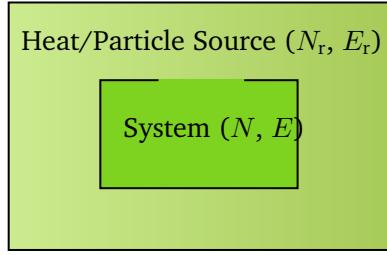


Fig. 61: The grand canonical ensemble is in a large heat and particle source, allowing for energy and particle exchange

Consider the ensemble and the heat and particle sources as a larger isolated system, where the total energy is the sum of the source energy (E_r) and the system energy E , and the total number of particles is the sum of the source particles (N_r) and the system particles N , both of which are constants

$$E_r + E = E_t = \text{const.}, \quad N_r + N = N_t = \text{const.} \quad (6.184)$$

6.5.1 Thermodynamic Characteristic Function: Grand Thermodynamic Potential

Satisfying the conditions of a large heat and particle source: $\frac{E}{E_t} = \left(1 - \frac{E_t}{E_t}\right) \ll 1$, $\frac{N}{N_t} = \left(1 - \frac{N_r}{N_t}\right) \ll 1$. According to the principle of equal probability, the probability ρ_s of the system being in state s is proportional to the number of microstates $\Omega_r(E_t - E_s)$ of the source with energy $E_t - E_s$, i.e.:

$$\rho_{gc,s} \propto \Omega_r(E_t - E_s, N_t - N_s) \quad (6.185)$$

Similarly, taking the logarithm and expanding the first-order term, we get

$$\ln \Omega_r(E_t - E_s, N_t - N_s) \simeq \ln \Omega_r(E_t, N_t) - \left(\frac{\partial \ln \Omega_r}{\partial E_r}\right)_{E_t, N_t} E_s - \left(\frac{\partial \ln \Omega_r}{\partial N_r}\right)_{E_t, N_t} N_s = \ln \Omega_r(E_t, N_t) - \beta E_s + \alpha N_s \quad (6.186)$$

where α, β are given by

$$\left(\frac{\partial \ln \Omega_r}{\partial E_r}\right)_{N_r, V_r} = \frac{1}{k_B} \left(\frac{\partial S_r}{\partial E_r}\right)_{N_r, V_r} = \frac{1}{k_B T} = \beta \quad (6.187a)$$

$$\left(\frac{\partial \ln \Omega_r}{\partial N_r}\right)_{N_r, V_r} = \frac{1}{k_B} \left(\frac{\partial S_r}{\partial N_r}\right)_{N_r, V_r} = -\frac{\mu}{k_B T} = -\alpha \quad (6.187b)$$

The state density function of the grand canonical ensemble (with normalization constant Ξ as the grand partition function) is obtained

$$\rho_{gc,s} = \frac{1}{\Xi} e^{-\beta E_s + \alpha N_s} \quad (6.188)$$

where the grand partition function is

$$\Xi = \sum_{N=0}^{\infty} \sum_s e^{-\beta E_s + \alpha N} \quad (6.189)$$

For classical physical systems, the phase space is continuous, and for a system with N particles, the phase space is divided into cells with a volume of h^{Nd} , where d is the degree of freedom of the system. Each cell corresponds to a physical state, and the state distribution function of the grand canonical ensemble is:

$$\rho_{gc}(q_i, p_i) d^{Nd} q d^{Nd} p = \frac{1}{N! h^{Nd}} \frac{e^{-\beta E(q_i, p_i) + \alpha N}}{\Xi} d\Omega \quad (6.190)$$

where the partition function of the grand canonical ensemble is:

$$\Xi = \sum_N \frac{e^{\alpha N}}{N! h^{Nd}} \int e^{-\beta E(q_i, p_i)} d^{Nd} q d^{Nd} p \quad (6.191)$$

Each cell $\Delta\Omega_{i,N}$ is of equal size, and it can be assumed that $\omega_{i,N}$ are all equal, resulting in the probability of finding the system in the i -th cell (corresponding to system energy E_i):

$$p_{gc,i,N} = \frac{n_{i,N}^*}{\mathcal{N}} = \frac{e^{-\beta E_i + \alpha N}}{\sum_{i,N} e^{-\beta E_i + \alpha N}} \quad (6.192)$$

Entropy is the ensemble average of the system's Gibbs entropy, where $\langle H \rangle = U$, $\langle N \rangle = \bar{N}$

$$\begin{aligned} S(V, \beta, \alpha) &= \langle -k_B \ln \rho_{gs} \rangle = \sum_{N=1}^{\infty} \int \rho_g [k_B \ln \Xi + k_B \beta H(q_i, p_i) - k_B \alpha N] d\Omega_N \\ &= k_B \ln \Xi(V, \beta, \alpha) + k_B \beta \langle H \rangle - k_B \alpha \langle N \rangle = k_B \ln \Xi + \frac{U - \mu \bar{N}}{T} \end{aligned} \quad (6.193)$$

The grand thermodynamic potential (grand potential) of the grand canonical ensemble is obtained as

$$J(V, T, \mu) = U - TS - \mu \bar{N} = -k_B T \ln \Xi(V, T, \mu) \quad (6.194)$$

According to the total differential of the grand potential J : $dJ(V, T, \mu) = -S dT - p dV - \bar{N} d\mu$, the thermodynamic quantities are obtained

$$p = - \left(\frac{\partial J}{\partial V} \right)_{T, \mu} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial V} \right)_{T, \mu} \quad (6.195a)$$

$$S = - \left(\frac{\partial J}{\partial T} \right)_{V, \mu} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial T} \right)_{V, \mu} \quad (6.195b)$$

$$\bar{N} = - \left(\frac{\partial J}{\partial \mu} \right)_{V, T} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{V, T} \quad (6.195c)$$

For a grand thermodynamic system composed of identical particles, the grand partition function of the system is:

$$\Xi(V, T, \mu) = \sum_{N=1}^{\infty} \frac{1}{N! h^{3N}} \iint d^{3N} q d^{3N} p \exp[-\beta H(q_\alpha, p_\alpha) + \alpha N] \quad (6.196)$$

It can be seen that the grand partition function is related to the canonical partition function $Z(T, V, N)$, i.e., the grand partition function is a weighted sum of canonical partition functions for different particle numbers N .

$$\Xi(V, T, \mu) = \sum_{N=1}^{\infty} [\exp(\mu/k_B T)]^N Z(T, V, N) \quad (6.197)$$

For an ideal gas, the canonical partition function $Z(T, V, N)$ is expressed using the single-particle partition function $Z_1(T, V)$ to obtain the system's grand partition function:

$$\Xi(V, T, \mu) = \sum_{N=1}^{\infty} \frac{1}{N!} [\exp(\mu/k_B T) Z_1(T, V)]^N = \exp[\exp(\mu\beta) Z_1], \quad Z(T, V, N) = \frac{1}{N!} [Z_1(T, V)]^N \quad (6.198)$$

6.5.2 Nearly Independent Particle Systems

For nearly independent particle systems, assume the energy level distribution is: $\{n_i\} = \{n_1, n_2, \dots, n_i, \dots\}$, then the total number of particles (N) and total energy (E) of the system satisfy Eq. 4.39 i.e., $N = \sum_i n_i$, $E_s = \sum_i n_i \varepsilon_i$. Additionally, given the energy level distribution $\{n_i\}$, the total number of microstates $W\{n_i\}$ of the nearly independent particle system equals the

product of the number of microstates W_i at each energy level (the distribution of particles at each energy level is independent).

$$W\{n_i\} = \prod_i W_i \quad (6.199)$$

Substituting into the microstate distribution function p_{N,E_s} of the grand canonical ensemble, we get:

$$p_{N,E_s} = \frac{1}{\Xi} W\{n_i\} e^{-\alpha N - \beta E_s} = \frac{1}{\Xi} W\{n_i\} e^{-\alpha \sum_i n_i - \beta \sum_i n_i \varepsilon_i} = \frac{1}{\Xi} \prod_i W_i e^{-(\alpha + \beta \varepsilon_i) n_i} \quad (6.200)$$

where the grand partition function Ξ is:

$$\begin{aligned} \Xi(\alpha, \beta, V) &= \sum_{N=0}^{\infty} \sum_{E_s} \sum_{\{n_i\}} W(\{n_i\}) e^{-\alpha \sum_i n_i - \beta \sum_i n_i \varepsilon_i} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \sum_{n_i=0}^{\infty} \dots \prod_i W_i e^{-(\alpha + \beta \varepsilon_i) n_i} \\ &= \prod_{i=1}^{\infty} \sum_{n_i=0}^{\infty} W_i e^{-(\alpha + \beta \varepsilon_i) n_i} = \prod_{i=1}^{\infty} \Xi_i(\alpha, \beta, V), \quad \Xi_i(\alpha, \beta, V) = \sum_{n_i=0}^{\infty} W_i e^{-(\alpha + \beta \varepsilon_i) n_i} \end{aligned} \quad (6.201)$$

In the grand canonical ensemble, the number of particles in the system is not fixed. Below, we calculate the ensemble average of the number of particles n_i at different energy levels:

$$\begin{aligned} \langle n_i \rangle &= \sum_{N=0}^{\infty} \sum_{E_s} n_i p_{N,E_s} = \frac{1}{\Xi} \sum_{N=0}^{\infty} \sum_{E_s} n_i W(\{n_i\}) e^{-\alpha N - \beta E_s} \\ &= \frac{1}{\Xi} \sum_{n_i=0}^{\infty} n_i W_i e^{-(\alpha + \beta \varepsilon_i) n_i} \prod_{j \neq i} \sum_{n_j=0}^{\infty} W_j e^{-(\alpha + \beta \varepsilon_j) n_j} \\ &= \sum_{n_i=0}^{\infty} n_i W_i e^{-(\alpha + \beta \varepsilon_i) n_i} \Big/ \sum_{n_i=0}^{\infty} W_i e^{-(\alpha + \beta \varepsilon_i) n_i} \\ &= -\frac{\partial \ln \Xi_i}{\partial \alpha} \end{aligned} \quad (6.202)$$

Next, we discuss the energy level distribution of particles in Boltzmann, Bose, and Fermi systems.

(1) Boltzmann Distribution: The system is non-degenerate, i.e., $\omega_i \gg n_i$. Given the energy level distribution $\{n_i\}$ of the system, the number of microstates of the system is:

$$W\{n_i\} = \prod_i W_i = \prod_i \frac{1}{n_i!} \omega_i^{n_i} \quad (6.203)$$

The grand partition function for the Boltzmann system is:

$$\Xi_i = \sum_{n_i=0}^{\infty} \frac{1}{n_i!} \omega_i^{n_i} e^{-(\alpha + \beta \varepsilon_i) n_i} = \sum_{n_i=0}^{\infty} \frac{1}{n_i!} [\omega_i e^{-(\alpha + \beta \varepsilon_i)}]^{n_i} = \exp [\omega_i e^{-(\alpha + \beta \varepsilon_i)}] \quad (6.204)$$

The ensemble average of the number of particles n_i is:

$$\langle n_i \rangle = -\frac{\partial \ln \Xi_i}{\partial \alpha} = \omega_i e^{-(\alpha + \beta \varepsilon_i)} \quad (6.205)$$

This is consistent with the Boltzmann distribution result, but the physical meaning is different. In Boltzmann statistical theory, $\{n_i\}$ is the most probable energy level distribution given the total

number of particles in the system, while the grand canonical ensemble gives the ensemble average of the energy level distribution.

(2) **Bose Distribution:** $\omega_i \sim n_i$. Given the energy level distribution $\{n_i\}$ of the system, the number of microstates is:

$$W_i = \binom{n_i + \omega_i - 1}{n_i} = \frac{(n_i + \omega_i - 1)!}{n_i! (\omega_i - 1)!} \quad (6.206)$$

The grand partition function for the Bose system is obtained using the binomial formula: $(1 - x)^{-n} = \sum_{m=0}^{\infty} C_{n+m-1}^m x^m$,

$$\Xi_i = \sum_{n_i=0}^{\infty} \binom{n_i + \omega_i - 1}{n_i} e^{-(\alpha + \beta \varepsilon_i) n_i} = [1 - e^{-(\alpha + \beta \varepsilon_i)}]^{-\omega_i} \quad (6.207)$$

The ensemble average of the number of particles n_i is:

$$\langle n_i \rangle = -\frac{\partial \ln \Xi_i}{\partial \alpha} = \frac{\omega_i}{e^{(\alpha + \beta \varepsilon_i)} - 1} \quad (6.208)$$

(3) **Fermi Distribution:** $\omega_i \sim n_i$. Given the energy level distribution $\{n_i\}$ of the system, the number of microstates is:

$$W_i = \binom{\omega_i}{n_i} = \frac{\omega_i!}{n_i! (n_i - \omega_i)!} \quad (6.209)$$

The grand partition function for the Fermi system is:

$$\Xi_i = \sum_{n_i=0}^{\infty} \binom{\omega_i}{n_i} e^{-(\alpha + \beta \varepsilon_i) n_i} = [1 + e^{-(\alpha + \beta \varepsilon_i)}]^{\omega_i} \quad (6.210)$$

The ensemble average of the number of particles n_i is:

$$\langle n_i \rangle = -\frac{\partial \ln \Xi_i}{\partial \alpha} = \frac{\omega_i}{e^{(\alpha + \beta \varepsilon_i)} + 1} \quad (6.211)$$

6.5.3 Ideal Gas

From Eq. 6.198 and the single-particle partition function $Z_1(T, V) = \frac{V}{\lambda_T^3}$, the grand partition function for a single-atom molecule of an ideal gas is:

$$\Xi(V, T, \mu) = \exp \left[\exp(\mu/k_B T) V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \quad (6.212)$$

The grand thermodynamic potential of the system is:

$$J(V, T, \mu) = -k_B T \ln \Xi(V, T, \mu) = -k_B T \exp(\mu/k_B T) V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \quad (6.213)$$

According to the total differential relationship of the grand thermodynamic potential: $dJ = -p dV - S dT - N d\mu$, the thermodynamic quantities are obtained:

$$p(T, V, \mu) = k_B T \exp(\mu/k_B T) \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \quad (6.214a)$$

$$S(T, V, \mu) = V \exp(\mu/k_B T) \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} k_B \left[\frac{5}{2} - \frac{\mu}{k_B T} \right] \quad (6.214b)$$

$$N(T, V, \mu) = V \exp(\mu/k_B T) \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \quad (6.214c)$$

Solving the last equation for μ , we obtain the expression $\mu(T, V, N)$ and substitute it into the above equations to obtain Eq. 6.97a, b, c.

6.5.4 Real Gas: Mayer Cluster Expansion

According to Eq. 6.101, the partition function of a real gas is:

$$Z(N, T, V) = \frac{1}{N! \lambda_T^{3N}} Q_N(T, V), \quad Q_N(V, T) = \int d^{3N} \mathbf{r} \prod_{i < j} \exp(-\beta V_{ij}) = \int d^{3N} \mathbf{r} \prod_{i < j} (1 + f_{ij}) \quad (6.215)$$

where the interaction factor is:

$$\begin{aligned} Q_N &= \int \prod_{i < j} (1 + f_{ij}) d\mathbf{r} = \int (1 + f_{12})(1 + f_{13}) \cdots (1 + f_{23})(1 + f_{24}) \cdots d\mathbf{r} \\ &= \int \left[1 + \sum_{i < j} f_{ij} + \sum_{i_1 < j_1; i_2 < j_2} f'_{i_1 j_1} f_{i_2 j_2} + \sum_{i_1 < j_1; i_2 < j_2; i_3 < j_3} f'_{i_1 j_1} f_{i_2 j_2} f_{i_3 j_3} + \cdots \right] d\mathbf{r} \end{aligned} \quad (6.216)$$

There are $2^{N(N-1)/2}$ terms in total, and a suitable method is needed to sum them; $\sum_{i_1 < j_1; i_2 < j_2; \dots} f'$ indicates that any pair $(i_p j_p) \neq (i_q j_q)$ in the sum. A cluster containing l particles is called an l -cluster, denoted as c_l . For a system with N particles, the smallest cluster is c_1 , and the largest cluster is c_N . Each N -particle cluster can be decomposed into different cluster combinations, represented by a set of numbers $(m_1, m_2, \dots, m_l, \dots, m_N)$, indicating that the graph contains m_1 c_1 clusters, m_2 c_2 clusters, m_l c_l clusters, and so on. The given cluster distribution satisfies:

$$\sum_{l=1}^N l \cdot m_l = N \quad (6.217)$$

N particles are distributed among different clusters. Each term in $S \{m_1, m_2, \dots, c_N\}$ has the same structure, equal to the product of different $[c_l]$ (where $[c_l]$ represents the integral value corresponding to the c_l cluster).

$$S \{m_1, m_2, \dots, c_N\} \text{ in any term} = \prod_{l=1}^N [m_l c_l] \quad (6.218)$$

The m_l l -clusters (c_l) are divided into K_l different configurations. Suppose there are K_l different types in c_l . For a given distribution (m_1, m_2, \dots, c_N) , suppose the m_l c_l can be divided into n_l

type 1, n_l type l , represented by a set of numbers $\{n_1, n_2, \dots, n_{K_l}\}$, called the type distribution of the c_l cluster. It satisfies:

$$\sum_{i=1}^{K_l} n_i = m_l \quad (6.219)$$

If the different configurations of the c_l cluster are denoted as $c_l^{(1)}, c_l^{(2)}, \dots, c_l^{(K_l)}$, then we have:

$$[m_l \uparrow c_l] = [n_1 \uparrow c_l^{(1)}] \cdot [n_2 \uparrow c_l^{(2)}] \cdots [n_{K_l} \uparrow c_l^{(K_l)}] = [c_l^{(1)}]^{n_1} \cdot [c_l^{(2)}]^{n_2} \cdots [c_l^{(K_l)}]^{n_{K_l}} \quad (6.220)$$

Next, we calculate Q_N , which involves summing over all possible N -particle configurations. First, given the cluster distribution $\{m_1, m_2, \dots, m_N\}$, there are many configurations for m_1 clusters of c_1 . We need to sum over all possible configurations $\{n_1, n_2, \dots, n_{K_1}\}$ while keeping m_1 constant:

$$\sum_{\{n_1, n_2, \dots, n_{K_1}\}} [m_1 \text{ clusters of } c_1] = \sum_{\{n_1, n_2, \dots, n_{K_1}\}} \prod_{i=1}^{K_1} \frac{[C_l^{(i)}]^{n_i}}{n_i!} \quad (6.221)$$

Next, sum over the cluster distribution $\{m_1, m_2, \dots, m_N\}$:

$$S \{m_1, m_2, \dots, m_N\} = N! \prod_{l=1}^N \frac{1}{(l!)^{m_l}} \sum_{\{n_1, n_2, \dots, n_{K_l}\}} \prod_{i=1}^{K_l} \frac{[C_l^{(i)}]^{n_i}}{n_i!} = N! \prod_{l=1}^N \frac{1}{(l!)^{m_l}} \frac{1}{m_l!} \left(\sum_{i=1}^{K_l} [C_l^{(i)}] \right)^{m_l} \quad (6.222)$$

Since $[c_l]$ comes from the volume integral of l particles in an l -particle cluster, the dimension of $[c_l]$ is the l -th power of volume. Using the center-of-mass coordinates of l particles and the relative coordinates between particles, first integrate over the volume of the center-of-mass coordinates, contributing a V , then integrate over the $l - 1$ relative coordinates, contributing a value with the dimension of volume to the $(l - 1)$ -th power, which is related to the range of interaction between particles. Generally, the thermal Compton wavelength of particles is non-dimensionalized, introducing the following dimensionless quantity b_l :

$$b_l(V, T) = \frac{1}{l! \lambda_T^{3(l-1)} V} \sum_{i=1}^{K_l} [C_l^{(i)}] \quad (6.223)$$

Thus, the interaction factor is obtained:

$$S \{m_1, m_2, \dots, m_N\} = N! \lambda_T^{3N} \prod_{l=1}^N \frac{1}{m_l!} \left(b_l \frac{V}{\lambda_T^3} \right)^{m_l} \quad (6.224a)$$

$$Q_N(V, T) = N! \lambda_T^{3N} \sum_{\{m_1, m_2, \dots, m_N\}} \prod_{l=1}^N \frac{1}{m_l!} \left(b_l \frac{V}{\lambda_T^3} \right)^{m_l} \quad (6.224b)$$

The corresponding canonical partition function is:

$$Z(T, V, N) = \sum_{\{m_1, m_2, \dots, m_N\}} \prod_{l=1}^N \frac{1}{m_l!} \left(b_l \frac{V}{\lambda_T^3} \right)^{m_l} \quad (6.225)$$

Since m_l in the above summation are not independent, considering the grand canonical distribution, the summation over the cluster $\{m_1, m_2, \dots, m_N\}$ can be simplified to a summation over

$m_l (l = 1, 2, \dots, N)$. Using Eq. 6.217 and according to the grand canonical ensemble theory, the ensemble partition function is:

$$\begin{aligned}\Xi(T, V, \mu) &= \sum_{N=0}^{\infty} e^{N\beta\mu} Z(T, V, N) \\ &= \sum_{N=0}^{\infty} \sum_{\{m_1, m_2, \dots, m_N\}} \prod_{l=1}^N \frac{1}{m_l!} \left(b_l e^{l\beta\mu} \frac{V}{\lambda_T^3} \right)^{m_l} = \sum_{m_1, m_2, \dots, m_N=0}^{\infty} \prod_{l=1}^N \frac{1}{m_l!} \left(b_l e^{l\beta\mu} \frac{V}{\lambda_T^3} \right)^{m_l} \\ &= \prod_{l=1}^{\infty} \exp \left(b_l e^{l\beta\mu} \frac{V}{\lambda_T^3} \right) = \exp \left(\frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} b_l e^{l\beta\mu} \right)\end{aligned}\quad (6.226)$$

The corresponding grand thermodynamic potential of the system is:

$$J(T, V, \mu) = -k_B T \ln \Xi = -k_B T \frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} b_l(V, T) e^{l\beta\mu} \quad (6.227)$$

Next, calculate the values of b_1, b_2, b_3 for the smallest particle clusters, using the center-of-mass coordinate $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ and the relative coordinate $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$

$$b_1 = \frac{1}{V} \int d^3 \mathbf{r}_1 = 1 \quad (6.228a)$$

$$b_2 = \frac{1}{2\lambda_T^3 V} \iint d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 f_{12} = \frac{1}{2\lambda_T^3} \int d^3 \mathbf{r}_{12} f_{12} = \frac{2\pi}{\lambda_T^3} \int_0^\infty dr r^2 \left(e^{-\frac{V(r)}{k_B T}} - 1 \right) \quad (6.228b)$$

$$b_3 = \frac{1}{6\lambda_T^6 V} \iiint d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 d^3 \mathbf{r}_3 (f_{12} f_{13} + f_{12} f_{23} + f_{13} f_{23} + f_{12} f_{13} f_{23}) \quad (6.228c)$$

$$\begin{aligned}&= \frac{1}{6\lambda_T^6 V} \int \left[\textcircled{1}-\textcircled{2} \textcircled{3} + \textcircled{1}-\textcircled{3} \textcircled{2} + \textcircled{1}-\textcircled{2} \textcircled{3} + \textcircled{1}-\textcircled{3} \textcircled{2} \right] \\ &= \frac{1}{6\lambda_T^6 V} \left[3V \int d^3 \mathbf{r}_{12} f_{12} \int d^3 \mathbf{r}_{13} f_{13} + V \iiint d^3 \mathbf{r}_{12} d\mathbf{r}_{13} d^3 \mathbf{r}_{23} f_{12} f_{13} f_{23} \right] \\ &= 2b_2^2 + \frac{1}{6\lambda_T^6 V} \iiint d^3 \mathbf{r}_{12} d\mathbf{r}_{13} d^3 \mathbf{r}_{23} f_{12} f_{13} f_{23}\end{aligned}$$

Here,  represents the contribution of the f_{12} factor. In the third step of Eq. 6.228b, it is assumed that the interaction between molecules depends only on the radius between them and is spherically symmetric. It can be proven that the integral of reducible diagrams can be further simplified to the product of irreducible diagrams. Additionally, the intermolecular interaction potential is extrapolated to infinity because as the distance between molecules increases, their interaction potential decays exponentially. When the system volume is relatively large, the volume integral over relative coordinates is approximately independent of the system volume and is only related to the range of interaction between molecules. Therefore, in the ideal gas approximation ($T \rightarrow \infty$ or $V \rightarrow \infty$),

$$\lim_{V \rightarrow \infty} b_l(V, T) = b_l(T) \quad (6.229)$$

After obtaining all the values of b_l , substitute them into the expression for the grand thermody-

namic potential J Eq. 6.227, and use the total differential relationship of J to obtain

$$\frac{p}{k_B T} = -\frac{1}{k_B T} \left(\frac{\partial J}{\partial V} \right)_{T,\mu} = \frac{1}{\lambda_T^3} \sum_{l=1}^{\infty} b_l \lambda^l \quad (6.230a)$$

$$\frac{N}{V} = -\frac{1}{V} \left(\frac{\partial J}{\partial \mu} \right)_{T,V} = \frac{1}{\lambda_T^3} \sum_{l=1}^{\infty} l b_l \lambda^l \quad (6.230b)$$

This is the Mayer cluster expansion formula, expressed as a function of fugacity $\lambda = \exp(\mu/k_B T)$. Next, we discuss the calculation of b_l . For low-density gases, in the thermodynamic limit, the probability of many particles forming a large cluster is very low, and $\lambda \ll 1$ corresponds to the cluster expansion only needing to expand to a few small terms. However, near phase transitions, many particles form a large cluster, so it is necessary to calculate the values of b_l for larger particle numbers. According to the Mayer cluster expansion formula, it can correspond to the Virial form of the real gas equation of state, which is the Virial expansion. By inverting Eq. 6.230b, we obtain the expression for fugacity λ :

$$\lambda = \sum_{l=1}^{\infty} c_l \left(\frac{\lambda_T^3}{v} \right)^l, \quad v = V/N \quad (6.231)$$

The undetermined coefficients c_l are functions only related to b_l . Substituting the above into Eq. 6.230a, we obtain the series expansion form:

$$\frac{p}{k_B T} = \frac{1}{\lambda_T^3} \sum_{l=1}^{\infty} b_l \left[\sum_{m=1}^{\infty} c_m \left(\frac{\lambda_T^3}{v} \right)^m \right]^l = \frac{1}{\lambda_T^3} \sum_{l=1}^{\infty} a_l \left(\frac{\lambda_T^3}{v} \right)^l \quad (6.232)$$

where the coefficients a_l are only related to b_l . For an ideal gas: $b_1 = 1, b_l = 0(l \geq 2)$, thus: $a_1 = 1, a_l = 0(l \geq 2)$. Below are the specific expressions for $a_l(l = 1, 2, \dots, N)$. According to the above relationship, we have:

$$\frac{p \lambda_T^3}{k_B T} = \sum_{l=1}^{\infty} b_l \lambda^l = \sum_{l=1}^{\infty} a_l \left[\sum_{n=1}^{\infty} n b_n \lambda^n \right]^l \quad (6.233)$$

Comparing the coefficients before λ^l , we obtain the expressions for b_l in terms of a_l :

$$b_1 = a_1 b_1 \quad (6.234a)$$

$$b_2 = 2a_1 b_2 + a_2 b_1^2 \quad (6.234b)$$

$$b_3 = 3a_1 b_3 + 4a_2 b_1 b_2 + a_3 b_1^3 \quad (6.234c)$$

$$b_4 = 4a_1 b_4 + a_2 (4b_2^2 + 6b_1 b_3) + 6a_3 b_1^2 b_2 + a_4 b_1^4 \quad (6.234d)$$

⋮

The expressions for a_l are:

$$a_1 = b_1 = 1 \quad (6.235a)$$

$$a_2 = -b_2 = -\frac{2\pi}{\lambda_T^3} \int_0^\infty dr r^2 \left(e^{-\frac{v(r)}{k_B T}} - 1 \right) \quad (6.235b)$$

$$a_3 = 4b_2^2 - 2b_3 \quad (6.235c)$$

$$a_4 = -20b_2^3 + 18b_2b_3 - 3b_4 \quad (6.235d)$$

⋮

Based on $a_1 = b_1 = 1$, approximating to the b_2 level, we obtain the equation of state for real gases:

$$\frac{pV}{Nk_B T} = 1 - b_2(T) \left(\frac{\lambda_T^3}{v} \right) \quad (6.236)$$

This result is consistent with the result obtained in Subsubsec. 6.4.3. Higher-order terms can also be given.

6.5.5 Grand Canonical Ensemble Fluctuations: Particle Number and Energy Fluctuations

For the grand canonical ensemble, the system exchanges particles and energy with a large particle source/large heat source, and the particle number and energy in the ensemble follow a certain probability distribution, i.e., the grand canonical distribution. The probability distribution causes fluctuations, and it is necessary to discuss the mean and variance. The following analysis shows that for the grand canonical ensemble, the most probable distribution corresponds to the particle number N^* and energy value E^* , which are equal to the ensemble average values of the system's particle number $\langle N \rangle$ and energy $\langle E \rangle$, and are equal to the corresponding thermodynamic quantities of the system. From this perspective, the grand canonical system is almost equivalent to the (micro)canonical ensemble.

If the Γ -space is divided into very small phase cells, the energy corresponding to the phase cell point i is E_i , then the probability of the grand canonical ensemble containing N particles and the system being exactly in the i -th phase cell is:

$$p_{gc,i,N} = \frac{1}{\Xi} \exp \{-\beta(E_i - \mu N)\}, \quad \Xi = \sum_{i,N} \exp \{-\beta(E_i - \mu N)\} \quad (6.237)$$

Introducing the state density $D_N(E)$ of unit energy for a given system particle number N , the number of systems with energy between $E \rightarrow E + dE$ is $D_N(E)dE$. Thus, according to the grand canonical system theory, the probability density of the system's particle number and energy being N, E in the ensemble is:

$$\rho_{gc}(N, E) = \frac{1}{\Xi} D_N(E) \exp \{-\beta(E - \mu N)\}, \quad \Xi = \sum_{N=1}^{\infty} \int_0^{\infty} dE D_N(E) \exp \{-\beta(E - \mu N)\} \quad (6.238)$$

For a given particle number N , the grand canonical ensemble is completely equivalent to the canonical ensemble. The grand canonical ensemble considers the distribution of the particle

number N on the basis of the canonical ensemble. (Microcanonical ensemble) Under the most probable system energy E^* and system particle number N^* ,

$$\frac{\partial \rho_{gc}(N, E)}{\partial E} \Big|_{E=E^*} = 0 \Rightarrow \frac{\partial D_N(E)}{\partial E} \Big|_{E=E^*} = \beta D_N(E^*) \Rightarrow \frac{\partial S}{\partial E} \Big|_{E=E^*} = \frac{1}{T} \quad (6.239)$$

where $D_N(E) \simeq \Omega(E, V, V)/\Delta E$, $S = k_B \ln \Omega$ is used. The partial derivative of $\rho_{gc}(N, E)$ with respect to the particle number is zero:

$$\frac{\partial p_{gc}(N, E)}{\partial N} \Big|_{N=N^*} = 0 \Rightarrow \frac{\partial D_N(E)}{\partial N} \Big|_{E=E^*} = -\beta \mu D_N(E^*) \Rightarrow \frac{\partial S}{\partial N} \Big|_{N=N^*} = -\frac{\mu}{T} \quad (6.240)$$

The ensemble average value of the system energy E is:

$$\bar{E} = \frac{1}{\Xi} \sum_{N=1}^{\infty} \int dE D_N(E) \exp\{-\beta(E - \mu N)\} E = J + TS + \mu N \equiv U \quad (6.241)$$

The ensemble average value of the system particle number N is:

$$\langle N \rangle = \sum_{i,N} N p_{i,N} = \frac{1}{\Xi} \sum_{i,N} N \exp\{-\beta(E_i - \mu N)\} = -\frac{\partial J}{\partial \mu} \Big|_{T,V} \equiv \bar{N} \quad (6.242)$$

The fluctuation of the system particle number: $\Delta N^2 \equiv \bar{N}^2 - \bar{N}^2$. First, calculate the mean square of the particle number $\langle N^2 \rangle$:

$$\begin{aligned} \bar{N}^2 &= \text{Tr} \left\{ \hat{N}^2 \hat{\rho} \right\} = \frac{1}{\Xi} \text{Tr} \left\{ \hat{N}^2 e^{-\beta \hat{H} + \beta \mu \hat{N}} \right\} \\ &= \frac{1}{\Xi} \text{Tr} \left\{ \left(\frac{\partial^2}{\partial(\beta\mu)^2} e^{-\beta \hat{H} + \beta \mu \hat{N}} \right)_{\beta,V} \right\} = \frac{1}{\Xi} \left(\frac{\partial^2}{\partial(\beta\mu)^2} \text{Tr} \left\{ e^{-\beta \hat{H} + \beta \mu \hat{N}} \right\} \right)_{\beta,V} \\ &= \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial(\beta\mu)^2} = \frac{\partial}{\partial \beta \mu} \left(\frac{1}{\Xi} \frac{\partial \Xi}{\partial \beta \mu} \right) - \frac{\partial(1/\Xi)}{\partial \beta \mu} \frac{\partial \Xi}{\partial \beta \mu} = \left(\frac{\partial^2 \ln \Xi}{\partial(\beta\mu)^2} \right) + \left(\frac{\partial \ln \Xi}{\partial \beta \mu} \right)^2 \end{aligned} \quad (6.243)$$

The variance of the particle number fluctuation is obtained:

$$\Delta N^2 = k_B T \frac{\partial \langle N \rangle}{\partial \mu} \Big|_{T,V} = k_B T \frac{\partial \bar{N}}{\partial \mu} \Big|_{T,V} \quad (6.244)$$

The relative fluctuation of the particle number:

$$\frac{\Delta N^2}{N^2} = \left(\frac{\partial^2 \ln \Xi}{\partial(\beta\mu)^2} \right) / \left(\frac{\partial N}{\partial \beta \mu} \right)_{\beta,V}^2 = \frac{k_B T}{N^2} \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \quad (6.245)$$

Rewriting the above equation in terms of more easily observable physical quantities, considering the specific entropy $s = S/N$ and specific volume $v = V/N$, and the total differential expression of Gibbs free energy G : $dG = -S dT + V dj + \mu dN$, using $G = \bar{N}\mu$, we obtain: $d\mu = v dp - s dT$. Thus, we obtain the Maxwell relation:

$$\left(\frac{\partial \mu}{\partial v} \right)_T = v \left(\frac{\partial p}{\partial v} \right)_T \quad (6.246)$$

Under the condition of keeping V constant, $dv = -V d\bar{N}/\bar{N}^2 = -v d\bar{N}/\bar{N}$, substituting into the above equation, we obtain:

$$-\frac{\bar{N}^2}{V} \left(\frac{\partial \mu}{\partial \bar{N}} \right)_{T,V} = v \left(\frac{\partial p}{\partial v} \right)_T \quad (6.247)$$

Substituting the above back into Eq. 6.245, we obtain:

$$\frac{\Delta N^2}{\bar{N}^2} = \frac{k_B T}{V} \kappa_T \quad (6.248)$$

where $\kappa_T = (\partial v / \partial p)_T / v$ is the compressibility, an intensive quantity. Under the condition of keeping the particle number density constant, both V and \bar{N} are extensive quantities, so the above equation is inversely proportional to the particle number \bar{N} . In the thermodynamic limit, the relative fluctuation of the particle number is almost zero. If the compressibility κ_T is not finite, the relative fluctuation of the particle number may be large, for example, at the critical point of liquid-gas phase transition, where the two phases coexist, the system's compressibility κ_T tends to infinity, and the relative fluctuation of the particle number in the liquid-gas two phases is also very large, resulting in the phenomenon of critical opalescence as seen in Fig. 28.

The ensemble average value of the system's energy E in the grand canonical ensemble is:

$$\langle E \rangle = \sum_{i,N} E_i p_{gc,i,N} = \frac{1}{\Xi} \sum_{i,N} E_i \exp \{-\beta(E_i - \mu N)\} = -\frac{1}{\Xi} \left(\frac{\partial \Xi}{\partial \beta} \right)_{\lambda, V} \quad (6.249)$$

For simplicity, during the differentiation process of the above equation, the fugacity $\lambda = e^{\beta \mu}$ is kept constant. Similarly, the mean square of the energy is:

$$\langle E^2 \rangle = \frac{1}{\Xi} \left(\frac{\partial^2 \Xi}{\partial \beta^2} \right)_{\lambda, V} = -\frac{1}{\Xi} \left(\frac{\partial(\Xi \langle E \rangle)}{\partial \beta} \right)_{\lambda, V} = \langle E \rangle^2 - \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{\lambda, V} \quad (6.250)$$

The fluctuation of energy is:

$$\begin{aligned} \Delta E^2 &= \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln \Xi}{\partial \beta^2} = - \left(\frac{\partial U}{\partial \beta} \right)_{\beta \mu, V} = - \frac{\partial(U, \beta \mu)}{\partial(\beta, \beta \mu)} \\ &= - \frac{\partial(U, \beta \mu)}{\partial(\beta, N)} \frac{\partial(\beta, N)}{\partial(\beta, \beta \mu)} = - \left[\left(\frac{\partial U}{\partial \beta} \right)_N - \left(\frac{\partial U}{\partial N} \right)_\beta \left(\frac{\partial \beta \mu}{\partial \beta} \right)_N \left(\frac{\partial N}{\partial \beta \mu} \right)_\beta \right] \end{aligned} \quad (6.251)$$

According to the total differential expression of the partition function, we have:

$$d \ln \Xi = \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\beta \mu} d\beta + \left(\frac{\partial \ln \Xi}{\partial \beta \mu} \right)_\beta d(\beta \mu) = -U d\beta + N d(\beta \mu) \Rightarrow \left(\frac{\partial \beta \mu}{\partial \beta} \right)_N = \left(\frac{\partial U}{\partial N} \right)_\beta \quad (6.252)$$

Substituting into the expression for the relative fluctuation of energy, we obtain:

$$\begin{aligned} \Delta E^2 &= - \left(\frac{\partial U}{\partial \beta} \right)_N + \left(\frac{\partial U}{\partial N} \right)_\beta^2 \left(\frac{\partial N}{\partial \beta \mu} \right)_\beta = k_B T^2 \left(\frac{\partial U}{\partial T} \right)_{NV} + \left(\frac{\partial U}{\partial N} \right)_{TV}^2 \Delta N^2 \\ &= k_B T^2 C_V + \left(\frac{\partial U}{\partial N} \right)_{TV}^2 \Delta N^2 = \Delta E_{\text{正则}}^2 + \left(\frac{\partial U}{\partial N} \right)_{TV}^2 \Delta N^2 \end{aligned} \quad (6.253)$$

In the parentheses, $\frac{\partial U}{\partial N}$ is an intensive quantity, $\Delta N^2 \propto \bar{N}$, and $U \propto \bar{N}$. In the thermodynamic limit, the relative energy fluctuation of the system $\Delta E^2 / U^2 \propto 1/\sqrt{\bar{N}} \rightarrow 0$ (as $\bar{N} \rightarrow \infty$). For the grand canonical ensemble, energy fluctuations and particle number fluctuations are correlated,

and it can be proven that $\langle EN \rangle \neq \langle E \rangle \langle N \rangle$.

$$\begin{aligned}\overline{NE} &= \text{Tr}\{\hat{N}\hat{H}\hat{\rho}\} = \frac{1}{\Xi} \text{Tr}\left\{\hat{N}\hat{H}e^{-\beta\hat{H}+\beta\mu\hat{N}}\right\} = -\frac{1}{\Xi} \frac{\partial^2}{\partial\beta\partial(\beta\mu)} \text{Tr}\left\{e^{-\beta\hat{H}+\beta\mu\hat{N}}\right\} \\ &= -\frac{1}{\Xi} \frac{\partial^2\Xi}{\partial\beta\partial(\beta\mu)} = -\frac{\partial}{\partial\beta} \left[\frac{1}{\Xi} \frac{\partial\Xi}{\partial(\beta\mu)} \right] + \left(\frac{\partial(1/\Xi)}{\partial\beta} \right)_{\beta\mu} \left(\frac{\partial\Xi}{\partial\beta\mu} \right)_\beta = -\frac{\partial}{\partial\beta} \left[\frac{1}{\Xi} \frac{\partial\Xi}{\partial(\beta\mu)} \right] - \frac{1}{\Xi^2} \left(\frac{\partial\Xi}{\partial\beta} \right)_{\beta\mu} \left(\frac{\partial\Xi}{\partial\beta\mu} \right)_\beta \\ &= -\frac{\partial^2\ln\Xi}{\partial\beta\partial(\beta\mu)} - \left(\frac{\partial\ln\Xi}{\partial\beta} \right)_{\beta\mu} \left(\frac{\partial\ln\Xi}{\partial\beta\mu} \right)_\beta = -\frac{\partial^2\ln\Xi}{\partial\beta\partial(\beta\mu)} + \bar{N}\bar{E}\end{aligned}\tag{6.254}$$

Thus, the covariance of fluctuations

$$\begin{aligned}\Delta N\Delta\bar{E} &= \overline{(N-\bar{N})(E-\bar{E})} = \overline{NE} - \bar{N}\bar{E} = -\frac{\partial^2\ln\Xi}{\partial\beta\partial(\beta\mu)} = -\left(\frac{\partial N}{\partial\beta}\right)_{\beta\mu V} = \left(\frac{\partial U}{\partial\beta\mu}\right)_{\beta V} = k_B T \left(\frac{\partial U}{\partial\mu}\right)_{TV} \\ &= k_B T \left(\frac{\partial U}{\partial N}\right)_{TV} \left(\frac{\partial N}{\partial\mu}\right)_{TV} = \left(\frac{\partial U}{\partial N}\right)_{TV} \Delta N^2\end{aligned}\tag{6.255}$$

The distribution of energy and particle number is given by

$$\begin{aligned}p(E, N) &= \sum_s p_s = \frac{1}{\Xi} \sum_{\{s|E_s=E, N_s=N\}} e^{-\beta E_s + \beta\mu N_s} = \frac{1}{\Xi} \Omega(E, N, V) e^{-\beta E + \beta\mu N} \\ &= \frac{1}{\Xi} e^{\ln\Omega(E, N, V) - \beta E + \beta\mu N} = \frac{1}{\Xi} e^{S(E, N, V)/k_B - \beta E + \beta\mu N} \\ &= e^{(-k_B T \ln\Xi + TS - E + \mu N)/(k_B T)} = e^{-(\bar{J} + J)/(k_B T)} = e^{-\Delta J/(k_B T)}\end{aligned}\tag{6.256}$$

where the generalized grand potential J and the equilibrium grand potential \bar{J} are defined as

$$J = J(T, \mu, V | E, N, V) = E - TS(E, N, V) - \mu N\tag{6.257a}$$

$$\bar{J} = J(T, \mu, V) = \bar{E} - TS(\bar{E}, \bar{N}, V) - \mu \bar{N}\tag{6.257b}$$

Using the expansion of the grand potential difference and the total differential expansion of entropy $dS = \frac{dU}{T} - \frac{\mu}{T}dN$

$$\begin{aligned}-\Delta J/T &= [S(E, N) - S(\bar{E}, \bar{N})] - (E - \bar{E})/T + \mu(N - \bar{N})/T \\ &= \left[\left(\frac{\partial S}{\partial E} \right)_N \Delta E + \left(\frac{\partial S}{\partial N} \right)_E \Delta N \right] + (-\Delta E + \mu\Delta N)/T + \frac{1}{2} \frac{\partial^2 S}{\partial U^2} \Delta E^2 + \frac{1}{2} \frac{\partial^2 S}{\partial N^2} \Delta N^2 + \frac{\partial^2 S}{\partial U \partial N} \Delta N \Delta E + \dots \\ &= \frac{1}{2} \left(\frac{\partial(1/T)}{\partial U} \right)_N \Delta E^2 + \frac{1}{2} \left(\frac{\partial(\mu/T)}{\partial N} \right)_U \Delta N^2 + \left(\frac{\partial(1/T)}{\partial N} \right)_U \Delta N \Delta E\end{aligned}\tag{6.258}$$

The probability density can still be written in the form of a Gaussian distribution

$$\begin{aligned}p(E, N) &= e^{-\Delta J/(k_B T)} \\ &= \frac{1}{C} \exp \left\{ \frac{1}{2k_B} \left(\frac{\partial(1/T)}{\partial U} \right)_N \Delta E^2 + \frac{1}{2k_B} \left(\frac{\partial(\mu/T)}{\partial N} \right)_U \Delta N^2 + \frac{1}{k_B} \left(\frac{\partial(1/T)}{\partial N} \right)_U \Delta N \Delta E \right\} \\ &= \frac{1}{C} \exp \left\{ -\frac{\Delta E^2}{2k_B T^2 C_V} - \frac{\Delta N^2}{2k_B T N^2 \kappa_T / V} - \frac{\Delta N \Delta E}{2k_B T N^2 (\partial U / \partial N)_{TV} \kappa_T / V} \right\}\end{aligned}\tag{6.259}$$

For a more general fluctuation theory, refer to the generalized ensemble theory of fluctuations Subsubsec. 7.4.1.

Chapter 7 Non-equilibrium Theory

7.1 Gas Transport

7.1.1 Particle Motion Parameters

The flux of particles Φ can be obtained by integrating Eq. 4.166

$$\begin{aligned}\Phi &= \int_0^\infty \int_0^{\pi/2} v \cos \theta \cdot n f(v) dv \frac{1}{2} \sin \theta d\theta \\ &= \frac{n}{2} \int_0^\infty dv v f(v) \int_0^{\pi/2} d\theta \cos \theta \sin \theta = \frac{1}{4} n \langle v \rangle\end{aligned}\quad (7.1)$$

According to Eq. 4.172, the particle number density is given by $n = p/(k_B T)$, and the average speed is given by Eq. 4.169, so the particle flux Φ can be written as

$$\Phi = \frac{1}{4} \frac{p}{k_B T} \sqrt{\frac{8 k_B T}{\pi m}} = \frac{p}{\sqrt{2 \pi m k_B T}} \quad (7.2)$$

The particle diffusion rate is (where A is the unit area)

$$\Phi A = \frac{p A}{\sqrt{2 \pi m k_B T}} \quad (7.3)$$

The volume swept by a particle per unit time is $\sigma v dt$, and the probability that a particle does not collide after time dt satisfies the differential equation

$$P(t + dt) = P(t) + \frac{dP}{dt} dt = P(t)(1 - n\sigma v dt), \quad \frac{1}{P} \frac{dP}{dt} = -n\sigma v \quad (7.4)$$

Thus, the probability that a particle does not collide after time t (with the normalization condition $\int_0^\infty e^{-n\sigma vt} n\sigma v dt = 1$) is given by

$$P(0) = 1, \quad P(t) = \exp(-n\sigma vt) \quad (7.5)$$

The average scattering time is obtained as

$$\begin{aligned}\tau &= \int_0^\infty t e^{-n\sigma vt} n\sigma v dt = \frac{1}{n\sigma v} \int_0^\infty (n\sigma vt) e^{-n\sigma vt} d(n\sigma vt) \\ &= \frac{1}{n\sigma v} \int_0^\infty x e^{-x} dx = \frac{1}{n\sigma v}\end{aligned}\quad (7.6)$$

The hard sphere potential between two spherical particles is abstracted as

$$V(R) = \begin{cases} 0 & R > a_1 + a_2 \\ \infty & R \leq a_1 + a_2 \end{cases}$$

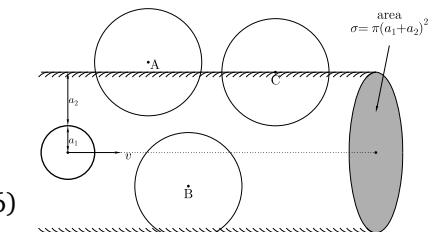


Fig. 62: Differential scattering cross-section of two types of spherical particles

For a collision (requiring the perpendicular closest distance collision parameter $b < a_1 + a_2$) between two spherical particles with radii a_1 and a_2 , the differential scattering cross-section is

$$\sigma = \pi (a_1 + a_2)^2 = \pi d^2 \quad (7.8)$$

The mean free path is

$$\lambda = \langle v \rangle \tau = \frac{\langle v \rangle}{n\sigma v} = \frac{1}{\sqrt{2}n\sigma} \quad (7.9)$$

where v uses the relative velocity $v \simeq v_r$, $\langle \cos^2 \theta \rangle = 0$, $v_r^2 = v_1^2 + v_2^2 - 2v_1 v_2 \cos \theta \Rightarrow \langle v_r^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle = 2 \langle v^2 \rangle$. Using the ideal gas equation of state $p = nk_B T$ and the differential scattering cross-section $\sigma = \pi d^2$, the mean free path can be written as

$$\lambda = \frac{k_B T}{\sqrt{2}\sigma p} = \frac{k_B T}{\sqrt{2}\pi d^2 p} \quad (7.10)$$

7.1.2 Transport/Diffusion Equation

1. Viscosity

Viscosity refers to the resistance phenomenon of a fluid under shear stress-induced deformation. For a parallel uniform fluid, the shear stress between layers is proportional to the velocity gradient perpendicular to the fluid layers, with the proportionality coefficient called the viscosity coefficient, denoted as η (dimension $\text{Nm}^{-2}\text{s}(\text{Pa} \cdot \text{s})$). Denoting the velocity of each layer as $\langle u_x \rangle$, the shear stress satisfies

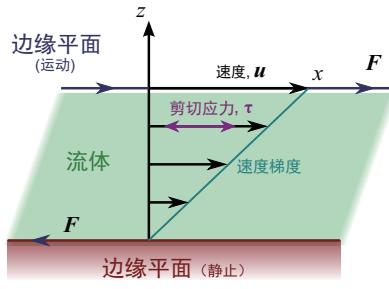


Fig. 63: Velocity gradient of fluid in the xz plane

The velocity gradient can derive a physical quantity, the momentum flux Π_z

$$\Pi_z = -\eta \frac{\partial \langle u_x \rangle}{\partial z} \quad (7.12)$$

Assuming the velocity v forms an angle θ with the z -axis, the momentum change between two fluid layers with a height difference of $\lambda \cos \theta$ is $-m(\partial \langle u_x \rangle / \partial z) \lambda \cos \theta$, then the momentum flux per unit time through a unit area in the direction perpendicular to the z -axis is

$$\begin{aligned} \Pi_z &= \int_0^\infty \int_0^\pi v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta \cdot m \left(-\frac{\partial \langle u_x \rangle}{\partial z} \right) \lambda \cos \theta \\ &= \frac{1}{2} nm \lambda \int_0^\infty v f(v) dv \left(-\frac{\partial \langle u_x \rangle}{\partial z} \right) \int_0^\pi \cos^2 \theta \sin \theta d\theta \\ &= -\frac{1}{3} nm \lambda \langle v \rangle \left(\frac{\partial \langle u_x \rangle}{\partial z} \right) \end{aligned} \quad (7.13)$$

Thus, the viscosity coefficient can be written as

$$\eta = \frac{1}{3} nm \lambda \langle v \rangle \quad (7.14)$$

2. Heat Flow

Considering the heat flow between two temperature gradients, the heat flux vector \mathbf{J} (reflecting

the amount of heat transferred per unit time per unit area, unit $\text{Js}^{-1} \text{m}^{-2} = \text{pm}^{-2}$) is given, then the heat flux in a certain direction is

$$J_z = -\kappa \left(\frac{\partial T}{\partial z} \right) \quad (7.15)$$

where κ is the thermal conductivity, unit $\text{pm}^{-1}\text{K}^{-1}$. Considering the heat capacity of each particle $C_n = C_V/N = mc_V$, the heat passing through a unit scattering cross-section during scattering is $C_n \cdot \Delta T = C_n \frac{\partial T}{\partial z} \lambda \cos \theta$, then the heat flux is

$$\begin{aligned} J_z &= \int_0^\infty dv \int_0^\pi \left(-C_n \frac{\partial T}{\partial z} \lambda \cos \theta \right) v \cos \theta n f(v) \frac{1}{2} \sin \theta d\theta \\ &= -\frac{1}{2} n C_n \lambda \int_0^\infty v f(v) dv \frac{\partial T}{\partial z} \int_0^\pi \cos^2 \theta \sin \theta d\theta \\ &= -\frac{1}{3} n C_n \lambda \langle v \rangle \frac{\partial T}{\partial z} \end{aligned} \quad (7.16)$$

Thus, the thermal conductivity is obtained as

$$\kappa = \frac{1}{3} C_V \lambda \langle v \rangle = c_V \eta \quad (7.17)$$

3. Diffusion

Below, we discuss the relationship between particle flux and diffusion flux. Fick's law states (where D is the diffusion coefficient)

$$\Phi = -D \nabla n^* \quad (7.18)$$

Discussing the inflow and outflow of a thin layer flux, the rate of change of particle flux is obtained as

$$\frac{\partial}{\partial t} (n^* A dz) = -A \frac{\partial \Phi_z}{\partial z} dz \quad (7.19)$$

Combining Fick's law, the diffusion equation for particle density is obtained as

$$\frac{\partial n^*}{\partial t} = -\frac{\partial \Phi_z}{\partial z}, \quad \frac{\partial n^*}{\partial t} = D \frac{\partial^2 n^*}{\partial z^2} \quad (7.20)$$

Fig. 64: Flux inflow and outflow of a thin layer

The particle flux per unit time per unit area is obtained as

$$\begin{aligned} \Phi_z &= \int_0^\pi d\theta \int_0^\infty dv v \cos \theta f(v) \frac{1}{2} \sin \theta \left(-\frac{\partial n^*}{\partial z} \lambda \cos \theta \right) \\ &= -\frac{1}{3} \lambda \langle v \rangle \frac{\partial n^*}{\partial z} \end{aligned} \quad (7.21)$$

Thus, the diffusion coefficient is

$$D = \frac{1}{3} \lambda \langle v \rangle = \frac{\eta}{nm} = \frac{\eta}{\rho} \quad (7.22)$$

The overall heat flow integral relation is

$$\int_S \mathbf{J} \cdot d\mathbf{S} = -\frac{\partial}{\partial t} \int_V CT dV = \int_V \nabla \cdot \mathbf{J} dV \quad (7.23)$$

From this, the heat diffusion equation is obtained as

$$\frac{\partial T}{\partial t} = D \nabla^2 T \quad (7.24)$$

where the thermal diffusion coefficient $D = \frac{\kappa}{C} (\text{m}^2 \text{s}^{-1})$, $C = \rho c (\text{JK}^{-1} \text{m}^{-3})$. The solution to this equation can be obtained by analogy with the method of separation of variables in electrodynamics.

In the one-dimensional case, the heat diffusion equation becomes

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2}, \quad k = 2\pi/\lambda, \quad \omega = 2\pi f \quad (7.25)$$

A wave-like solution is given as

$$T(x, t) \propto \exp(i(kx - \omega t)) \quad (7.26)$$

Solving gives

$$k^2 = \frac{i\omega}{D}, \quad k = \pm(1 + i)\sqrt{\frac{\omega}{2D}} \quad (7.27)$$

Ignoring the solution that diverges as $x \rightarrow \infty$, the first form of the solution is chosen. Therefore, the general solution for $x \geq 0$ can be written as

$$T(x, t) = \sum_{\omega} A(\omega) \exp(-i\omega t) \exp\left((i-1)\sqrt{\frac{\omega}{2D}}x\right) \quad (7.28)$$

Solving the one-dimensional problem of a sinusoidal temperature wave entering the ground, the boundary condition can be written as

$$T(0, t) = T_0 + \Delta T \cos \Omega t \quad (7.29)$$

At $x = 0$, the general solution for temperature becomes

$$T(0, t) = \sum_{\omega} A(\omega) \exp(-i\omega t) \quad (7.30)$$

Comparing gives the only non-zero values of $A(\omega)$ as $A(0) = T_0$, $A(-\Omega) = \frac{\Delta T}{2}$, and $A(\Omega) = \frac{\Delta T}{2}$. Therefore, the solution for the region $x \geq 0$ is

$$T(x, t) = T_0 + \frac{\Delta T}{2} e^{-x/\delta} \cos\left(\Omega t - \frac{x}{\delta}\right) \quad (7.31)$$

where the penetration depth/skin depth is given as

$$\delta = \sqrt{\frac{2D}{\Omega}} = \sqrt{\frac{2\kappa}{\Omega C}} \quad (7.32)$$

7.2 Boltzmann Equation

To describe the evolution of a system in a non-equilibrium state, a set of equations describing the dynamics of a system of many interacting particles, namely the BBGKY (Bogoliubov-Born-Green-Kirkwood-Yvon) hierarchy, is introduced, which will be given from the perspective of distribution density. Considering the single-particle distribution function $f_1(\mathbf{q}, \mathbf{p}, t) = N\rho_1(\mathbf{q}, \mathbf{p}, t)$, it satisfies

$$f_1(\mathbf{q}, \mathbf{p}, t) = \left\langle \sum_{i=1}^N \delta^3(\mathbf{q} - \mathbf{q}_i) \delta^3(\mathbf{p} - \mathbf{p}_i) \right\rangle = N \int \prod_{i=2}^N d^3\mathbf{q}_i d^3\mathbf{p}_i \rho(\mathbf{q} = \mathbf{q}_1, \dots, \mathbf{p} = \mathbf{p}_1, \dots, t) \quad (7.33)$$

A more general s -particle density function is:

$$\rho_s(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_s, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_s, t) = \int \prod_{i=s+1}^N d^3\mathbf{q}_i d^3\mathbf{p}_i \rho(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{p}_1, \mathbf{p}_2, \dots, t), \quad f_s = \frac{N!}{(N-s)!} \rho_s \quad (7.34)$$

ρ_n is normalized by integrating over all variables. Next, the total Hamiltonian of a system containing N gas molecules is written as:

$$H(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) = \sum_{i=1}^N \left[\frac{\mathbf{p}_i^2}{2m} + V(\mathbf{q}_i) \right] + \frac{1}{2} \sum_{i=1}^N V^{\text{int}}(\mathbf{q}_i - \mathbf{q}_j) \quad (7.35)$$

It is split into single-particle and interaction parts:

$$H = H_s + H_{N-s} + H_{\text{int}} \quad (7.36)$$

The Hamiltonians for each part are obtained as:

$$H_s = H(\mathbf{q}_1, \dots, \mathbf{q}_s, \mathbf{p}_1, \dots, \mathbf{p}_s) = \sum_{i=1}^s \left[\frac{\mathbf{p}_i^2}{2m} + V(\mathbf{q}_i) \right] + \frac{1}{2} \sum_{i,j=1}^s V^{\text{int}}(\mathbf{q}_i - \mathbf{q}_j) \quad (7.37a)$$

$$H_{N-s} = H(\mathbf{q}_{s+1}, \dots, \mathbf{q}_N, \mathbf{p}_{s+1}, \dots, \mathbf{p}_N) = \sum_{i=s+1}^N \left[\frac{\mathbf{p}_i^2}{2m} + V(\mathbf{q}_i) \right] + \frac{1}{2} \sum_{i,j=s+1}^N V^{\text{int}}(\mathbf{q}_i - \mathbf{q}_j) \quad (7.37b)$$

$$H_{\text{int}} = \sum_{i=1}^s \sum_{j=s+1}^N V^{\text{int}}(\mathbf{q}_i - \mathbf{q}_j) \quad (7.37c)$$

According to Liouville's theorem Eq. 6.10, the partial derivative of the density distribution ρ_s with respect to time t is:

$$\frac{\partial \rho_s}{\partial t} = \int \prod_{i=s+1}^N d^3\mathbf{q}_i d^3\mathbf{p}_i \frac{\partial \rho}{\partial t} = - \int \prod_{i=s+1}^N d^3\mathbf{q}_i d^3\mathbf{p}_i [\rho, H_s + H_{N-s} + H_{\text{int}}] \quad (7.38)$$

The first two Poisson brackets are zero (containing only phase space terms), and the third Poisson bracket is:

$$\begin{aligned}
 [\rho_s, H_{\text{int}}] &= \int \prod_{i=s+1}^N d^3\mathbf{q}_i d^3\mathbf{p}_i \left[\sum_{j=1}^s \sum_{l=s+1}^N \frac{\partial \rho}{\partial \mathbf{p}_j} \cdot \frac{\partial}{\partial \mathbf{q}_l} V^{\text{int}}(\mathbf{q}_j - \mathbf{q}_l) \right] \\
 &= (N-s) \int \prod_{i=s+1}^N d^3\mathbf{q}_i d^3\mathbf{p}_i \sum_{j=1}^s \frac{\partial \rho}{\partial \mathbf{p}_j} \cdot \frac{\partial}{\partial \mathbf{q}_j} V^{\text{int}}(\mathbf{q}_j - \mathbf{q}_{s+1}) \\
 &= (N-s) \sum_{j=1}^n \int d^3\mathbf{q}_{s+1} d^3\mathbf{p}_{s+1} \frac{\partial V^{\text{int}}(\mathbf{q}_j - \mathbf{q}_{s+1})}{\partial \mathbf{q}_j} \cdot \frac{\partial}{\partial \mathbf{p}_j} \left[\int \prod_{i=s+2}^N d^3\mathbf{q}_i d^3\mathbf{p}_i \rho \right] \\
 &= (N-s) \sum_{j=1}^s \int d^3\mathbf{q}_{s+1} d^3\mathbf{p}_{s+1} \frac{\partial V^{\text{int}}(\mathbf{q}_j - \mathbf{q}_{s+1})}{\partial \mathbf{q}_j} \cdot \frac{\partial \rho_{s+1}}{\partial \mathbf{p}_j}
 \end{aligned} \tag{7.39}$$

Thus, the BBGKY hierarchy is obtained (Eq. 7.40b expands the commutator with the potential energy term)

$$\frac{\partial \rho_s}{\partial t} + [\rho_s, H_s] = (N-s) \sum_{i=1}^s \int d^3\mathbf{q}_{s+1} d^3\mathbf{p}_{s+1} \frac{\partial V^{\text{int}}(\mathbf{q}_i - \mathbf{q}_{s+1})}{\partial \mathbf{q}_i} \cdot \frac{\partial \rho_{s+1}}{\partial \mathbf{p}_i} \tag{7.40a}$$

$$\left[\frac{\partial}{\partial t} + \sum_{i=1}^s \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{q}_i} - \sum_{i=1}^s \left(\frac{\partial V}{\partial \mathbf{q}_i} + \frac{\partial V^{\text{int}}}{\partial \mathbf{q}_i} \right) \cdot \frac{\partial}{\partial \mathbf{p}_i} \right] f_s = \sum_{i=1}^s \int d^3\mathbf{q}_{s+1} d^3\mathbf{p}_{s+1} \frac{\partial V^{\text{int}}(\mathbf{q}_i - \mathbf{q}_{s+1})}{\partial \mathbf{q}_i} \cdot \frac{\partial f_{s+1}}{\partial \mathbf{p}_i} \tag{7.40b}$$

7.2.1 Boltzmann Integral-Differential Equation

Considering the first two terms of equation Eq. 7.40b

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1} - \frac{\partial V}{\partial \mathbf{q}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} \right] f_1 = \int d^3\mathbf{q}_2 d^3\mathbf{p}_2 \frac{\partial V^{\text{int}}(\mathbf{q}_1 - \mathbf{q}_2)}{\partial \mathbf{q}_1} \cdot \frac{\partial f_2}{\partial \mathbf{p}_1} \tag{7.41}$$

The dimensions of all terms in the square brackets are the inverse of time: $1/\tau$. The characteristic speed of room temperature gas is $v \simeq 10^2 \text{ ms}^{-1}$. The different force ranges of the external potential V and the two-body interaction potential V^{int} give the corresponding characteristic lengths. External force time scale:

$$\frac{1}{\tau_V} \sim \frac{\partial V}{\partial \mathbf{q}} \cdot \frac{\partial}{\partial \mathbf{p}} \sim \frac{V/p}{q} \sim \frac{v}{L} \tag{7.42}$$

The macroscopic scale L is the typical force range of the external potential V . Taking $L = 10^{-3} \text{ m}$, then: $\tau_V \simeq L/v \simeq 10^{-5} \text{ s}$. Collision time scale:

$$\frac{1}{\tau_c} \sim \frac{\partial V^{\text{int}}}{\partial \mathbf{q}} \cdot \frac{\partial}{\partial \mathbf{p}} \sim \frac{V^{\text{int}}/p}{q} \sim \frac{v}{d} \tag{7.43}$$

where d is the typical force range of the two-body interaction potential V^{int} . The Van der Waals gas has short-range interactions between molecules, with a force range approximately equal to the distance between molecules, taking $d = 10^{-10} \text{ m}$, then: $\tau_c \simeq d/v \simeq 10^{-12} \text{ s}$. In contrast,

the charged particles in a plasma have Coulomb interactions, which are long-range interactions, requiring the solution of the Vlasov equation. The collision time scale dependent on f_{s+1} is:

$$\frac{1}{\tau_x} \sim \int dV \left(\frac{\partial V^{\text{int}}}{\partial \mathbf{q}} \cdot \frac{\partial}{\partial \mathbf{p}} \right) \frac{f_{s+1}}{f_s} \sim \frac{d^3}{\tau_c} n \quad (7.44)$$

The above equation is non-zero only when integrated over the volume of the interaction range d , thus obtaining the average free time as:

$$\tau_x \simeq \frac{\tau_c}{nd^3} \simeq \frac{1}{nvd} \quad (7.45)$$

Taking $n = 10^{26} \text{ m}^{-3}$, for short-range forces, then: $n d^3 \simeq 10^{-4}$, therefore $\tau_x \simeq 10^{-8} \text{ s} \gg \tau_c$. In the time between microscopic long and macroscopic short ($\tau_c < t < \tau_v$), particles collide sufficiently, and the system is in a steady state ($\partial/\partial t = 0$), ignoring the $1/\tau v$ term and the $\partial/\partial t$ term, the equation satisfied by f_2 can be simplified as:

$$\left[\frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1} + \frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{q}_2} - \frac{\partial V^{\text{int}}(\mathbf{q}_1 - \mathbf{q}_2)}{\partial \mathbf{q}_1} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) \right] f_2 = 0 \quad (7.46)$$

Since the function $f(\mathbf{q}_1, \mathbf{q}_2)$ is a slowly varying function of the center of mass $\mathbf{Q} = (\mathbf{q}_1 + \mathbf{q}_2)/2$ and a rapidly varying function of the particle separation $\mathbf{q} = \mathbf{q}_1 - \mathbf{q}_2$, it is expanded as

$$\frac{\partial f_2}{\partial \mathbf{q}} \gg \frac{\partial f_2}{\partial \mathbf{Q}}, \quad \frac{\partial f_2}{\partial \mathbf{q}_2} \simeq -\frac{\partial f_2}{\partial \mathbf{q}_1} \simeq \frac{\partial f_2}{\partial \mathbf{q}} \quad (7.47)$$

Further obtaining:

$$\frac{\partial V^{\text{int}}(\mathbf{q}_1 - \mathbf{q}_2)}{\partial \mathbf{q}_1} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) f_2 = - \left(\frac{\mathbf{p}_1 - \mathbf{p}_2}{m} \right) \cdot \left(\frac{\partial}{\partial \mathbf{q}} \right) f_2 \quad (7.48)$$

For the right side of equation Eq. 7.41, the collision term is written as

$$\begin{aligned} \frac{df_1}{dt} \Big|_c &= \int d^3 \mathbf{q}_2 d^3 \mathbf{p}_2 \frac{\partial V^{\text{int}}(\mathbf{q}_1 - \mathbf{q}_2)}{\partial \mathbf{q}_1} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) f_2 \simeq - \int d^3 \mathbf{q}_2 d^3 \mathbf{p}_2 \left(\frac{\mathbf{p}_1 - \mathbf{p}_2}{m} \right) \cdot \left(\frac{\partial}{\partial \mathbf{q}} \right) f_2 \\ &= \int d^3 \mathbf{p}_2 d^2 \Omega \left| \frac{d\sigma}{d\Omega} \right| \cdot |\mathbf{v}_1 - \mathbf{v}_2| [f_2(\mathbf{q}_1, \mathbf{b}, a = -\infty, \mathbf{p}'_1, \mathbf{p}'_2; t) - f_2(\mathbf{q}_1, \mathbf{b}, a = -\infty, \mathbf{p}_1, \mathbf{p}_2; t)] \end{aligned} \quad (7.49)$$

The single-particle probability distribution function f_1 satisfies the Boltzmann equation:

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1} - \frac{\partial V}{\partial \mathbf{q}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} \right] f_1 = - \int d^3 \mathbf{p}_2 d^2 \Omega \left| \frac{d\sigma}{d\Omega} \right| \cdot |\mathbf{v}_1 - \mathbf{v}_2| [f_1(\mathbf{q}_1, \mathbf{p}_1, t) \cdot f_1(\mathbf{q}_1, \mathbf{p}_2, t) - f_1(\mathbf{q}_1, \mathbf{p}'_1, t) \cdot f_1(\mathbf{q}_1, \mathbf{p}'_2, t)] \quad (7.50)$$

The general form of the probability density function $f(\mathbf{r}, \mathbf{p}, t)$ satisfies the Boltzmann equation:

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla f + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \quad (7.51)$$

The collision term on the right represents the rate of change of the distribution function due to molecular collisions, related to the collision mechanism of molecules. Considering a two-body collision model, the collision term can be written as:

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = \iint g I(g, \Omega) [f(\mathbf{r}, \mathbf{p}'_A, t) f(\mathbf{r}, \mathbf{p}'_B, t) - f(\mathbf{r}, \mathbf{p}_A, t) f(\mathbf{r}, \mathbf{p}_B, t)] d\Omega d^3 \mathbf{p}_B, \quad g = |\mathbf{p}_B - \mathbf{p}_A| = |\mathbf{p}'_B - \mathbf{p}'_A| \quad (7.52)$$

7.2.2 Boltzmann Equation Relaxation Time Approximation

When the system is in local equilibrium, the distribution function of molecules also has the form of local equilibrium. For a classical dilute gas, the local equilibrium distribution of molecules has the following form:

$$f^{(0)}(\mathbf{q}, \mathbf{p}, t) = n(\mathbf{q}, t) \left[\frac{m}{2\pi kT(\mathbf{q}, t)} \right]^{\frac{3}{2}} \exp \left\{ -\frac{1}{2mkT(\mathbf{q}, t)} [\mathbf{p} - \mathbf{p}_0(\mathbf{q}, t)]^2 \right\} \quad (7.53)$$

In the case where the local equilibrium approximation holds, molecular collisions first bring the system to local equilibrium. Therefore, the collision term $\left(\frac{\partial f}{\partial t} \right)_{\text{coll}}$ can be linearized through the relaxation time approximation, which can be expressed as

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = -\frac{f - f^{(0)}}{\tau} \quad (7.54)$$

where τ is the time required for molecules to reach local equilibrium, called the relaxation time, or expressed using the molecular collision frequency $\nu = 1/\tau$. This equation indicates that at $t = \tau$, the value of $f - f^{(0)}$ is $\frac{1}{e}$ of the initial value. Substituting the above equation into the Boltzmann equation, the Boltzmann equation under the relaxation time approximation (Bhatnagar-Gross-Krook, BGK form) is obtained:

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla f + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} = -\frac{f - f^{(0)}}{\tau} \quad (7.55)$$

Assuming that in unit time, the number of molecules with velocity in the range $\mathbf{v} \sim \mathbf{v} + d\mathbf{v}$ passing through the unit area of the x_0 plane from the negative side to the positive side is $d\Gamma = uf d\mathbf{v}$, where f is the abbreviation of the distribution function $f(\mathbf{r}, \mathbf{v}, t)$. u, v, w are the velocities in the x, y, z directions, respectively. The momentum transported from the negative side to the positive side through the unit area of the x_0 plane in unit time by molecules with velocity in the range $d\mathbf{v}$ is $mv d\Gamma = muvf d\mathbf{v}$. Assuming that the gas is not subject to external forces, the macroscopic flow velocity v_0 of the gas is along the y direction, and v_0 is only a function of x , then the local equilibrium distribution function of the gas is

$$f^{(0)} = n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT} [u^2 + (v - v_0(x))^2 + w^2]} \quad (7.56)$$

In the steady state of the gas, $\frac{\partial f}{\partial t} = 0$, and f is only a function of x , independent of y and z . In the relaxation time approximation, the Boltzmann equation is rewritten as

$$u \frac{\partial f}{\partial x} = -\frac{f - f^{(0)}}{\tau} \quad (7.57)$$

The approximation near equilibrium $f^{(1)} = f - f^{(0)}$, $f^{(1)} \ll f^{(0)}$, when retaining the first-order small quantity, Eq. 7.57 can be simplified as

$$f^{(1)} = -\tau u \frac{\partial f}{\partial x} \simeq -\tau u \frac{\partial f^{(0)}}{\partial x} = \tau u \frac{\partial f^{(0)}}{\partial v} \frac{dv_0}{dx} \quad (7.58)$$

Thus, the distribution function is approximately solved as

$$f = f^{(0)} + \tau u \frac{\partial f^{(0)}}{\partial v} \frac{dv_0}{dx} \quad (7.59)$$

The momentum flux transported from the positive side to the negative side through the unit area of the x_0 plane in unit time is obtained as

$$\begin{aligned} \Pi_z &= - \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dumuvf \\ &= - \iiint muv \left[f^{(0)} + \tau u \frac{\partial f^{(0)}}{\partial v} \frac{dv_0}{dx} \right] du dv dw \\ &= - \iiint mu^2 v \tau \frac{\partial f^{(0)}}{\partial v} du dv dw \frac{dv_0}{dx} \end{aligned} \quad (7.60)$$

From Eq. 7.13, the viscosity coefficient of the gas is obtained as

$$\eta = - \iiint mu^2 v \tau \frac{\partial f^{(0)}}{\partial v} du dv dw = nm\tau \bar{u}^2 = nkT\tau \quad (7.61)$$

When the gas is close to equilibrium, it can be proven that the viscosity coefficient returns to Eq. 7.14

7.2.3 Electrical Conductivity/Thermal Conductivity

For simplicity, first discuss the pure electrical conductivity problem in metals without temperature and density inhomogeneities. Assume that under the action of a constant external electric field E along the x direction, the free electrons in the metal acquire a directional velocity, and there is a current passing through the metal. Experiments show that the current density J_e is proportional to the electric field strength E , i.e., Ohm's law (where the proportionality coefficient σ is the electrical conductivity of the metal)

$$J_e = \sigma E \quad (7.62)$$

From a microscopic perspective, the current density J_e equals the number of electrons passing through the unit cross-sectional area of the metal per unit time multiplied by the electron charge $-e$. Due to the random thermal motion of electrons, electrons can move in the positive x direction or the negative x direction. Let the distribution function of electrons be f , then the current density $J_e^{+/-}$ generated by electrons moving in the positive (negative) x direction is

$$J_e^+ = -e \int_0^{\infty} du \int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dw (+u)f, \quad J_e^- = -e \int_{-\infty}^0 du \int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dw (-u)f \quad (7.63)$$

The net current density flowing in the positive x direction is obtained by subtracting the above equations as

$$J_e = J_e^+ - J_e^- = -e \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dw u f \quad (7.64)$$

If there is no external electric field, the electron gas is in equilibrium. Free electrons are a strongly degenerate Fermi gas. Therefore, the local equilibrium distribution is

$$f^{(0)} dv = \frac{2m^3}{h^3} \frac{1}{e^{(\varepsilon - \mu)/kT} + 1} dv = \frac{2m^3}{h^3} f_F dv, \quad f_F = \frac{1}{e^{(\varepsilon - \mu)/kT} + 1} \quad (7.65)$$

The electron energy $\varepsilon = \frac{m}{2}(u^2 + v^2 + w^2)$. If the $f^{(0)}$ of Eq. 7.65 is substituted into the net current density, $J_e = 0$ is obtained because the integrand is an odd function of u . Now, with a weak external electric field E applied in the x direction, $J_e \neq 0$ under the action of the electric field force $-eE$. To obtain the current density, the distribution function f needs to be known, for which the Boltzmann equation needs to be solved. If the external electric field is removed, the collision of electrons will cause the metal to tend towards equilibrium (a relaxation process occurs). In the relaxation time approximation, applying Eq. 7.54, considering that the system reaches a steady state, $\frac{\partial f}{\partial t} = 0$. Ignoring the inhomogeneity of temperature/density caused by the electric field, f is independent of r , and the Boltzmann equation simplifies to

$$-\frac{eE}{m} \frac{\partial f}{\partial u} = -\frac{f - f^{(0)}}{\tau} \quad (7.66)$$

The distribution function is solved as

$$f = f^{(0)} + \frac{\tau eE}{m} \frac{\partial f}{\partial u} \simeq f^{(0)} + \frac{\tau eE}{m} \frac{\partial f^{(0)}}{\partial u} \quad (7.67)$$

In the case of a weak electric field, the second term is a small correction term to the distribution function after the electric field is applied, $f^{(1)} \ll f^{(0)}$, substituting into Eq. 7.64 gives

$$J_e = -\frac{e^2 E}{m} \iiint_{\tau} u \frac{\partial f^{(0)}}{\partial u} du dv dw \quad (7.68)$$

Using the polar coordinates in velocity space, taking the u direction as the polar axis, $u = |v| \cos \theta$, the above equation can be rewritten as

$$\begin{aligned} J_e &= -2e^2 E \left(\frac{m}{h}\right)^3 \iiint \tau u^2 \frac{\partial f_F}{\partial \varepsilon} du dv dw = -e^2 E \left(\frac{m}{h}\right)^3 \left(\frac{2}{m}\right)^{\frac{5}{2}} \int_0^\infty \int_0^\pi \int_0^{2\pi} \tau \varepsilon^{\frac{3}{2}} \frac{\partial f_F}{\partial \varepsilon} \cos^2 \theta \sin \theta d\varepsilon d\theta d\varphi \\ &= -\frac{16\pi}{3h^3} e^2 E \sqrt{2m} \int_0^\infty \tau \varepsilon^{3h} \frac{\partial f_F}{\partial \varepsilon} d\varepsilon = -\frac{16\pi}{3h^3} e^2 E m \int_0^\infty l \varepsilon \frac{\partial f_F}{\partial \varepsilon} d\varepsilon \end{aligned} \quad (7.69)$$

where $\tau = \frac{l(v)}{v}$, l is the electron mean free path, related to the electron speed v and energy ε . The current density J_e in the metal is calculated in different cases.

Case 1. $T = 0$ K

At absolute zero, the Fermi distribution is a step function, when $\varepsilon < \varepsilon_F$, $f_F = 1$, when $\varepsilon > \varepsilon_F$, $f_F = 0$, the derivative is a δ function

$$\frac{\partial f_F}{\partial \varepsilon} = -\delta(\varepsilon - \varepsilon_F), \quad \varepsilon_F = \mu_0 = \frac{h^2}{2m} \left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \quad (7.70)$$

ε_F is the Fermi energy level of the electron gas at absolute zero, from the above equation, the current density in the metal is obtained as

$$J_e = \frac{ne^2 l(\varepsilon_F)}{mv(\varepsilon_F)} E = \frac{ne^2 \tau(\varepsilon_F)}{m} E \quad (7.71)$$

Comparing with Ohm's law Eq. 7.62, the electrical conductivity of the metal is obtained as

$$\sigma = \frac{ne^2\tau(\varepsilon_F)}{m} = \frac{ne^2l(\varepsilon_F)}{mv(\varepsilon_F)} \quad (7.72)$$

This shows that the electrical conductivity is proportional to $n\tau(\varepsilon_F)$.

Case 2. $T \neq 0$ K

Since the Fermi temperature T_F of the electron gas is as high as 10^4 K, at normal temperatures $T \ll T_F$, i.e., $\frac{kT}{\varepsilon_F} \ll 1$, at this time, the energy integral in Eq. 7.69 can be approximately expressed using the Sommerfeld expansion Eq. 5.117

$$I = - \int_0^\infty g(\varepsilon) \frac{\partial f_F}{\partial \varepsilon} d\varepsilon \simeq g(\mu) - g(0) + \frac{\pi^2}{6} (kT)^2 g''(\mu), \quad T \ll T_F \quad (7.73)$$

Taking $l(\varepsilon) \simeq l(\mu)$, $g(\varepsilon) = \varepsilon$, using the above approximation, the current density is obtained as

$$J_e = \frac{16\pi}{3h^3} e^2 m l(\mu) \mu E \quad (7.74)$$

where $l(\mu) \simeq l(\varepsilon_F) \simeq v_F \tau(\varepsilon_F)$, the chemical potential μ is

$$\mu = \mu_0 \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\mu_0} \right)^2 \right] \quad (7.75)$$

The electrical conductivity of the metal at temperature T is obtained as

$$\sigma = \frac{16\pi}{3h^3} e^2 m l(\mu) \mu \simeq \frac{ne^2\tau(\varepsilon_F)}{m} \left(\frac{\mu}{\varepsilon_F} \right)^{\frac{3}{2}} = \frac{ne^2\tau(\varepsilon_F)}{m} \left[1 - \frac{\pi^2}{8} \left(\frac{kT}{\varepsilon_F} \right)^2 \right] \quad (7.76)$$

Case 3. Consider the complex situation where there is both an external electric field and a temperature gradient in the metal. In this case, the effects of the external electric field E (along the x direction) and the temperature gradient $\frac{dT}{dx}$ on the electron distribution function must be considered simultaneously: Due to the temperature gradient $\frac{dT}{dx}$ along the x direction inside the metal, heat will flow from the high-temperature region to the low-temperature region. Experiments have found that the heat J_q passing through a unit cross-section perpendicular to the x axis per unit time is proportional to the temperature gradient, i.e., Eq. 7.15

$$J_q = -\kappa \frac{dT}{dx} \quad (7.77)$$

The proportionality coefficient κ is the thermal conductivity, and the negative sign indicates that the direction of heat transfer is opposite to the direction of the temperature gradient, towards the direction of decreasing temperature. This is called Fourier's law of heat conduction. In the process of heat conduction, the heat transferred by electrons is the kinetic energy of electrons

$$\varepsilon = \frac{1}{2} mv^2 = \frac{1}{2} m (u^2 + v^2 + w^2) \quad (7.78)$$

Replacing $-e$ in Eq. 7.64 with ε , the statistical expression of heat flow J_q is obtained as

$$J_q = \int \varepsilon u f dv = \iiint \frac{1}{2} m (u^2 + v^2 + w^2) uf du dv dw \quad (7.79)$$

Since the electric field E and the temperature gradient $\frac{dT}{dx}$ inside the metal are both along the x direction, the distribution function f is only a function of x , independent of y and z

$$\frac{\partial f}{\partial x} \neq 0, \quad \frac{\partial f}{\partial y} = \frac{\partial f}{\partial z} = 0 \quad (7.80)$$

Electrons are subjected to a constant electric field, with acceleration only in the x direction

$$F_x = -\frac{eE}{m}, \quad F_y = F_z = 0 \quad (7.81)$$

The conduction and heat conduction processes in the metal reach stability, with $\frac{\partial f}{\partial t} = 0$. Rewriting Eq. 7.66, the Boltzmann equation under the relaxation time approximation is obtained as

$$u \frac{\partial f}{\partial x} - \frac{eE}{m} \frac{\partial f}{\partial u} = -\frac{f - f^{(0)}}{\tau} \quad (7.82)$$

where $f^{(0)}$ is the local equilibrium Fermi distribution Eq. 7.65, with temperature $T = T(x)$ and chemical potential $\mu = \mu(n, T(x))$. Solving gives

$$f = f^{(0)} + \tau \left(\frac{eE}{m} \frac{\partial f}{\partial u} - u \frac{\partial f}{\partial x} \right) \quad (7.83)$$

Assuming that the external electric field E and the temperature gradient dT are both small, f and the local equilibrium distribution function $f^{(0)}$ differ only slightly. In the first-order approximation, the f on the right side of the above equation can be replaced by $f^{(0)}$, thus obtaining

$$f = f^{(0)} + \tau \left(\frac{eE}{m} \frac{\partial f^{(0)}}{\partial u} - u \frac{\partial f^{(0)}}{\partial x} \right) \quad (7.84)$$

From Eq. 7.65, the differential form of the Fermi equilibrium distribution function $f^{(0)}$ is

$$\frac{\partial f^{(0)}}{\partial u} = 2 \left(\frac{m}{h} \right)^3 m u \frac{\partial f_F}{\partial \varepsilon} \quad (7.85a)$$

$$\frac{\partial f^{(0)}}{\partial x} = T \frac{\partial f^{(0)}}{\partial \varepsilon} \frac{\partial}{\partial x} \left(\frac{\varepsilon - \mu}{T} \right) = -2 \left(\frac{m}{h} \right)^3 \left[\frac{\varepsilon}{T} \frac{dT}{dx} + T \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) \right] \frac{\partial f_F}{\partial \varepsilon} \quad (7.85b)$$

Substituting into Eq. 7.84, the distribution function is obtained as

$$f = f^{(0)} + 2 \left(\frac{m}{h} \right)^3 \tau u \left[eE + \frac{\varepsilon}{T} \frac{dT}{dx} + T \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) \right] \frac{\partial f_F}{\partial \varepsilon} \quad (7.86)$$

From this and using $\tau = \frac{l}{v}$, the heat flow density and current density are obtained as

$$J_q = 2 \left(\frac{m}{h} \right)^3 \int \frac{l}{v} u^2 \varepsilon^2 \frac{\partial f_F}{\partial \varepsilon} dv \frac{1}{T} \frac{dT}{dx} + 2 \left(\frac{m}{h} \right)^3 \left[eE + T \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) \right] \int \frac{l}{v} u^2 \varepsilon \frac{\partial f_F}{\partial \varepsilon} dv \quad (7.87a)$$

$$J_e = -2e \left(\frac{m}{h} \right)^3 \int \frac{l}{v} u^2 \varepsilon \frac{\partial f_F}{\partial \varepsilon} dv \frac{1}{T} \frac{dT}{dx} - 2e \left(\frac{m}{h} \right)^3 \left[eE + T \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) \right] \int \frac{l}{v} u^2 \frac{\partial f_F}{\partial \varepsilon} dv \quad (7.87b)$$

Below, the integrals in the two flow densities are simplified. Using the polar coordinates in velocity space, taking the u direction as the polar axis, $u = |v| \cos \theta$, then

$$\int \frac{l}{v} u^2 \frac{\partial f_F}{\partial \varepsilon} dv = \frac{2}{m^2} \int_0^\infty \int_0^\pi \int_0^{2\pi} l \varepsilon \frac{\partial f_F}{\partial \varepsilon} \cos^2 \theta \sin \theta d\varepsilon d\theta d\varphi = \frac{8\pi}{3m^2} \int_0^\infty l \varepsilon \frac{\partial f_F}{\partial \varepsilon} d\varepsilon \quad (7.88)$$

Using the relationship between flow and driving force in irreversible thermodynamics, the two flow densities are rewritten as

$$J_q = L_{11} \left(-\frac{1}{T} \frac{dT}{dx} \right) + L_{12} \left[E + \frac{T}{e} \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) \right] \quad (7.89a)$$

$$J_e = L_{21} \left(-\frac{1}{T} \frac{dT}{dx} \right) + L_{22} \left[E + \frac{T}{e} \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) \right] \quad (7.89b)$$

where the coefficients L_{ij} are

$$L_{11} = -2 \left(\frac{m}{h} \right)^3 \int \frac{l}{v} u^2 \varepsilon^2 \frac{\partial f_F}{\partial \varepsilon} dv = -\frac{16\pi m}{3h^3} \int_0^\infty l \varepsilon^3 \frac{\partial f_F}{\partial \varepsilon} d\varepsilon \quad (7.90a)$$

$$L_{12} = 2e \left(\frac{m}{h} \right)^3 \int \frac{l}{v} u^2 \varepsilon \frac{\partial f_F}{\partial \varepsilon} dv = \frac{16\pi me}{3h^3} \int_0^\infty l \varepsilon^2 \frac{\partial f_F}{\partial \varepsilon} d\varepsilon = L_{21} \quad (7.90b)$$

$$L_{22} = -2e^2 \left(\frac{m}{h} \right)^3 \int \frac{l}{v} u^2 \frac{\partial f_F}{\partial \varepsilon} dv = -\frac{16\pi me^2}{3h^3} \int_0^\infty l \varepsilon \frac{\partial f_F}{\partial \varepsilon} d\varepsilon \quad (7.90c)$$

The above equations show that when the system is not far from equilibrium, the driving flows J_q and J_e and the forces $-\frac{1}{T} \frac{dT}{dx}$ and $E + \frac{T}{e} \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right)$ have a linear relationship; moreover, the cross coefficients between heat flow and current are equal, $L_{12} = L_{21}$, thus providing the Onsager reciprocal relations using statistical physics.

When measuring the thermal conductivity κ , it is usually done under open-circuit conditions without current in the metal, i.e., $J_e = 0$, from Eq. 7.89b, it is obtained as

$$\left[E + \frac{T}{e} \frac{d}{dT} \left(\frac{\mu}{T} \right) \right] = \frac{L_{21}}{L_{22}} \left(\frac{1}{T} \frac{dT}{dx} \right) \quad (7.91)$$

Substituting this into Eq. 7.89a, it is obtained as

$$J_q = - \left(L_{11} - \frac{L_{12}^2}{L_{22}} \right) \frac{1}{T} \frac{dT}{dx} \quad (7.92)$$

Comparing with Fourier's law Eq. 7.77, the thermal conductivity is obtained as

$$\kappa = \left(L_{11} - \frac{L_{12}^2}{L_{22}} \right) \frac{1}{T} \quad (7.93)$$

Using the Sommerfeld expansion for approximate integration, the coefficients L_{ij} are rewritten as

$$L_{11} = \frac{16\pi m}{3h^3} l(\mu) \mu^3 \left[1 + \pi^2 \left(\frac{kT}{\mu} \right)^2 \right] \quad (7.94a)$$

$$L_{12} = -\frac{16\pi me}{3h^3} l(\mu) \mu^2 \left[1 + \frac{\pi^2}{3} \left(\frac{kT}{\mu} \right)^2 \right] \quad (7.94b)$$

$$L_{22} = \frac{16\pi me^2}{3h^3} l(\mu) \mu \quad (7.94c)$$

Substituting the approximated L_{ij} into the thermal conductivity Eq. 7.93, it is obtained as

$$\kappa = \frac{16\pi^3 m k^2 T}{9h^3} l(\mu) \mu \simeq \frac{\pi^2 k^2 T}{3} \frac{n\tau(\varepsilon_F)}{m} \left(\frac{\mu}{\varepsilon_F} \right)^{\frac{3}{2}} \simeq \frac{\pi^2 k^2 T}{3} \frac{n\tau(\mu_0)}{m} \quad (7.95)$$

The Lorentz constant gives the ratio of thermal conductivity to electrical conductivity (using Eq. 7.76 and Eq. 7.95)

$$L = \frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k}{e} \right)^2 = 2.443 \times 10^{-8} \Omega \cdot K^{-2} \quad (7.96)$$

The Lorentz constant is a universal constant, and this equation is called the Wiedemann-Franz law. The experimental value of L varies with temperature and differs for different metals.

7.3 H-Theorem

The H -theorem is a natural result of the kinetic equation derived by Boltzmann, reflecting the relationship of entropy change, satisfying that the f_1 satisfying the Boltzmann equation indeed irreversibly reaches its equilibrium state. The specific statement of the H theorem is: If $f_1(\mathbf{q}, \mathbf{p}, t)$ satisfies the Boltzmann equation, then the H -theorem is expressed as

$$\frac{dH(t)}{dt} \leq 0 \quad (7.97)$$

where $H(t)$ is a functional of $f_1(\mathbf{q}, \mathbf{p}, t)$:

$$H(t) \equiv \int d^3\mathbf{q} d^3\mathbf{p} f_1(\mathbf{q}, \mathbf{p}, t) \ln f_1(\mathbf{q}, \mathbf{p}, t) = N \bar{\ln} f_1 \quad (7.98)$$

$N = d^3\mathbf{q} d^3\mathbf{p} f_1(\mathbf{q}, \mathbf{p}, t)$ is the number of gas molecules, a constant that does not change with time. H is a function of time, and its rate of change with time is

$$\frac{dH}{dt} = \frac{1}{2} \int d^3\mathbf{q}_1 d^3\mathbf{p}_1 \frac{\partial f_1}{\partial t} (\ln f_1 + 1) = \frac{1}{2} \int d^3\mathbf{q}_1 d^3\mathbf{p}_1 \frac{\partial f_1}{\partial t} \ln f_1 \quad (7.99)$$

Substituting the single-particle distribution function f_1 into the Boltzmann equation Eq. 7.50, we obtain (the first term of the integral is zero)

$$\begin{aligned} \frac{dH}{dt} &= - \int d^3\mathbf{q}_1 d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^2\mathbf{b} |\mathbf{v}_1 - \mathbf{v}_2| [f_1(\mathbf{q}_1, \mathbf{p}_1, t) \cdot f_1(\mathbf{q}_1, \mathbf{p}_2, t) - f_1(\mathbf{q}_1, \mathbf{p}'_1, t) \cdot f_1(\mathbf{q}_1, \mathbf{p}'_2, t)] \ln f_1(\mathbf{q}_1, \mathbf{p}_1, t) \\ &= - \frac{1}{2} \int d^3\mathbf{q} d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^2\mathbf{b} |\mathbf{v}_1 - \mathbf{v}_2| [f_1(\mathbf{q}_1, \mathbf{p}'_1) f_1(\mathbf{q}_1, \mathbf{p}'_2) - f_1(\mathbf{q}_1, \mathbf{p}_1) f_1(\mathbf{q}_1, \mathbf{p}_2)] \ln (f_1(\mathbf{q}_1, \mathbf{p}'_1) f_1(\mathbf{q}_1, \mathbf{p}'_2)) \\ &= - \frac{1}{4} \int d^3\mathbf{q} d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^2\mathbf{b} |\mathbf{v}_1 - \mathbf{v}_2| [f_1(\mathbf{q}_1, \mathbf{p}_1) f_1(\mathbf{q}_1, \mathbf{p}_2) - f_1(\mathbf{q}_1, \mathbf{p}'_1) f_1(\mathbf{q}_1, \mathbf{p}'_2)] [\ln (f_1^{\mathbf{p}_1} f_1^{\mathbf{p}_2}) - \ln (f_1^{\mathbf{p}'_1} f_1^{\mathbf{p}'_2})] \end{aligned} \quad (7.100)$$

In the exchange process, the condition $|\mathbf{v}_1 - \mathbf{v}_2| = |\mathbf{v}'_1 - \mathbf{v}'_2|$ is applied, so $((\mathbf{p}'_1, \mathbf{p}'_2, \mathbf{b}'))$ and $(\mathbf{p}_1, \mathbf{p}_2, \mathbf{b})$ are exchanged. From the above equation, it is clear that whether $f_1(\mathbf{q}_1, \mathbf{p}_1) f_1(\mathbf{q}_1, \mathbf{p}_2) > f_1(\mathbf{q}_1, \mathbf{p}'_1) f_1(\mathbf{q}_1, \mathbf{p}'_2)$ or $f_1(\mathbf{q}_1, \mathbf{p}_1) f_1(\mathbf{q}_1, \mathbf{p}_2) < f_1(\mathbf{q}_1, \mathbf{p}'_1) f_1(\mathbf{q}_1, \mathbf{p}'_2)$, the two quantities in the square brackets are greater than 0, thus proving the H -theorem Eq. 7.97.

7.3.1 Detailed Balance Principle

After the gas reaches equilibrium, the H function no longer decreases with time, so the necessary condition for $dH/dt = 0$ is:

$$f_1(\mathbf{q}_1, \mathbf{p}_1) f_1(\mathbf{q}_1, \mathbf{p}_2) = f_1(\mathbf{q}_1, \mathbf{p}'_1) f_1(\mathbf{q}_1, \mathbf{p}'_2) \quad (7.101a)$$

$$\ln f_1(\mathbf{q}_1, \mathbf{p}_1) + \ln f_1(\mathbf{q}_1, \mathbf{p}_2) = \ln f_1(\mathbf{q}_1, \mathbf{p}'_1) + \ln f_1(\mathbf{q}_1, \mathbf{p}'_2) \quad (7.101b)$$

At any position \mathbf{q} , the gas reaches thermal equilibrium, and the particles at each point in phase space cancel each other out in forward and reverse collisions, maintaining balance. This condition is called the detailed balance condition. Below, we discuss the properties when the gas reaches equilibrium. Eq. 7.101b indicates that when the gas reaches overall equilibrium, $\ln f$ is a conserved quantity. Elastic collisions have five conservation quantities: particle number, three components of momentum, and energy. Generally, f_1 is taken as

$$\ln f_1 = \alpha(\mathbf{q}) - \boldsymbol{\alpha}(\mathbf{q}) \cdot \mathbf{p} - \beta(\mathbf{q}) \left(\frac{\mathbf{p}^2}{2m} \right) \quad (7.102)$$

Introducing external potential energy gives:

$$f_1(\mathbf{q}, \mathbf{p}) = \mathcal{N}(\mathbf{q}) \exp \left[-\boldsymbol{\alpha}(\mathbf{q}) \cdot \mathbf{p} - \beta(\mathbf{q}) \left(\frac{\mathbf{p}^2}{2m} + V(\mathbf{q}) \right) \right] \quad (7.103)$$

The distribution function f_1 depends on position \mathbf{q} , called local equilibrium. Although this local equilibrium distribution remains unchanged during collisions, f_1 will continuously evolve due to the flow term. When $[H_1, f_1] = 0$, f_1 reaches overall equilibrium, requiring \mathcal{N}, β to be constants, and $\boldsymbol{\alpha} = 0$.

If f_1 is only a function of H_1 or other conserved quantities, then $[H_1, f_1] = 0$ is satisfied. In Eq. 7.102, as long as \mathcal{N}, β are constants, and $\boldsymbol{\alpha} = 0$, $[H_1, f_1] = 0$ is satisfied. According to the normalization of f_1 to the number of particles $N = d^3 \mathbf{q} d^3 \mathbf{p} f_1(\mathbf{q}, \mathbf{p}, t)$, we obtain

$$f_1(\mathbf{q}, \mathbf{p}) = n \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp \left[-\frac{\beta (\mathbf{p} - \mathbf{p}_0)^2}{2m} \right] \quad (7.104)$$

where $\mathbf{p}_0 = \langle \mathbf{p} \rangle = m\boldsymbol{\alpha}/\beta$ is the average momentum of the gas. If the container is stationary, the average momentum is zero. The variance of momentum is calculated as:

$$\langle \mathbf{p}^2 \rangle = \langle p_x^2 + p_y^2 + p_z^2 \rangle = \frac{3m}{\beta} \quad (7.105)$$

Consider the properties when a mixed gas composed of two gases reaches equilibrium. Assume there are gases a and b in the system, moving in the same external field, with the interaction potential between the two bodies as: $V_{\alpha,\beta}(\mathbf{q}^{(\alpha)} - \mathbf{q}^{(\beta)})$, $\alpha, \beta = a, b$. The single-particle distribution functions of the two gases are $f_1^{(a)}$ and $f_1^{(b)}$, respectively. The collision term between gas particles can be obtained as:

$$C_{\alpha,\beta} = - \int d^3 \mathbf{p}_2 d^2 \Omega \left| \frac{d\sigma_{\alpha,\beta}}{d\Omega} \right| \cdot |\mathbf{v}_1 - \mathbf{v}_2| \left[f_1^{(\alpha)}(\mathbf{q}_1, \mathbf{p}_1, t) \cdot f_1^{(\beta)}(\mathbf{q}_1, \mathbf{p}_2, t) - f_1^{(\alpha)}(\mathbf{q}_1, \mathbf{p}'_1, t) \cdot f_1^{(\beta)}(\mathbf{q}_1, \mathbf{p}'_2, t) \right] \quad (7.106)$$

Therefore, the evolution equations for $f_1^{(a)}$ and $f_1^{(b)}$ are transformed into the following generalized Boltzmann equations:

$$\frac{\partial f_1^{(a)}}{\partial t} = - \left[f_1^{(a)}, H_1^{(a)} \right] + C_{a,a} + C_{a,b}, \quad (7.107a)$$

$$\frac{\partial f_1^{(b)}}{\partial t} = - \left[f_1^{(b)}, H_1^{(b)} \right] + C_{b,a} + C_{b,b}. \quad (7.107b)$$

If the right side of the above equations equals zero, the system reaches a steady state: $\partial f_1^{(a)}/\partial t = \partial f_1^{(b)}/\partial t = 0$, then gases a and b reach equilibrium separately: $f_1^{(a)} \propto e^{-\beta_a H_1^{(a)}}$, $f_1^{(b)} \propto e^{-\beta_b H_1^{(b)}}$. If $C_{a,b} = C_{b,a} = 0$, i.e., there are no collisions between different particles, the requirement $C_{a,b} = C_{b,a} = 0$ leads to the following constraint:

$$f_1^{(a)}(\mathbf{q}_1, \mathbf{p}_1, t) \cdot f_1^{(b)}(\mathbf{q}_1, \mathbf{p}_2, t) = f_1^{(a)}(\mathbf{q}_1, \mathbf{p}'_1, t) \cdot f_1^{(b)}(\mathbf{q}_1, \mathbf{p}'_2, t) \quad (7.108)$$

Thus, the equilibrium condition between different gases is obtained:

$$\beta_a H_1^{(a)}(\mathbf{p}_1) + \beta_b H_1^{(b)}(\mathbf{p}_2) = \beta_a H_1^{(a)}(\mathbf{p}'_1) + \beta_b H_1^{(b)}(\mathbf{p}'_2) \quad (7.109)$$

Since the total energy of the system $H_1^{(a)} + H_1^{(b)}$ is conserved, the equilibrium condition between different gases is $\beta_a = \beta_b = \beta_0$. In a more straightforward form, the average kinetic energy of the two gas molecules is equal:

$$\left\langle \frac{\mathbf{p}_a^2}{2m_a} \right\rangle = \left\langle \frac{\mathbf{p}_b^2}{2m_b} \right\rangle = \frac{3}{2\beta} \quad (7.110)$$

From the above equation, it can be seen that the physical meaning of β is related to the empirical temperature of the system. The relationship between β and temperature T is written, and using molecular kinetic theory, the pressure of the gas can be obtained as: $P = n/\beta$, and similarly, the coldness $\beta = 1/k_B T$ can be obtained.

7.3.2 H-Theorem and Entropy Function

The Boltzmann entropy is introduced through the H function

$$S_B(t) = -k_B H(t) \quad (7.111)$$

According to the H -theorem, during the evolution of the system from a non-equilibrium state to an equilibrium state, the Boltzmann entropy of the system can only increase. Since $H(t)$ is a functional of the single-particle distribution function f_1 , the definition of Boltzmann entropy is more universal and applicable to both non-equilibrium and equilibrium states.

$$\begin{aligned} H &= V \int d^3 \mathbf{p} f_1(\mathbf{p}) \ln f_1(\mathbf{p}) \\ &= V \int d^3 p n (2\pi m k_B T)^{-3/2} \exp\left(-\frac{p^2}{2m k_B T}\right) \left[\ln\left(\frac{n}{(2\pi m k_B T)^{3/2}}\right) - \frac{p^2}{2m k_B T} \right] \\ &= N \left[\ln\left(\frac{n}{(2\pi m k_B T)^{3/2}}\right) - \frac{3}{2} \right] \end{aligned} \quad (7.112)$$

The Boltzmann entropy is obtained as

$$S_B = -k_B H(t) = N k_B \left[\frac{3}{2} + \frac{3}{2} \ln(2\pi m k_B T) - \ln\left(\frac{N}{V}\right) \right] \quad (7.113)$$

7.3.3 Conservation Laws/Fluid Dynamics Equations

First, discuss the microscopic conservation quantities during two-body collisions, for example, the conservation quantity χ satisfies:

$$\chi(\mathbf{q}, \mathbf{p}_1, t) + \chi(\mathbf{q}, \mathbf{p}_2, t) = \chi(\mathbf{q}, \mathbf{p}'_1, t) + \chi(\mathbf{q}, \mathbf{p}'_2, t) \quad (7.114)$$

Here, $(\mathbf{p}_1, \mathbf{p}_2)$ and $(\mathbf{p}'_1, \mathbf{p}'_2)$ are the momenta of the two particles before and after the collision, respectively. The microscopic conservation quantities satisfy the following macroscopic properties:

$$J_\chi(\mathbf{q}, t) = \int d^3\mathbf{p} \chi(\mathbf{q}, \mathbf{p}, t) \frac{df_1}{dt} \Big|_c (\mathbf{q}, \mathbf{p}, t) = 0 \quad (7.115)$$

Substituting into the Boltzmann equation Eq. 7.50, we obtain

$$\begin{aligned} J_\chi(\mathbf{q}, t) &= \int d^3\mathbf{p} \chi(\mathbf{q}, \mathbf{p}, t) \left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1} + \mathbf{F} \cdot \frac{\partial}{\partial \mathbf{p}_1} \right] f_1(\mathbf{q}, \mathbf{p}, t) = 0 \\ &= \int d^3\mathbf{p} \left\{ \left[\partial_t + \frac{1}{m} p_\alpha \partial_\alpha + F_\alpha \frac{\partial}{\partial p_\alpha} \right] (\chi f_1) - f_1 \left[\partial_t + \frac{1}{m} p_\alpha \partial_\alpha + F_\alpha \frac{\partial}{\partial p_\alpha} \right] \chi \right\} = 0 \end{aligned} \quad (7.116)$$

In the above equation, the third term is the total derivative term (divergence) in momentum space, and after integrating over momentum space, the volume integral becomes a surface integral at infinity, resulting in zero. Using the average value in momentum space, the above equation is rewritten as:

$$\partial_t(n\langle\chi\rangle) + \partial_\alpha \left(n \left\langle \frac{p_\alpha}{m} \chi \right\rangle \right) - n \langle \partial_t \chi \rangle - n \left\langle \frac{p_\alpha}{m} \partial_\alpha \chi \right\rangle - n F_\alpha \left\langle \frac{\partial \chi}{\partial p_\alpha} \right\rangle = 0 \quad (7.117)$$

1. Particle Number Conservation Equation. Taking $\chi = 1$, we have the particle number conservation equation

$$\partial_t n + \partial_\alpha (n u_\alpha) = 0 \quad (7.118)$$

where \mathbf{u} is the average velocity of the fluid element. Introducing the mass density of particles $\rho \equiv nm$, the above equation is rewritten as the mass conservation equation

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (7.119)$$

2. Momentum Conservation Equation. According to the random motion velocity of molecules in the fluid element: $\mathbf{V} \equiv \mathbf{p}/m - \mathbf{u}$ (where \mathbf{V} is the velocity of molecules in the fluid element after subtracting the average velocity \mathbf{u}). Taking $\chi = \mathbf{V}$ and substituting into Eq. 7.117, we obtain:

$$\partial_\beta (n \langle (u_\beta + V_\beta) V_\alpha \rangle) + n \partial_t u_\alpha + n \partial_\beta u_\alpha \langle (u_\beta + V_\beta) \rangle - n \frac{F_\alpha}{m} = 0 \quad (7.120)$$

Here, the independence of the variables $(\mathbf{q}, \mathbf{p}, t)$ is used, i.e., $\partial_t p_\alpha = \partial_\alpha p_\beta = 0$. Using $\langle V_\alpha \rangle = 0$, the momentum conservation equation of the fluid is obtained:

$$\partial_t u_\alpha + u_\beta \partial_\beta u_\alpha = \frac{F_\alpha}{m} - \frac{1}{mn} \partial_\beta \mathcal{P}_{\alpha\beta} \quad (7.121)$$

Introducing the pressure tensor

$$\mathcal{P}_{\alpha\beta} \equiv mn \langle V_\alpha V_\beta \rangle = \rho \langle V_\alpha V_\beta \rangle \quad (7.122)$$

The momentum conservation equation of the fluid is written in tensor form:

$$D_t \mathbf{u} \equiv (\partial_t + \mathbf{u} \cdot \nabla) \mathbf{u} = \mathbf{f} - \frac{1}{\rho} \nabla \cdot \mathcal{P} \quad (7.123)$$

In the equation, $\mathbf{f} \equiv \mathbf{F}/m$ is the external force per unit mass of the fluid element. $D_t \equiv \partial_t + \mathbf{u} \cdot \nabla$ is the material derivative or substantial derivative, which physically means the derivative of the macroscopic physical quantity of the fluid observed by an observer moving with the fluid element over time.

3. Energy Conservation Equation. First, define the internal energy of a unit volume of the fluid element as:

$$\varepsilon \equiv n \left\langle \frac{mV^2}{2} \right\rangle = \frac{\rho}{m} \left\langle \frac{mV^2}{2} \right\rangle \quad (7.124)$$

Taking $\chi = mV^2/2$ and substituting into Eq. 7.117, using $\mathbf{p}/m = \mathbf{u} + \mathbf{V}$, and $\langle V_o \rangle = 0$, we obtain:

$$\partial_t \varepsilon + \partial_\alpha (u_\alpha \varepsilon) + \partial_\alpha \left(n \left\langle V_\alpha \frac{mV^2}{2} \right\rangle \right) + P_{\alpha\beta} \partial_\alpha u_\beta = 0 \quad (7.125)$$

Introducing the energy flow vector \mathbf{q} of the fluid element:

$$q_\alpha \equiv \frac{nm}{2} \langle V_\alpha V^2 \rangle = \frac{1}{2} \rho \langle V_\alpha V^2 \rangle \quad (7.126)$$

Substituting into Eq. 7.125, the energy conservation equation of the fluid is obtained:

$$\partial_t \varepsilon + \partial_\alpha (\varepsilon u_\alpha) = -\partial_\alpha q_\alpha - \mathcal{P}_{\alpha\beta} \partial_\alpha u_\beta = -\partial_\alpha q_\alpha - \frac{1}{2} \mathcal{P}_{\alpha\beta} (\partial_\alpha u_\beta + \partial_\beta u_\alpha) \quad (7.127)$$

Introducing the velocity deformation tensor \mathcal{S} :

$$\mathcal{S}_{\alpha\beta} = \frac{1}{2} (\partial_\alpha u_\beta + \partial_\beta u_\alpha) \quad (7.128)$$

The energy conservation equation is rewritten in tensor form:

$$\partial_t \varepsilon + \nabla \cdot (c \mathbf{u}) = -\nabla \cdot \mathbf{q} - \mathcal{P} : \mathcal{S} \quad (7.129)$$

The equations Eq. 7.119, Eq. 7.123, and Eq. 7.129 form the set of fluid dynamics equations. If the pressure tensor \mathcal{P} and the heat flux vector \mathbf{q} are functions of the density, velocity, and temperature (internal energy) of the fluid element, then the set of fluid dynamics equations is closed.

7.4 Fluctuation Theory

7.4.1 Generalized Ensemble Theory of Fluctuations

For a series of extensive quantities: X_1, X_2, \dots ; corresponding intensive quantities y_1, y_2, \dots , the total differential of the physical quantity is written as $S = S(X_1, X_2, \dots)$, $dS = y_1 dX_1 + y_2 dX_2 + \dots$. Consider a microcanonical grand ensemble containing a system and environment, where the total extensive quantities of the system and environment are conserved, and the intensive quantities are the same. The basis vector is chosen as $|T\rangle = |s \otimes R\rangle$, satisfying the eigenvalue

equation and entropy condition

$$\hat{X}_i|T\rangle = \hat{X}_i|s \otimes R\rangle = [X_i(s) + X_i^R(R)]|s \otimes R\rangle \quad (7.130a)$$

$$S_T(\{X_i + X_i^R\}) = k_B \ln \Omega_T(\{X_i + X_i^R\}) \quad (7.130b)$$

The probability is given as

$$\begin{aligned} p_s &= \sum_{|R\rangle} \frac{1}{\Omega_T} = \frac{\Omega_R(\{X_i^R\})}{\Omega_T(\{X_i^T\})} = \frac{1}{\Omega_T} e^{S_R(\{X_i^T - X_i(s)\})/k_B} \\ &= \frac{1}{\Omega_T} e^{S_R[\{\bar{X}_i^R - (X_i(s) - \bar{X}_i)\}/k_B]} = \frac{1}{\Omega_T} \exp \left\{ \frac{\bar{S}_R}{k_B} - \frac{X_i(s) - \bar{X}_i}{k_B} \left(\frac{\partial \bar{S}_R}{\partial \bar{X}_i^R} \right) + \dots \right\} \\ &= \frac{1}{\Omega_T} e^{\bar{S}_R/k_B - \sum_i y_i(X_i - \bar{X}_i)/k_B} = \frac{1}{\Xi} e^{-\sum_i y_i X_i(s)/k_B} \end{aligned} \quad (7.131)$$

Among them, the generalized partition function

$$\Xi(y_1, y_2, \dots) = \sum e^{-\sum_i y_i X_i(S)/k_B} \quad (7.132)$$

The average value of the physical quantity

$$\begin{aligned} \bar{X}_l &= \sum_s X_l(s) p_s = \frac{1}{\Xi} \sum_s X_l(s) e^{-\sum_i y_i X_i(s)/k_B} \\ &= \frac{1}{\Xi} \sum_s (-k_B) \frac{\partial}{\partial y_l} e^{-\sum_i y_i X_i(s)/k_B} = \frac{1}{\Xi} (-k_B) \frac{\partial}{\partial y_l} \sum_s e^{-\sum_i y_i X_i(s)/k_B} \\ &= -k_B \frac{1}{\Xi} \frac{\partial \Xi}{\partial y_l} = -k_B \left(\frac{\partial \ln \Xi}{\partial y_l} \right)_{\{y_i \neq l\}} \end{aligned} \quad (7.133)$$

According to the product of averages

$$\begin{aligned} \overline{X_l X_m} &= \frac{1}{\Xi} \sum_s X_l(s) X_m(s) e^{\sum_i y_i X_i(s)/k_B} = k_B^2 \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial y_l \partial y_m} \\ &= k_B^2 \frac{\partial^2 \ln \Xi}{\partial y_l \partial y_m} + k_B^2 \left(\frac{\partial \ln \Xi}{\partial y_l} \right) \left(\frac{\partial \ln \Xi}{\partial y_m} \right) = k_B^2 \frac{\partial^2 \ln \Xi}{\partial y_l \partial y_m} + \bar{X}_l \bar{X}_m \end{aligned} \quad (7.134)$$

The variance of the average is obtained as

$$\begin{aligned} \overline{\Delta X_l \Delta X_m} &= \overline{(X_l - \bar{X}_l)(X_m - \bar{X}_m)} = \overline{X_l X_m} - \bar{X}_l \bar{X}_m = k_B^2 \frac{\partial^2 \ln \Xi}{\partial y_l \partial y_m} \\ &= -k_B \left(\frac{\partial X_l}{\partial y_m} \right)_{\{y_i \neq m\}} = -k_B \left(\frac{\partial X_m}{\partial y_l} \right)_{\{y_i \neq l\}} \end{aligned} \quad (7.135)$$

If the functions satisfy $f = f(\{X_l\})$ and $g = g(\{X_l\})$, the general variance of the average is given as

$$\begin{aligned} \overline{\Delta f \Delta g} &= \sum_{lm} \left(\frac{\partial f}{\partial X_l} \right) \left(\frac{\partial g}{\partial y_m} \right) \overline{\Delta X_l \Delta y_m} = - \sum_{lm} \left(\frac{\partial f}{\partial X_l} \right) \left(\frac{\partial g}{\partial y_m} \right) k_B \delta_{lm} \\ &= -k_B \sum_l \left(\frac{\partial f}{\partial X_l} \right) \left(\frac{\partial g}{\partial y_l} \right) = -k_B \sum_l \left(\frac{\partial f}{\partial y_l} \right) \left(\frac{\partial g}{\partial X_l} \right) \\ &= -k_B \sum_l \sum_m \left(\frac{\partial f}{\partial X_l} \right) \left(\frac{\partial g}{\partial X_m} \right) \left(\frac{\partial X_l}{\partial y_l} \right) = -k_B \sum_l \sum_m \left(\frac{\partial f}{\partial y_l} \right) \left(\frac{\partial g}{\partial y_m} \right) \left(\frac{\partial y_m}{\partial X_l} \right) \end{aligned} \quad (7.136)$$

For example, consider the total differential relationship: $dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$

(1) In the canonical ensemble, keeping T, V, N constant, we obtain

$$\overline{\Delta E^2} = -k_B \left(\frac{\partial U}{\partial [1/T]} \right)_{NV} = k_B T^2 C_V \quad (7.137)$$

(2) In the grand canonical ensemble, keeping T, V, μ constant, we obtain

$$\overline{\Delta N^2} = -k_B \left(\frac{\partial N}{\partial [-\mu/T]} \right)_{T,V} = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{TV} = \frac{k_B T N^2 \kappa_T}{V} \quad (7.138a)$$

$$\overline{\Delta E^2} = -k_B \left(\frac{\partial U}{\partial [1/T]} \right)_{\mu/T,V} = k_B T^2 C_V + \left(\frac{\partial U}{\partial N} \right)_{TV}^2 \overline{\Delta N^2} \quad (7.138b)$$

$$\overline{\Delta E \Delta N} = -k_B \left(\frac{\partial U}{\partial [-\mu/T]} \right)_{TV} = k_B T \left(\frac{\partial U}{\partial \mu} \right)_{TV} = k_B T \left(\frac{\partial U}{\partial N} \right)_{TV} \left(\frac{\partial N}{\partial \mu} \right)_{TV} = \left(\frac{\partial U}{\partial N} \right)_{TV} \overline{\Delta N^2} \quad (7.138c)$$

(3) In the generalized ensemble, keeping T, p, μ constant, we obtain

$$\overline{\Delta V^2} = \overline{\Delta N^2 v^2} = \overline{\Delta N^2 v^2} = \frac{k_B T N^2}{V} \kappa_T \frac{V^2}{N^2} = k_B T V \kappa_T \quad (7.139a)$$

$$\overline{\Delta T \Delta V} = 0 \quad (7.139b)$$

Or from the perspective of energy expansion, expand $E(S, V)$ around (\bar{S}, \bar{V}) up to the second-order terms of ΔS and ΔV , we have

$$\begin{aligned} \Delta E &= E(S, V) - \bar{E}(\bar{S}, \bar{V}) = \left(\frac{\partial E}{\partial S} \right)_V \Delta S + \left(\frac{\partial E}{\partial V} \right)_S \Delta V + \frac{1}{2} \left[\left(\frac{\partial^2 E}{\partial S^2} \right)_V (\Delta S)^2 + 2 \frac{\partial^2 E}{\partial S \partial V} \Delta S \Delta V + \left(\frac{\partial^2 E}{\partial V^2} \right)_S (\Delta V)^2 \right] \\ &= T \Delta S - p \Delta V + \frac{1}{2} (\Delta T \Delta S - \Delta p \Delta V) \end{aligned} \quad (7.140)$$

The probability of the system having deviations $\Delta p, \Delta V, \Delta T, \Delta S$ is

$$p = p_m \exp \frac{-\Delta E + p \Delta S - p \Delta V}{kT} = p_m \exp \left(\frac{\Delta p \Delta V - \Delta T \Delta S}{2kT} \right) \quad (7.141)$$

To find the fluctuations in temperature and volume, we can take T, V as variables, then ΔS and Δp can be expressed as functions of ΔT and ΔV

$$\Delta S = \left(\frac{\partial S}{\partial T} \right)_V \Delta T + \left(\frac{\partial S}{\partial V} \right)_T \Delta V = \frac{C_V}{T} \Delta T + \left(\frac{\partial p}{\partial T} \right)_V \Delta V \quad (7.142a)$$

$$\Delta p = \left(\frac{\partial p}{\partial T} \right)_V \Delta T + \left(\frac{\partial p}{\partial V} \right)_T \Delta V \quad (7.142b)$$

Substituting into Eq. 7.141, we obtain

$$p(\Delta T, \Delta V) = p_m \exp \left[-\frac{C_V}{2kT^2} (\Delta T)^2 + \frac{1}{2kT} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right] \quad (7.143)$$

The fluctuation of the system's temperature is

$$\begin{aligned} \overline{(\Delta T)^2} &= \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\Delta T)^2 p(\Delta T, \Delta V) d(\Delta T) d(\Delta V)}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(\Delta T, \Delta V) d(\Delta T) d(\Delta V)} \\ &= \frac{\int_{-\infty}^{\infty} (\Delta T)^2 \exp \left[-\frac{C_V}{2kT^2} (\Delta T)^2 \right] d(\Delta T)}{\int_{-\infty}^{\infty} \exp \left[-\frac{C_V}{2kT^2} (\Delta T)^2 \right] d(\Delta T)} = \frac{kT^2}{C_V} \end{aligned} \quad (7.144)$$

The fluctuation of the system's volume is

$$\begin{aligned}\overline{(\Delta V)^2} &= \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\Delta V)^2 \exp \left[\frac{1}{2kT} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[\frac{1}{2kT} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)} \\ &= -kT \left(\frac{\partial V}{\partial p} \right)_T = kTV\kappa_T\end{aligned}\quad (7.145)$$

The correlation function of fluctuations in T and V (the correlation function $\overline{\Delta x \Delta y}$ measures the statistical correlation between x and y)

$$\begin{aligned}\overline{\Delta T \Delta V} &= \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Delta T \Delta V \exp \left[-\frac{C_V}{2kT^2} (\Delta T)^2 + \frac{1}{2kT} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta T) d(\Delta V)}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[-\frac{C_V}{2kT^2} (\Delta T)^2 + \frac{1}{2kT} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta T) d(\Delta V)} \\ &= \frac{\int_{-\infty}^{\infty} \Delta T \exp \left[-\frac{C_V}{2kT^2} (\Delta T)^2 \right] d(\Delta T) \int_{-\infty}^{\infty} \Delta V \exp \left[\frac{1}{2kT} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)}{\int_{-\infty}^{\infty} \exp \left[-\frac{C_V}{2kT^2} (\Delta T)^2 \right] d(\Delta T) \int_{-\infty}^{\infty} \exp \left[\frac{1}{2kT} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)} = 0\end{aligned}\quad (7.146)$$

The relative fluctuations of temperature and volume

$$\frac{\overline{(\Delta T)^2}}{T^2} = \frac{k}{C_V}, \quad \overline{(\Delta V)^2} = \frac{kT\kappa_T}{V} \quad (7.147)$$

The fluctuation of particle number density is related to the fluctuation of volume because $N = nV$

$$\frac{\Delta n}{n} + \frac{\Delta V}{V} = 0, \quad \frac{\overline{(\Delta n)^2}}{n^2} = \frac{\overline{(\Delta V)^2}}{V^2} = \frac{kT}{V}\kappa_T \quad (7.148)$$

To find the fluctuations in entropy and pressure, we can choose S and p as variables, and express ΔT and ΔV as functions of ΔS and Δp

$$\Delta T = \left(\frac{\partial T}{\partial S} \right)_p \Delta S + \left(\frac{\partial T}{\partial p} \right)_S \Delta p = \frac{T}{C_p} \Delta S + \left(\frac{\partial T}{\partial p} \right)_S \Delta p \quad (7.149a)$$

$$\Delta V = \left(\frac{\partial V}{\partial S} \right)_p \Delta S + \left(\frac{\partial V}{\partial p} \right)_S \Delta p = \left(\frac{\partial V}{\partial p} \right)_S \Delta S + \left(\frac{\partial V}{\partial p} \right)_S \Delta p \quad (7.149b)$$

Substituting into Eq. 7.141, we obtain

$$p(\Delta S, \Delta p) = p_m \exp \left[-\frac{1}{2kC_p} (\Delta S)^2 + \frac{1}{2kT} \left(\frac{\partial V}{\partial p} \right)_S (\Delta p)^2 \right] \quad (7.150)$$

The fluctuation of the system's entropy is

$$\begin{aligned}\overline{(\Delta S)^2} &= \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\Delta S)^2 p(\Delta S, \Delta p) d(\Delta S) d(\Delta p)}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(\Delta S, \Delta p) d(\Delta S) d(\Delta p)} = \frac{\int_{-\infty}^{\infty} (\Delta S)^2 \exp \left[-\frac{1}{2kC_p} (\Delta S)^2 \right] d(\Delta S)}{\int_{-\infty}^{\infty} \exp \left[-\frac{1}{2kC_p} (\Delta S)^2 \right] d(\Delta S)} = kC_p\end{aligned}\quad (7.151)$$

The fluctuation of pressure is

$$\begin{aligned}\overline{(\Delta p)^2} &= \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\Delta p)^2 p(\Delta S, \Delta p) d(\Delta S) d(\Delta p)}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(\Delta S, \Delta p) d(\Delta S) d(\Delta p)} = \frac{\int_{-\infty}^{\infty} (\Delta p)^2 \exp \left[\frac{1}{2kT} \left(\frac{\partial V}{\partial p} \right)_S (\Delta p)^2 \right] d(\Delta p)}{\int_{-\infty}^{\infty} \exp \left[\frac{1}{2kT} \left(\frac{\partial V}{\partial p} \right)_S (\Delta p)^2 \right] d(\Delta p)} = -kT \left(\frac{\partial p}{\partial V} \right)_S\end{aligned}\quad (7.152)$$

The correlation function of entropy and pressure fluctuations

$$\overline{\Delta S \Delta p} = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Delta S \Delta p p(\Delta S, \Delta p) d(\Delta S) d(\Delta p)}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(\Delta S, \Delta p) d(\Delta S) d(\Delta p)} = 0 \quad (7.153)$$

Some dependent statistical quantities' fluctuations can be given, such as the fluctuations of temperature and entropy

$$\overline{\Delta T \Delta S} = \left(\frac{\partial S}{\partial T} \right)_V \overline{(\Delta T)^2} + \left(\frac{\partial S}{\partial V} \right)_T \overline{\Delta T \Delta V} = \frac{C_V}{T} \overline{(\Delta T)^2} = kT \quad (7.154a)$$

$$\overline{\Delta p \Delta V} = \left(\frac{\partial p}{\partial V} \right)_T \overline{(\Delta V)^2} + \left(\frac{\partial p}{\partial T} \right)_V \overline{\Delta T \Delta V} = -kT \quad (7.154b)$$

$$\overline{\Delta S \Delta V} = \left(\frac{\partial V}{\partial T} \right)_p \overline{(\Delta T)^2} + \left(\frac{\partial V}{\partial p} \right)_T \overline{\Delta S \Delta p} = \frac{kT}{C_V} \left(\frac{\partial V}{\partial T} \right)_p \quad (7.154c)$$

$$\overline{\Delta T \Delta p} = \left(\frac{\partial p}{\partial T} \right)_V \overline{(\Delta T)^2} + \left(\frac{\partial p}{\partial V} \right)_T \overline{\Delta T \Delta V} = \frac{kT^2}{C_V} \left(\frac{\partial p}{\partial T} \right)_V \quad (7.154d)$$

7.4.2 Spatial/Temporal Correlation of Fluctuations

1. Spatial Correlation of Fluctuations:

Due to the interactions between particles in the system and the influence of particle indistinguishability, a disturbance at one point in the system space will affect the fluctuations at another point. Taking the correlation of density fluctuations as an example, suppose there are two small volume elements dV and dV' in the system, with position vectors \mathbf{r} and \mathbf{r}' , respectively. The particle number densities at these two small volume elements are $n(\mathbf{r})$ and $n(\mathbf{r}')$. The average of the difference between $n(\mathbf{r})$ and its statistical average $\bar{n}(\mathbf{r})$ is zero

$$\overline{\Delta n} = \overline{n(\mathbf{r}) - \bar{n}(\mathbf{r})} = 0 \quad (7.155)$$

Define the spatial correlation function of density

$$g(\mathbf{r}, \mathbf{r}') = \overline{[n(\mathbf{r}) - \bar{n}(\mathbf{r})][n(\mathbf{r}') - \bar{n}(\mathbf{r}')]}$$

If the fluctuations at different points in space are independent, then

$$g(\mathbf{r}, \mathbf{r}') = \overline{[n(\mathbf{r}) - \bar{n}(\mathbf{r})][n(\mathbf{r}') - \bar{n}(\mathbf{r}')]}) = 0, \quad \mathbf{r} \neq \mathbf{r}' \quad (7.157)$$

Conversely, if $g(\mathbf{r}, \mathbf{r}') \neq 0$, it indicates that there is a correlation between density fluctuations at different points in space. For homogeneous systems, such as gases or liquids, the correlation function $g(\mathbf{r}, \mathbf{r}')$ is only a function of the distance $r = |\mathbf{r} - \mathbf{r}'|$ between \mathbf{r} and \mathbf{r}' , $g(\mathbf{r}, \mathbf{r}') = g(r)$, $g(r)$ is

$$g(r) = \overline{[n(r) - \bar{n}][n(0) - \bar{n}]}, \quad \bar{n} = \bar{n}(r) = \bar{n}(0) \quad (7.158)$$

Generally, the greater the distance between two points, the smaller the mutual influence, and the correlation function $g(r)$ decreases with increasing r . If the correlation is significant within a distance $r \sim \xi$, and $g(r)$ is very small for $r > \xi$, so small that it can be ignored, then the quantity

ξ can be used as a measure of the spatial correlation range, defining ξ as the correlation length. To find the correlation function $g(\mathbf{r})$, perform a Fourier expansion of the density deviation Δn

$$\Delta n = n(\mathbf{r}) - \bar{n} = \frac{1}{V} \sum_k n_k e^{i\mathbf{k}\cdot\mathbf{r}}, \quad n_k = \int [n(\mathbf{r}) - \bar{n}] e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \quad (7.159)$$

where V is the volume of the system, and n_k is the Fourier component of Δn . Since Δn is a real number, taking the complex conjugate on both sides of the equation, we get

$$\Delta n = \frac{1}{V} \sum_k n_k^* e^{-i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{V} \sum_k n_{-k}^* e^{i\mathbf{k}\cdot\mathbf{r}} \quad (7.160)$$

Comparing the two equations, we get

$$n_k = n_{-k}^* \quad (7.161)$$

Write

$$|n_k|^2 = \iint d\mathbf{r} d\mathbf{r}' [n(\mathbf{r}) - \bar{n}] [n(\mathbf{r}') - \bar{n}] e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \quad (7.162)$$

Taking the statistical average, and considering that the order of integration and averaging can be exchanged, we get

$$\overline{|n_k|^2} = \iint d\mathbf{r} d\mathbf{r}' g(|\mathbf{r} - \mathbf{r}'|) e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \int d\mathbf{r}' \int d\mathbf{R} g(\mathbf{R}) e^{-i\mathbf{k}\cdot\mathbf{R}} = V g_k \quad (7.163)$$

where $\mathbf{R} = \mathbf{r} - \mathbf{r}'$, g_k is the Fourier component of the correlation function $g(\mathbf{r})$

$$g_k = \int d\mathbf{r} g(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \quad (7.164)$$

The inverse transform is

$$g(\mathbf{r}) = \frac{1}{V} \sum_k g_k e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{V^2} \sum_k \overline{|n_k|^2} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (7.165)$$

Taking the fluid system as an example to find the correlation function $g(\mathbf{r})$. Choose temperature T and density n as independent variables. Due to the statistical independence of temperature and volume, when considering density fluctuations, the system's temperature T can be assumed to be constant, and the system's volume can be assumed to remain unchanged. According to the quasi-thermodynamic theory of fluctuations, the probability of the system's free energy deviation $\Delta F = F - \bar{F} = \Delta E - T\Delta S$ is given by Eq. 7.141 as:

$$p(\Delta F) \propto e^{-\frac{\Delta F}{k_B T}}, \quad \Delta F = \int (f - \bar{f}) d\mathbf{r} \quad (7.166)$$

ΔF is expressed as the volume integral of the free energy density deviation $\Delta f = f - \bar{f}$, where the integral covers the entire fluid volume. Expand Δf into a power series of the density deviation Δn and the density gradient ∇n . Since the total number of particles in the fluid is constant, regardless of whether Δn is greater than zero or less than zero, fluctuations always increase the system's free energy, and the free energy is minimal at equilibrium. Therefore, the coefficient of the Δn term in the expansion must be zero, and the lowest order term related to Δn in the expansion of Δf

is the square term $(\Delta n)^2$. For a spatially uniform fluid, there is no specific direction in space, so the expansion of Δf cannot contain linear terms of the density gradient ∇n , and the lowest order term containing ∇n is the square term $(\nabla n)^2$. Therefore, the expansion of Δf retaining the lowest order terms of Δn and ∇n is:

$$\Delta f = f - \bar{f} = \frac{a}{2}(\Delta n)^2 + \frac{b}{2}(\nabla n)^2 \quad (7.167)$$

where a and b are coefficients related to temperature. It can be obtained that $a = \left(\frac{\partial^2 f}{\partial n^2}\right)_T$.

Considering $\mu = \left(\frac{\partial f}{\partial n}\right)_T$ and $d\mu = -s dT + v dp$, where μ , s , and v are the chemical potential, entropy, and volume of a molecule, respectively, a can be expressed as:

$$a = \left(\frac{\partial^2 f}{\partial n^2}\right)_T = \left(\frac{\partial \mu}{\partial n}\right)_T = v \left(\frac{\partial p}{\partial n}\right)_T = \frac{1}{n} \left(\frac{\partial p}{\partial n}\right)_T \quad (7.168)$$

In thermodynamics, the condition for equilibrium stability requires $\left(\frac{\partial p}{\partial v}\right)_T < 0$, which means $\left(\frac{\partial p}{\partial n}\right)_T > 0$, thus $a > 0$. At the critical point, $\left(\frac{\partial P}{\partial n}\right)_T = 0$, $a = 0$, so a should be chosen as $a \geq 0$. According to this, Landau assumes near the critical point that $a = a_0 |T - T_c|$, where $a_0 > 0$ and is a constant independent of temperature T . For a homogeneous fluid, n being a constant uniform state is the most probable state, and the free energy takes a minimum value at this point. Therefore, near the critical point, b is taken as a positive constant. From the Fourier transform of Eq. 7.159, the Fourier transforms of $(\Delta n)^2$ and $(\nabla n)^2$ are obtained as follows:

$$\begin{aligned} [\Delta n(\mathbf{r})]^2 &= \frac{1}{V^2} \sum_{k,k'} n_k^* n_{k'} e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} \\ [\nabla n(\mathbf{r})]^2 &= \frac{1}{V^2} \sum_{k,k'} n_k^* n_{k'} \mathbf{k} \cdot \mathbf{k}' e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} \end{aligned} \quad (7.169)$$

The deviation of the free energy density is obtained as

$$\Delta f = \frac{1}{2V^2} \sum_{k,k'} n_k^* n_{k'} (a + b \mathbf{k} \cdot \mathbf{k}') e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} \quad (7.170)$$

Thus, the deviation of the free energy is

$$\Delta F = \frac{1}{2V^2} \sum_{k,k'} n_k^* n_{k'} (a + b \mathbf{k} \cdot \mathbf{k}') \int e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} d\mathbf{r} = \frac{1}{2V} \sum_k (a + b k^2) |n_k|^2 \quad (7.171)$$

The above derivation uses the formula $\frac{1}{V} \int e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} d\mathbf{r} = \delta_{k,k'}$. Substituting ΔF into the probability Eq. 7.166, we get

$$p(\Delta F) \propto \exp \left[-\frac{1}{2V k_B T} \sum_k (a + b k^2) |n_k|^2 \right] = \prod_k \exp \left[-\frac{1}{2V k_B T} (a + b k^2) |n_k|^2 \right] \quad (7.172)$$

It is known that p is the product of Gaussian distribution functions of each Fourier component n_k of the density deviation $\Delta n(\mathbf{r})$, and each n_k contributes statistically independently to the fluctuations. Therefore, the probability of the Fourier component n_k of the density deviation Δn

is

$$p(n_k) \propto \exp\left(-\frac{1}{2Vk_B T} (a + bk^2) |n_k|^2\right) \quad (7.173)$$

Using the integral formula of the Gaussian distribution function, the fluctuation of n_k is obtained as

$$\overline{|n_k|^2} = \frac{\int_{-\infty}^{\infty} \exp\left[-\frac{1}{2Vk_B T} (a + bk^2) |n_k|^2\right] |n_k|^2 dn_k}{\int_{-\infty}^{\infty} \exp\left[-\frac{1}{2Vk_B T} (a + bk^2) |n_k|^2\right] dn_k} = \frac{Vk_B T}{a + bk^2} \quad (7.174)$$

Substituting into the correlation function Eq. 7.165, the correlation function is obtained (the wave vector \mathbf{k} in the macroscopic scale volume V can be considered quasi-continuous, and the sum can be converted into an integral over k)

$$g(\mathbf{r}) = \frac{k_B T}{V} \sum_k \frac{1}{a + bk^2} e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{k_B T}{(2\pi)^3} \int \frac{1}{a + bk^2} e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k} = \frac{k_B T}{4\pi b} \frac{1}{r} e^{-\frac{r}{\xi}} \quad (7.175)$$

where we define

$$\xi = \sqrt{\frac{b}{a}} \quad (7.176)$$

Eq. 7.175 describes the correlation of density fluctuations between two points separated by a distance r . The correlation mainly occurs within the range $r \leq \xi = \sqrt{\frac{b}{a}}$. When $r > \xi$, the correlation function $g(r)$ rapidly decays to zero as r increases. Therefore, ξ is called the correlation length. In Landau's theory, $a = a_0|T - T_c|$, where $a_0 > 0$ and $b > 0$. Let $t = \frac{T - T_c}{T_c}$, then near the critical point, the correlation length can be expressed as

$$\xi \sim |t|^{-\nu}, \quad \nu = \frac{1}{2} \quad (7.177)$$

This equation indicates that as the temperature $T \rightarrow T_c$, the correlation length tends to infinity. This means that when the system's temperature approaches the critical temperature, there is significant correlation in the density fluctuations throughout the system. At this time, the correlation function can be expressed as

$$g(r) \simeq \frac{k_B T}{4\pi b r} \propto \frac{1}{r} \quad (7.178)$$

As the temperature approaches the critical temperature, the correlation length tends to infinity, which is a fundamental characteristic of critical phenomena. Many properties of the system near the critical point are closely related to the divergence of the correlation length. According to Eq. 7.158, the fluctuation of the number of molecules is calculated as

$$\overline{(N - \bar{N})^2} = \iint d\mathbf{r} d\mathbf{r}' [\bar{n}(\mathbf{r}) - \bar{n}] [\bar{n}(\mathbf{r}') - \bar{n}] = \iint d\mathbf{r} d\mathbf{r}' g(\mathbf{r} - \mathbf{r}') = V \int d\mathbf{R} g(\mathbf{R}) \quad (7.179)$$

Substituting into Eq. 7.175, we get

$$\overline{(N - \bar{N})^2} = \frac{V k_B T}{4\pi b} \int d\mathbf{R} \frac{1}{R} e^{-\frac{R}{\xi}} = \frac{V k_B T}{b} \xi^2 \quad (7.180)$$

This indicates that the anomalous increase in the fluctuation of the number of molecules near the critical point is closely related to the divergence of the correlation length. By substituting into Eq. 7.148, we obtain

$$\kappa_T = \frac{1}{b} \left(\frac{V}{\bar{N}} \right)^2 \xi^2 \quad (7.181)$$

This shows that the divergence of the isothermal compressibility near the critical point is also closely related to the divergence of the correlation length. Considering the relationship with the correlation length, we get

$$\kappa_T \sim |t|^{-2\nu} \quad (7.182)$$

Thus, according to Landau's theory, near the critical point $\kappa_T \sim |t|^{-\gamma}$, and the critical exponent γ is related to ν as follows:

$$\gamma = 2\nu \quad (7.183)$$

2. **Temporal Correlation of Fluctuations**

The temporal correlation of fluctuations indicates the influence of a disturbance at one moment on the fluctuations at another moment. Corresponding to the correlation length, there is also a correlation time in temporal correlation, indicating the time scale over which this influence can extend. Assume x is a physical quantity describing the macroscopic properties of the system. Its average value is \bar{x} , and as time t changes, x fluctuates around the average value, being a time-dependent fluctuating function. Let the random variable $\alpha(t)$ represent the deviation of the physical quantity $x(t)$ from its average value at time t

$$\alpha(t) = x(t) - \bar{x} \quad (7.184)$$

The deviation $\alpha(t)$ of the physical quantity x at a certain time t will affect its deviation $\alpha(t + \tau)$ at time $t + \tau$. Define the temporal correlation function

$$g(\tau) = \overline{\alpha(t)\alpha(t + \tau)} \quad (7.185)$$

Ensemble theory has already assumed that ensemble averages and time averages are equal in a statistical sense, so the temporal correlation function $g(\tau)$ can be understood as both the ensemble average of $\alpha(t)\alpha(t + \tau)$ and the time average of $\alpha(t)\alpha(t + \tau)$ over a long time T for a given time interval τ

$$g(\tau) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \alpha(t)\alpha(t + \tau) dt \quad (7.186)$$

The temporal correlation function $g(\tau)$ has the following properties:

- (1) $g(\tau)$ is only a function of the time interval τ , independent of time t ;
- (2) $g(0)$ is the fluctuation $\overline{\alpha(t)^2}$ of the physical quantity $x(t)$, therefore

$$g(0) = \overline{\alpha(t)^2} > 0 \quad (7.187a)$$

$$|g(\tau)| \leq g(0) \quad (7.187b)$$

- (3) $|g(\tau)| < g(0)$, because

$$\overline{[\alpha(t + \tau) \pm \alpha(t)]^2} = \overline{\alpha(t)^2} + \overline{\alpha(t + \tau)^2} \pm 2\overline{\alpha(t + \tau)\alpha(t)} = 2[g(0) \pm g(\tau)] \geq 0 \quad (7.188)$$

- (4) $g(\tau)$ is an even function, i.e.,

$$g(\tau) = g(-\tau) \quad (7.189)$$

because

$$g(\tau) = \overline{\alpha(t)\alpha(t+\tau)} = \overline{\alpha(t_1-\tau)\alpha(t_1)} = g(-\tau) \quad (7.190)$$

(5) As the time interval τ increases, the value of the temporal correlation function $g(\tau)$ decreases. When τ exceeds a certain characteristic time τ^* , the values of $\alpha(t)$ and $\alpha(t+\tau)$ do not affect each other, i.e., when $\tau > \tau^*$, $g(\tau) = \overline{\alpha(t)\alpha(t+\tau)} = \overline{\alpha(t)\alpha(t+\tau)} = 0$. At this time, $\alpha(t)$ is uncorrelated, and τ^* is called the correlation time. If the correlation time τ^* is extremely short, tending to 0 in macroscopic time, $\alpha(t)$ is said to be uncorrelated, and the temporal correlation function can be written as

$$g(\tau) = \overline{\alpha(t)\alpha(t+\tau)} = a\delta(\tau) \quad (7.191)$$

The above equation means that the deviations $\alpha(t)$ at different times are uncorrelated, and at $\tau = 0$, $g(0) = \overline{\alpha(t)^2} = a$, where a represents the mean square deviation of the physical quantity x , i.e., the fluctuation of x . The larger a is, the greater the fluctuation of x ; below, the temporal correlation function is illustrated using Brownian motion as an example. The equation of motion for a Brownian particle in a certain direction on a horizontal plane is given by Eq. 7.211, rewritten as

$$\dot{v} = -\gamma v + A(t) \quad (7.192)$$

where v is the velocity of the Brownian particle, $\gamma = \frac{\alpha}{m}$, and $A(t) = \frac{X(t)}{m}$ is the fluctuating force acting on a unit mass Brownian particle. The motion of the Brownian particle is the result of both viscous resistance and fluctuating force. Assume that at $t = 0$, the velocity of the Brownian particle is $v(0)$, then integrating the above equation gives

$$v(t) = v(0)e^{-\gamma t} + e^{-\gamma t} \int_0^t A(\xi)e^{\gamma \xi} d\xi \quad (7.193)$$

This equation holds for all Brownian particles. Since $A(t)$ is the fluctuating force, when averaged over a large number of Brownian particles, $\overline{A(t)} = 0$, thus we have

$$\overline{v(t)} = \overline{v(0)}e^{-\gamma t} = v_0 e^{-\gamma t} \quad (7.194)$$

where $v_0 = \overline{v(0)}$ is the average initial velocity of the Brownian particles. This equation shows that due to the viscous resistance of the fluid, the average velocity of the Brownian particles decays exponentially, with a relaxation time of $\frac{1}{\gamma} = \frac{m}{\alpha} \approx 10^{-7}$ s. The deviation of the particle's velocity is

$$\Delta v = v(t) - \overline{v(t)} = \int_0^t A(\xi)e^{-\gamma(t-\xi)} d\xi \quad (7.195)$$

The time correlation function of the velocity is

$$\overline{\Delta v(t)\Delta v(t')} = \overline{[v(t) - \overline{v(t)}][v(t') - \overline{v(t')}] = \int_0^t d\xi \int_0^{t'} d\xi' \overline{A(\xi)A(\xi')} e^{-\gamma(t-\xi)-\gamma(t'-\xi')}} \quad (7.196)$$

Since the fluctuating force $A(t)$ experienced by the Brownian particles is a rapidly changing random variable over time, the correlation time τ^* of $\overline{A(\xi)A(\xi')}$ should be very short, roughly estimated by the average collision time of the Brownian particles with surrounding liquid molecules.

For liquids, $\tau^* \sim 10^{-19}$ s, $\tau^* \ll \frac{1}{\gamma}$, thus the correlation function of the fluctuating force $\overline{A(\xi)A(\xi')}$ has a delta function form. If a represents the measure of the fluctuation magnitude of the random force $A(t)$ in the random motion of the particles, then $\overline{A(\xi)A(\xi')} = a\delta(\xi' - \xi)$, substituting into the above equation gives

$$\overline{\Delta v(t)\Delta v(t')} = a \int_0^t d\xi \int_0^{t'} d\xi' \delta(\xi' - \xi) e^{-\gamma(t-\xi)-\gamma(t'-\xi')} \quad (7.197)$$

If $t > t'$, integrate with respect to $d\xi$ first, and then with respect to $d\xi'$, obtaining

$$\overline{\Delta v(t)\Delta v(t')} = a \int_0^{t'} d\xi' e^{-\gamma(t+t'-2\xi')} = \frac{a}{2\gamma} [e^{-\gamma(t-t')} - e^{-\gamma(t+t')}] \quad (7.198)$$

If $t < t'$, integrate with respect to $d\xi'$ first, and then with respect to $d\xi$, obtaining

$$\overline{\Delta v(t)\Delta v(t')} = \frac{a}{2\gamma} [e^{-\gamma(t'-t)} - e^{-\gamma(t+t')}] \quad (7.199)$$

The above two equations can be unified into the velocity correlation function

$$\overline{\Delta v(t)\Delta v(t')} = \frac{a}{2\gamma} [e^{-\gamma|t-t'|} - e^{-\gamma(t+t')}] \quad (7.200)$$

When $t = t'$, the velocity fluctuation is

$$\overline{[\Delta v(t)]^2} = \frac{a}{2\gamma} [1 - e^{-2\gamma t}] \quad (7.201)$$

If the time $t \ll \frac{1}{\gamma}$, the value inside the brackets approximates $1 - e^{-2\gamma t} \simeq 2\gamma t$, resulting in

$$\overline{[\Delta v(t)]^2} = at, \quad t \ll \frac{1}{\gamma} \quad (7.202)$$

Thus, when $t \ll \frac{1}{\gamma}$, the velocity fluctuation $\overline{[\Delta v]^2}$ is proportional to time t , as detailed in the explanation of Brownian motion in Subsubsec. 7.4.3. Therefore, the above equation shows that due to the action of the fluctuating force $A(t)$, the velocity of the Brownian particles diffuses, with a velocity diffusion coefficient of $D_v = \frac{a}{2}$.

If $t \gg \frac{1}{\gamma}$, from Eq. 7.194 we have $\overline{v(t)} \approx 0$, meaning the influence of the initial velocity has disappeared, and the Brownian particles have reached thermal equilibrium with the fluid medium. From the velocity fluctuation Eq. 7.201, the equilibrium value of $\overline{v(t)^2}$ is obtained as

$$\overline{v(t)^2} = \frac{a}{2\gamma} = \frac{kT}{m}, \quad t \gg \frac{1}{\gamma} \quad (7.203)$$

Using the equipartition theorem Eq. 4.176 $\frac{1}{2}mv^2 = \frac{1}{2}kT$, we can obtain

$$a = \frac{2kT\gamma}{m} = \frac{2\alpha kT}{m^2} \quad (7.204)$$

Theorem 7.1 (Fluctuation-Dissipation Theorem). *On the left, a represents the magnitude of the fluctuation of the random force experienced by the particles or the magnitude of the fluctuation of the particle's acceleration. It originates from the irregular fluctuating force experienced by the Brownian particles and is a measure of the magnitude of random motion fluctuations; on the right, α comes from the damping force, which is a measure of the damping force experienced by the Brownian particles moving in the fluid, i.e., a measure of the dissipation magnitude. This equation links fluctuation and dissipation. The stronger the dissipation in the system, the larger α , and the larger a , indicating a stronger fluctuating force, and vice versa. This result is called the Fluctuation-Dissipation Theorem.*

When $t, t' \gg \frac{1}{\gamma}$, $\overline{v(t)} = 0$, the second term in Eq. 7.200 can be ignored, thus obtaining

$$\overline{v(t)v(t')} = \frac{a}{2\gamma} e^{-\gamma|t-t'|} = \frac{kT}{m} e^{-\gamma|t-t'|} \quad (7.205)$$

This indicates that although the fluctuating forces at different times are not correlated, the velocities (or momenta) of Brownian particles at different times are correlated. This is because the velocity is the result of both viscous resistance and fluctuating forces.

The fluctuation of the displacement of Brownian particles is calculated using the velocity time correlation function. After a time interval t , the distance traveled by the Brownian particle is

$$\Delta x = x(t) - x(0) = \int_0^t v(\xi) d\xi \quad (7.206)$$

where $\overline{\Delta x} = \int_0^t \overline{v(\xi)} d\xi = 0$. Noting that $\gamma t \gg 1$, the fluctuation of the displacement is

$$\overline{(\Delta x)^2} = \int_0^t d\xi \int_0^t d\xi' \overline{v(\xi)v(\xi')} = \frac{kT}{m} \int_0^t d\xi \int_0^t d\xi' e^{-\gamma|\xi-\xi'|} \quad (7.207)$$

The above integral can be divided into two parts, $\xi > \xi'$ and $\xi < \xi'$, giving two integration regions, resulting in the integral

$$\begin{aligned} \overline{(\Delta x)^2} &= \frac{kT}{m} \left[\int_0^t d\xi \int_0^\xi d\xi' e^{-\gamma|\xi-\xi'|} + \int_0^t d\xi \int_\xi^t d\xi' e^{-\gamma|\xi-\xi'|} \right] \\ &= \frac{kT}{m\gamma} \left[\int_0^t d\xi (1 - e^{-\gamma\xi}) + \int_0^t d\xi (1 - e^{-\gamma(t-\xi)}) \right] \\ &= \frac{2kT}{m\gamma} t = 2Dt \end{aligned} \quad (7.208)$$

The diffusion coefficient $D = \frac{kT}{\gamma m} = \frac{kT}{\alpha}$, $a = 2\gamma^2 D$, consistent with Eq. 7.221, thus obtaining the solution to the Langevin equation through the velocity time correlation function.

7.4.3 Brownian Motion

1. Langevin Theory: The forces acting on Brownian particles from the surrounding medium are divided into two parts: one is the average force exerted by fluid molecules on the Brownian particles (manifested as macroscopic viscous resistance); the other is the fluctuating force from

collisions of fluid molecules in the background of the average force.

When a Brownian particle moves with velocity v , it will collide with more fluid molecules in its forward direction, so on average, it will experience viscous resistance opposite to its velocity direction. When the velocity v is not large, the magnitude of the resistance is proportional to the magnitude of the particle's velocity. The viscous resistance can be expressed as $f = -\alpha v$, where α is the damping coefficient. If the Brownian particle is considered as a small sphere with radius a , and the fluid's viscosity coefficient is η , then (under small Reynolds numbers) the damping coefficient α is given by Stokes' law

$$\alpha = 6\pi a \eta \quad (7.209)$$

The fluctuating force $\mathbf{F}(t)$ comes from the irregular thermal motion of fluid molecules exerting a fluctuating force on the Brownian particle, equivalent to the net force from collisions of fluid molecules with a stationary Brownian particle, with random magnitude and direction, and its average value $\bar{\mathbf{F}} = 0$. If the system is in an external force field, the Brownian particle also experiences the external force \mathbf{F}_{ext} . Assuming the mass of the Brownian particle is m , its equation of motion is

$$m\ddot{r} = -\alpha\dot{r} + \mathbf{F}(t) + \mathbf{F}_{\text{ext}} \quad (7.210)$$

This is called the Langevin equation. The Brownian particle moves under the combined action of regular forces and fluctuating forces. Since the fluctuating force $\mathbf{F}(t)$ varies randomly with time t , the motion of particles under the action of fluctuating forces requires statistical treatment and can only be described probabilistically, i.e., only the average results of the motion of a large number of Brownian particles can be discussed. For simplicity, consider only the one-dimensional motion of a Brownian particle in the x direction on a horizontal plane, without an external force field, $\mathbf{F}_{\text{ext}} = 0$. In this case, the Langevin equation can be rewritten as

$$m\ddot{x} = -\alpha\dot{x} + X(t) \quad (7.211)$$

where $X(t)$ is the x component of the fluctuating force. Multiply both sides of the equation by x , considering

$$x\ddot{x} = \frac{1}{2} \frac{d^2}{dt^2} x^2 - \dot{x}^2, \quad x\dot{x} = \frac{1}{2} \frac{d}{dt} x^2 \quad (7.212)$$

we obtain

$$\frac{m}{2} \frac{d^2}{dt^2} x^2 - m\dot{x}^2 = -\frac{\alpha}{2} \frac{d}{dt} x^2 + xX(t) \quad (7.213)$$

Taking the average over a large number of Brownian particles, denoted by a bar over the physical quantity, we have

$$\frac{m}{2} \frac{d^2}{dt^2} \bar{x}^2 - m\bar{\dot{x}}^2 = -\frac{\alpha}{2} \frac{d}{dt} \bar{x}^2 + \bar{x}X(t) \quad (7.214)$$

where it has been considered that the order of averaging over particles and differentiating with respect to time can be exchanged. The fluctuating force $X(t)$ is independent of the particle position x , so

$$\bar{x}X(t) = \bar{x}\bar{X}(t) = 0 \quad (7.215)$$

According to the equipartition theorem Eq. 4.176, the average kinetic energy of the Brownian particle is

$$\frac{1}{2}m\bar{x}^2 = \frac{1}{2}kT \quad (7.216)$$

Substituting these results into Eq. 7.214 and rearranging, we obtain

$$\frac{d^2}{dt^2}\bar{x}^2 + \frac{\alpha}{m}\frac{d}{dt}\bar{x}^2 - \frac{2kT}{m} = 0 \quad (7.217)$$

This is a second-order non-homogeneous ordinary differential equation with constant coefficients for \bar{x}^2 , whose general solution is

$$\bar{x}^2 = \frac{2kT}{\alpha}t + C_1 e^{-\frac{\alpha}{m}t} + C_2 \quad (7.218)$$

C_1 and C_2 are integration constants, which can be determined by initial conditions. At $t = 0$, all Brownian particles are stationary at $x = 0$, i.e., $\bar{x}^2(0) = 0$, $\frac{d}{dt}\bar{x}^2(0) = 0$, then the solution to equation Eq. 7.217 is

$$\bar{x}^2 = \frac{2kT}{m\left(\frac{\alpha}{m}\right)^2} \left[\frac{\alpha}{m}t + \left(e^{-\frac{\alpha}{m}t} - 1 \right) \right] \quad (7.219)$$

If the time is very short, such that $\frac{\alpha}{m}t \ll 1$, then

$$\bar{x}^2 \simeq \frac{kT}{m}t^2 = \bar{v}^2 t^2 \quad (7.220)$$

indicating that within a very short time interval, the Brownian particle moves at an average speed $\bar{v} = \sqrt{\frac{kT}{m}}$.

If the time t is not very short, such that $\frac{\alpha}{m}t \gg 1$, then the term in parentheses in equation Eq. 7.219 can be ignored, and its solution is

$$\bar{x}^2 = \frac{2kT}{\alpha}t = 2Dt \quad (7.221)$$

where the proportionality coefficient D (which can be proven to be the diffusion coefficient of Brownian particles by Eq. 7.4.3)

$$D = \frac{kT}{\alpha} = \frac{kT}{6\pi a\eta} \quad (7.222)$$

indicating that \bar{x}^2 is proportional to time t , not t^2 . Now let's estimate the magnitude of $\frac{\alpha}{m}$, assuming the Brownian particle is a small sphere with radius a and density ρ , then

$$\frac{\alpha}{m} = \frac{9\eta}{2a^2\rho} \quad (7.223)$$

In Perrin's experiment, the density of Brownian particles is $\rho = 1.19 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$, the average radius a is $3.69 \times 10^{-7} \text{ m}$, and the fluid medium is water, with a viscosity coefficient $\eta = 1.14 \times 10^{-3} \text{ Pa} \cdot \text{s}$. Substituting these data into the above equation gives $\frac{\alpha}{m} = 3.2 \times 10^7 \text{ s}^{-1}$. Therefore, after a very short time, such as $t > 0.1 \text{ ms}$, the average value of the square of the Brownian particle's displacement can be expressed by Eq. 7.221.

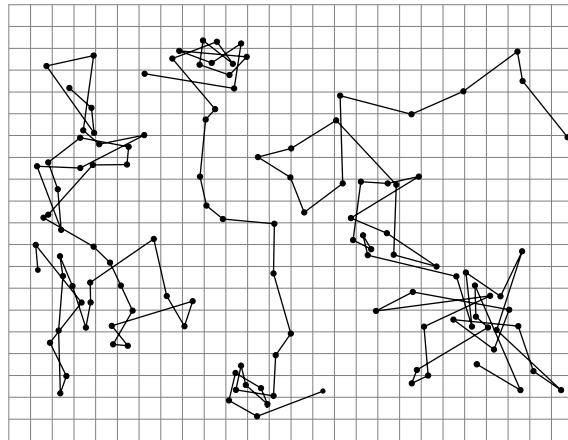


Fig. 65: Brownian motion of three particles in Perrin's experiment, with a point plotted every 30 seconds

2. Einstein-Smoluchowski Theory

Brownian motion is studied as a "random walk problem." The discussion is simplified to one-dimensional motion, assuming that at $t = 0$, the Brownian particle is at position $x(0) = 0$. It is assumed that each collision between fluid molecules and the Brownian particle causes the Brownian particle to move a small distance δ along the positive or negative direction of the x -axis, i.e., $\Delta x = \pm\delta$, with equal probability of moving in the positive and negative directions. On average, a collision occurs every τ^* time interval, and the collisions of the Brownian particle are uncorrelated. Under these conditions, the probability of the Brownian particle moving to position x at time t is sought. During time t , the total number of movements due to collisions is $n = \frac{t}{\tau^*}$, and the number of movements in the positive x direction is more than in the negative direction by $m = \frac{x}{\delta}$. Therefore, the number of movements in the positive x direction is $\frac{1}{2}(n + m)$, and in the negative x direction is $\frac{1}{2}(n - m)$. The probability of the Brownian particle moving to position x at time t is given by the binomial distribution

$$p_n(m) = \left(\frac{1}{2}\right)^n \frac{n!}{\left(\frac{n+m}{2}\right)! \left(\frac{n-m}{2}\right)!} \quad (7.224)$$

Since t and x are macroscopic quantities, while τ^* and δ are microscopic quantities, n and m are both integers much greater than 1, and n and m have the same parity. If n is odd, then m can only be odd; if n is even, then m can only be even. The interval of possible values for m is $\Delta m = 2$. From the binomial distribution, we obtain

$$\bar{m} = \sum_{m=-n}^n m p_n(m) = 0 \quad (7.225a)$$

$$\overline{m^2} = \sum_{m=-n}^n m^2 p_n(m) = n \quad (7.225b)$$

Therefore, after time t , the average displacement and the mean square displacement of the Brow-

nian particle are

$$\overline{x(t)} = \bar{m}\delta = 0 \quad (7.226a)$$

$$\overline{x^2(t)} = \overline{m^2}\delta^2 = n\delta^2 = \frac{\delta^2}{\tau^*}t \quad (7.226b)$$

$\overline{x^2(t)} \propto t$, consistent with the Langevin theory. Comparing this with Eq. 7.221, we obtain the diffusion coefficient

$$D = \frac{1}{2} \frac{\delta^2}{\tau^*} \quad (7.227)$$

It can be proven that when t is very large, the binomial distribution transitions to a Gaussian distribution. When n is a very large number, $\ln n!$ can be approximated using Stirling's approximation Eq. 4.6

$$\ln n! \simeq n(\ln n - 1) + \frac{1}{2} \ln(2\pi n), \quad n \gg 1 \quad (7.228)$$

Taking the logarithm of both sides of Eq. 7.224, we get (the second step simplifies using $n \gg m$)

$$\begin{aligned} \ln p_n(m) &\simeq \left(n + \frac{1}{2}\right) \ln n - \frac{1}{2}(n+m+1) \ln \left[\frac{1}{2}(n+m)\right] - \frac{1}{2}(n-m+1) \ln \left[\frac{1}{2}(n-m)\right] - n \ln 2 - \frac{1}{2} \ln(2\pi) \\ &\simeq \ln \frac{2}{\sqrt{2\pi n}} - \frac{m^2}{2n} \end{aligned} \quad (7.229)$$

Thus, we obtain

$$p_n(m) = \sqrt{\frac{2}{\pi n}} e^{-\frac{m^2}{2n}} \quad (7.230)$$

If x and t are taken as continuous variables, and noting that $\Delta m = 2$, the above expression can be rewritten in the form of a Gaussian distribution function

$$p(x)dx = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) dx \quad (7.231)$$

indicating the probability that at time t , the Brownian particle is within the range $x \sim x + dx$, where the coefficient D is given by Eq. 7.4.3. The mean square value of x^2 is obtained as

$$\overline{x^2} = \int_{-\infty}^{\infty} x^2 p(x)dx = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} x^2 e^{-\frac{x^2}{4Dt}} dx = 2Dt \quad (7.232)$$

consistent with the Langevin theory's Eq. 7.221, where the diffusion coefficient D of the Brownian particle in the fluid medium satisfies Eq. 7.4.3, linking the macroscopic diffusion coefficient D with the microscopic free path of the particle. Einstein considered Brownian motion as a diffusion phenomenon of Brownian particles in a fluid medium.

3. **Diffusion Theory**: Assume the number density of Brownian particles in the fluid is $n(\mathbf{r}, t)$, then the flux density of Brownian particles is $j(\mathbf{r}, t) = n(\mathbf{r}, t) \cdot v(\mathbf{r}, t)$. When the particle number density n is non-uniform, particles will diffuse in the fluid, and the macroscopic law of diffusion is given by Fick's law Eq. 7.18

$$\mathbf{j}(\mathbf{r}, t) = -D \nabla n(\mathbf{r}, t) \quad (7.233)$$

where D is the diffusion coefficient. The continuity equation of the fluid is

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) + \nabla \cdot j(\mathbf{r}, t) = 0 \quad (7.234)$$

Combining the above two equations gives the diffusion equation for particle density $n(\mathbf{r}, t)$ Eq. 7.20

$$\frac{\partial}{\partial t}n(\mathbf{r}, t) = D\nabla^2 n(\mathbf{r}, t) \quad (7.235)$$

For one-dimensional Brownian motion, the diffusion equation simplifies to

$$\frac{\partial}{\partial t}n(x, t) = D\frac{\partial^2}{\partial x^2}n(x, t) \quad (7.236)$$

Assume that at $t = 0$, the Brownian particle is at $x = 0$, and the number of Brownian particles per unit cross-sectional area is n_0 , so n satisfies the initial condition

$$n(x, 0) = n_0\delta(x) \quad (7.237)$$

Using the Fourier transform method to solve the diffusion equation Eq. 7.236, let

$$g(\xi, t) = \int_{-\infty}^{\infty} n(x, t)e^{ix\xi} dx \quad (7.238)$$

The inverse transform is

$$n(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} g(\xi, t)e^{-ix\xi} d\xi \quad (7.239)$$

Multiplying both sides of the diffusion equation Eq. 7.236 by $e^{ix\xi}$ and integrating over x , we get

$$\int_{-\infty}^{\infty} \frac{\partial}{\partial t}n(x, t)e^{ix\xi} dx = \frac{\partial}{\partial t}g(\xi, t) \quad (7.240a)$$

$$\int_{-\infty}^{\infty} \frac{\partial^2}{\partial x^2}n(x, t)e^{ix\xi} dx = -\xi^2 g(\xi, t) \quad (7.240b)$$

Equating both sides gives

$$\frac{\partial}{\partial t}g(\xi, t) = -D\xi^2 g(\xi, t) \quad (7.241)$$

The solution to the equation is

$$g(\xi, t) = g(\xi, 0)e^{-D\xi^2 t} \quad (7.242)$$

where $g(\xi, 0)$ is the Fourier transform of $n(x, 0)$

$$g(\xi, 0) = \int_{-\infty}^{\infty} n(x, 0)e^{ix\xi} dx = n_0 \quad (7.243)$$

Substituting into the inverse transform equation Eq. 7.239, we get

$$n(x, t) = \frac{n_0}{2\pi} \int_{-\infty}^{\infty} e^{-D\xi^2 t - ix\xi} d\xi = \frac{n_0}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}} \quad (7.244)$$

where the integral formula

$$\int_{-\infty}^{\infty} e^{-ax^2 + bx} dx = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}}, \quad a > 0 \quad (7.245)$$

is used. Eq. 7.244 indicates that the number density n of Brownian particles is distributed according to a Gaussian distribution function with respect to position x and is time-dependent. The

average displacement and mean square displacement of Brownian particles can be obtained as

$$\bar{x} = \frac{1}{n_0} \int_{-\infty}^{\infty} xn(x, t) dx = 0 \quad (7.246a)$$

$$\bar{x^2} = \frac{1}{n_0} \int_{-\infty}^{\infty} x^2 n(x, t) dx = 2Dt \quad (7.246b)$$

consistent with the Langevin theory's Eq. 7.221 and Einstein's theory Eq. 7.232, thus proving that the motion of Brownian particles under the influence of fluctuating forces is a diffusion phenomenon. If the initial distribution of Brownian particles is non-uniform, the diffusion of particles will lead them to a uniform distribution. Therefore, the theory of Brownian motion provides a theoretical basis for how a system transitions from a non-equilibrium state to an equilibrium state.

7.4.4 Fokker-Planck Equation

The following proves that the probability distribution function of particle displacement satisfies the diffusion equation. The diffusion equation was initially derived by Einstein and later generalized by Fokker-Planck, hence it is called the Fokker-Planck equation. The Fokker-Planck equation is an equation for the time evolution of the probability distribution function, essentially a non-equilibrium problem.

Discuss the change in the probability distribution function in a Markov process (where the probability of the system at time t depends only on the state of the system at time t and the immediately preceding time). For such a process, most of the memory and influence during the evolution of the system will be ignored. We derive the Fokker-Planck equation using Brownian motion as an example, although its application is not limited to Brownian motion.

Discuss the one-dimensional motion of Brownian particles without external forces. Since the motion of particles is random, assume that at time τ , the probability of the particle being within the range $x \sim x + dx$ is $p(x, \tau)dx$. Assume this probability depends only on the position x_0 of the particle at the previous time τ_0 , and not on any earlier history. Therefore, the motion of Brownian particles can be considered a Markov process. The relationship between the probability distribution function $p(x, \tau)dx$ and the parameters τ , x , τ_0 , and x_0 can be expressed in the form of conditional probability, i.e.

$$p(x, \tau)dx = p(x, \tau | x_0, \tau_0)dx \quad (7.247)$$

The above equation represents the probability of a particle being at position x_0 at time τ_0 and within the range $x \sim x + dx$ at time τ . The conditional probability can be expressed as

$$p(x, \tau | x_0, \tau_0) = \int_{-\infty}^{\infty} p(x, \tau | x', \tau') p(x', \tau' | x_0, \tau_0) dx' \quad (7.248)$$

The characteristic of a Markov process is that $p(x, \tau | x', \tau')$ depends only on x' and τ' , and not on x_0 and τ_0 . Since p depends only on the time interval $t = \tau - \tau_0$, and not on the starting point of measurement τ_0 , it can be rewritten as

$$p(x, \tau | x_0, \tau_0)dx = p(x, t | x_0)dx \quad (7.249)$$

indicating the probability of a particle initially at position x_0 moving to within the range $x \sim x + dx$ after time t .

The probability distribution function satisfies the following conditions:

$$p(x, \tau | x_0, \tau_0) \geq 0 \quad (7.250a)$$

$$\int_{-\infty}^{\infty} p(x, \tau | x_0, \tau_0) dx = 1 \quad (7.250b)$$

$$\lim_{t \rightarrow 0} p(x, t | x_0) = \delta(x - x_0) \quad (7.250c)$$

Besides the probability distribution function for position x , we can also consider the following two probability distribution functions:

$$p(u, \tau | u_0, \tau_0) du = p(u, t | u_0) du \quad (7.251)$$

indicating the probability of a particle having velocity u_0 at time τ_0 and velocity within the range $u \sim u + du$ at time τ . And

$$p(x, u, \tau | x_0, u_0, \tau_0) dx du = p(x, u, t | x_0, u_0) dx du \quad (7.252)$$

indicating the probability of a particle being at position x_0 and velocity u_0 at time τ_0 , and within the range $x \sim x + dx$ and velocity $u \sim u + du$ at time τ .

At time t , the number of particles within the range $x \sim x + dx$ per unit cross-sectional area is $n(x, t)dx$. For a Markov process, $n(x, t)$ equals the total number of particles that were at x_0 at time t_0 and transitioned to x after time $\tau = t - t_0$, i.e.,

$$n(x, t) = \int_{-\infty}^{\infty} p(x, t | x_0, t_0) n(x_0, t_0) dx_0 \quad (7.253)$$

Next, we discuss the change in the probability distribution function $p(x, t | x_0)$ over time. At time t , the probability of being within the range $x \sim x + dx$ is $p(x, t | x_0) dx$. After an arbitrary small time interval Δt , the increment in probability is $\frac{\partial p}{\partial t} \Delta t dx$. The increase in p is caused by two factors: one is the transition of particles from within the range $x \sim x + dx$ at time t to within the range $x_1 \sim x_1 + dx_1$ during the time interval Δt , with probability $p(x_1, \Delta t | x) dx_1$, which decreases the probability of being within $x \sim x + dx$; the other factor is the transition of particles from within the range $x_1 \sim x_1 + dx_1$ at time t to within the range $x \sim x + dx$ during the time interval Δt , with probability $p(x, \Delta t | x_1) dx$, which increases the probability of being within $x \sim x + dx$. Therefore, the increment in probability during the time interval Δt is

$$\frac{\partial p}{\partial t} \Delta t dx = - \int_{x_1} p(x, t | x_0) p(x_1, \Delta t | x) dx dx_1 + \int_{x_1} p(x_1, t | x_0) p(x, \Delta t | x_1) dx dx_1 \quad (7.254)$$

The first integral represents all transitions from position x to another position x_1 during the time interval $t \sim t + \Delta t$, which decreases the probability at x ; similarly, the second integral represents all transitions from position x_1 to position x during the time interval $t \sim t + \Delta t$, which increases the probability at x . The net increment in probability is the difference between these two integrals.

The derivation of this equation does not involve the dynamics of the transition process, nor does it involve whether the system follows quantum or classical mechanics, so the conclusion is general. The specific form of the probability distribution function $p(x, t | x_0)$ depends on the system's dynamics. The first integral is

$$\int_{x_1} p(x, t | x_0) p(x_1, \Delta t | x) dx dx_1 = p(x, t | x_0) dx \quad (7.255)$$

In the second integral, let $x_1 = x - \xi$, then

$$\int_{x_1} p(x_1, t | x_0) p(x, \Delta t | x_1) dx dx_1 = dx \int_{-\infty}^{\infty} p(x - \xi, t | x_0) p(x, \Delta t | x - \xi) d\xi \quad (7.256)$$

Substituting the above two equations into Eq. 7.254, we get

$$\frac{\partial p}{\partial t} \Delta t = -p(x, t | x_0) + \int_{-\infty}^{\infty} p(x - \xi, t | x_0) p(x, \Delta t | x - \xi) d\xi \quad (7.257)$$

Typically, the probability distribution function $p(x, t | x_0)$ rapidly decreases with increasing $|\xi| = |x - x_0|$. For example, in Brownian motion, the mass of a Brownian particle is about 10^6 times that of a molecule. After time Δt , the change in position $|\xi|$ of the Brownian particle due to the residual force from collisions with fluid molecules is very small. Therefore, the probability distribution function $p(x, \Delta t | x - \xi)$ has significant values only when $|\xi|$ is small, and it rapidly decays to zero as $|\xi|$ increases. In other words, the probability distribution function $p(x, \Delta t | x - \xi)$ has a sharp peak near $\xi = 0$ and rapidly decays to zero with increasing $|\xi|$. Therefore, the integrand $p(x - \xi, t | x_0) p(x, \Delta t | x - \xi)$ in Eq. 7.257 can be expanded into a Taylor series in ξ around $\xi = 0$.

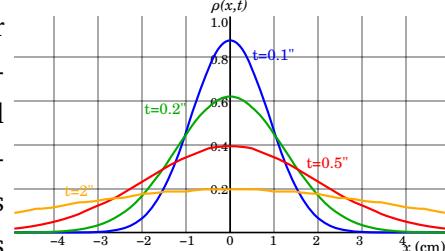


Fig. 66: Characteristic bell curve of Brownian particle diffusion

$$p(x - \xi, t | x_0) p(x, \Delta t | x - \xi) = p(x, t | x_0) p(x + \xi, \Delta t | x) + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} [p(x, t | x_0) p(x + \xi, \Delta t | x)] \xi^n \quad (7.258)$$

Substituting the above equation into Eq. 7.257, we get

$$\begin{aligned} \frac{\partial p}{\partial t} \Delta t &= -p(x, t | x_0) + p(x, t | x_0) \int_{-\infty}^{\infty} p(x + \xi, \Delta t | x) d\xi + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} \left[p(x, t | x_0) \int_{-\infty}^{\infty} \xi^n p(x + \xi, \Delta t | x) d\xi \right] \\ &= \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} \left[p(x, t | x_0) \int_{-\infty}^{\infty} \xi^n p(x + \xi, \Delta t | x) d\xi \right] \end{aligned} \quad (7.259)$$

// ... existing code ... where the first term and the second term cancel each other out using Eq. 7.250b. As $\Delta t \rightarrow 0$, the terms with $n > 2$ in the summation will tend to zero faster than

Δt . Therefore, within an infinitesimal time interval Δt , only the terms with $n = 1, 2$ need to be retained in the summation.

$$\frac{\partial p}{\partial t} = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \sum_{n=1}^2 \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} \left[p(x, t | x_0) \int_{-\infty}^{\infty} \xi^n p(x + \xi, \Delta t | x) d\xi \right] \quad (7.260)$$

Define

$$a(x, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{-\infty}^{\infty} \Delta x p(x + \Delta x, \Delta t | x) d(\Delta x) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \overline{[\Delta x(\Delta t)]} \quad (7.261a)$$

$$b(x, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{-\infty}^{\infty} (\Delta x)^2 p(x + \Delta x, \Delta t | x) d(\Delta x) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \overline{[\Delta x(\Delta t)]^2} \quad (7.261b)$$

where $\Delta x(\Delta t) = x(\Delta t) - x(0)$. Then Eq. 7.260 can be simplified to

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x} (ap) - \frac{1}{2} \frac{\partial^2}{\partial x^2} (bp) = 0 \quad (7.262)$$

This is the Fokker–Planck equation, reflecting the time evolution of the probability distribution function, which is of significant importance in the study of Brownian motion and fluctuation theory. If the variable x in Eq. 7.260 is replaced with velocity $v = \dot{x}$, the differential equation satisfied by the probability distribution function $p(v, t | v_0)$ at time t can be obtained.

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial v} (Ap) - \frac{1}{2} \frac{\partial^2}{\partial v^2} (Bp) = 0 \quad (7.263)$$

where

$$A(x, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{-\infty}^{\infty} \Delta v p(v + \Delta v, \Delta t v | v) d(\Delta v) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \overline{[\Delta v(\Delta t)]} \quad (7.264a)$$

$$B(x, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{-\infty}^{\infty} (\Delta v)^2 p(v + \Delta v, \Delta t | v) d(\Delta v) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \overline{[\Delta v(\Delta t)]^2} \quad (7.264b)$$

where $\Delta v = v(\Delta t) - v(0)$, Eq. 7.263 is the Fokker–Planck equation in velocity space. The equation satisfied by the probability distribution function $p(x, v, t | x_0, v_0)$ with position x and velocity v as variables is

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x} (ap) + \frac{\partial}{\partial v} (Ap) - \frac{1}{2} \frac{\partial^2}{\partial x^2} (bp) - \frac{1}{2} \frac{\partial^2}{\partial v^2} (Bp) - \frac{\partial^2}{\partial x \partial v} (Cp) = 0 \quad (7.265)$$

where

$$a(x, v, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \iint \Delta x p(x + \Delta x, v + \Delta v, \Delta t | x, v) d(\Delta x) d(\Delta v) \quad (7.266a)$$

$$b(x, v, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \iint (\Delta x)^2 p(x + \Delta x, v + \Delta v, \Delta t | x, v) d(\Delta x) d(\Delta v) \quad (7.266b)$$

$$A(x, v, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \iint \Delta v p(x + \Delta x, v + \Delta v, \Delta t | x, v) d(\Delta x) d(\Delta v) \quad (7.266c)$$

$$B(x, v, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \iint (\Delta v)^2 p(x + \Delta x, v + \Delta v, \Delta t | x, v) d(\Delta x) d(\Delta v) \quad (7.266d)$$

$$C(x, v, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \iint \Delta x \Delta v p(x + \Delta x, v + \Delta v, \Delta t | x, v) d(\Delta x) d(\Delta v) \quad (7.266e)$$

To obtain the solution p of the differential equation, the specific forms of quantities such as $\overline{\Delta x}$, $\overline{(\Delta x)^2}$, $\overline{\Delta v}$, $\overline{(\Delta v)^2}$, $\overline{\Delta x \Delta v}$, and $\overline{(\Delta x)^2}$ must be known.

Next, we will solve the Fokker - Planck equations Eq. 7.262 and Eq. 7.263 for the motion of Brownian particles without external forces.

(1) Solution of the Fokker - Planck equation in momentum space Eq. 7.262: Using Eq. 7.246, $\overline{\Delta x} = 0$, $\overline{(\Delta x)^2} = 2D\Delta t$, with diffusion coefficient $D = \frac{kT}{\alpha} = \frac{kT}{\gamma m}$, we get $a = 0$, $b = 2D$. Substituting a and b into Eq. 7.262, we obtain the equation satisfied by the probability distribution function

$$\frac{\partial p}{\partial t} - D \frac{\partial^2 p}{\partial x^2} = 0 \quad (7.267)$$

From Eq. 7.253, the equation satisfied by the particle number density $n(x, t)$ is

$$\frac{\partial n}{\partial t} - D \frac{\partial^2 n}{\partial x^2} = 0 \quad (7.268)$$

This is Einstein's diffusion equation. The initial condition for equation Eq. 7.267 is given by Eq. 7.250c, and its solution is

$$p(x, t | x_0) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{(x-x_0)^2}{4Dt}} \quad (7.269)$$

If at $t = 0$ all particles are at x_0 , the initial condition for the particle number density is $n(x, 0) = n_0 \delta(x - x_0)$. The particle number density is

$$n(x, t) = \int p(x, t | \xi) n(\xi, 0) d\xi = \frac{n_0}{\sqrt{4\pi Dt}} e^{-\frac{(x-x_0)^2}{4Dt}} \quad (7.270)$$

From the probability distribution function Eq. 7.269, the average displacement and the mean square displacement are

$$\bar{x} = x_0, \quad \overline{x^2} = x_0^2 + 2Dt \quad (7.271)$$

(2) Solution of the Fokker - Planck equation in velocity space Eq. 7.263: From Eq. 7.201 and Eq. 7.194, the average value of velocity and the mean square deviation of velocity are given as $\overline{v(t)} = v_0 e^{-\gamma t}$ and $\overline{[\Delta v(t)]^2} = \frac{a}{2\gamma} (1 - e^{-2\gamma t})$. When t is a small quantity Δt , we have

$$\overline{\Delta v} = \overline{[v(\Delta t) - v_0]} = -\gamma v_0 \Delta t, \quad \overline{(\Delta v)^2} = a \Delta t = 2D\gamma^2 \Delta t \quad (7.272)$$

Comparing the above with Eq. 7.264, we get $A = -\gamma v$, $B = 2D\gamma^2$. Substituting into Eq. 7.263, we get

$$\frac{\partial p}{\partial t} - \gamma \frac{\partial}{\partial v} (vp) - D\gamma^2 \frac{\partial^2 p}{\partial v^2} = 0 \quad (7.273)$$

Perform the following function transformation $f = pe^{-\gamma t}$, then the above equation transforms into a differential equation for f

$$\frac{\partial f}{\partial t} - \gamma v \frac{\partial f}{\partial v} - D\gamma^2 \frac{\partial^2 f}{\partial v^2} = 0 \quad (7.274)$$

Perform a variable transformation: $\xi = ve^{xt}$, $\tau = D\gamma^2 \int_0^t e^{2xt} dt = \frac{D\gamma}{2} (e^{2xt} - 1)$, then the equation for $f(\xi, \tau)$ simplifies to

$$\frac{\partial f}{\partial \tau} - \frac{\partial^2 f}{\partial \xi^2} = 0 \quad (7.275)$$

This is a diffusion equation with diffusion coefficient $D = 1$. The initial condition for $f(\xi, \tau)$ can be obtained from Eq. 7.250c

$$f(\xi, 0) = p(v, 0 | v_0) = \delta(v - v_0) = \delta(\xi - \xi_0) \quad (7.276)$$

where $\xi_0 = v_0$. The solution to the diffusion equation is

$$f(\xi, \tau) = \frac{1}{\sqrt{4\pi\tau}} e^{-\frac{(\xi-\xi_0)^2}{4\tau}} \quad (7.277)$$

Transforming back to the original variables, the probability distribution function in velocity space is

$$p(v, t | v_0) = \frac{1}{\sqrt{2\pi D\gamma(1-e^{-2\gamma})}} \exp\left\{-\frac{(v-v_0e^{-\gamma t})^2}{2D\gamma(1-e^{-2\gamma})}\right\} \quad (7.278)$$

As $t \rightarrow \infty$, we have

$$\lim_{t \rightarrow \infty} p(v, t | v_0) = \frac{1}{\sqrt{2\pi D\gamma}} \exp\left(-\frac{v^2}{2D\gamma}\right) \quad (7.279)$$

Substituting $D = \frac{kT}{\gamma m}$, we obtain the one-dimensional Maxwell velocity distribution, returning to Eq. 4.162

$$f(v) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv^2}{2kT}\right) \quad (7.280)$$

This reflects the velocity distribution function in equilibrium.

AppendixA Exam Topics

1. Special forms and relationships of thermodynamic characteristic functions
2. Rules for partial derivatives and simplification
3. Connection between physical concepts and their physical and mathematical expressions
4. Integration and series operations of partition functions
5. Interdisciplinary knowledge transfer and integration

$$S = \ln \Omega \quad (\text{A.1})$$

AppendixB Mathematical and Physical Knowledge

class	dimension	Symmetry	α	β	γ	δ	ν	η
3-state Potts	2	S_3	$\frac{1}{3}$	$\frac{1}{9}$	$\frac{13}{9}$	14	$\frac{5}{6}$	$\frac{4}{15}$
Ashkin - Teller (4-state Potts)	2	S_4	$\frac{2}{3}$	$\frac{1}{12}$	$\frac{7}{6}$	15	$\frac{2}{3}$	$\frac{1}{4}$
Ordinary percolation	1	1	1	0	1	∞	1	$\frac{1}{5}$
	2	1	$-\frac{2}{3}$	$\frac{5}{36}$	$\frac{43}{18}$	$\frac{91}{5}$	$\frac{4}{3}$	$\frac{24}{24}$
	3	1	-0.625(3)	0.4181(8)	1.793(3)	5.29(6)	0.87619(12)	0.46(8) or 0.59(9)
	4	1	-0.756(40)	0.657(9)	1.422(16)	3.9 or 3.198(6)	0.689(10)	-0.0944(28)
	5	1	≈ -0.85	0.830(10)	1.185(5)	3.0	0.569(5)	-0.075(20) or -0.0565
	6 ⁺	1	-1	1	1	2	$\frac{1}{2}$	0
Directed percolation	1	1	0.159464(6)	0.276486(8)	2.277730(5)	0.159464(6)	1.096854(4)	0.313686(8)
	2	1	0.451	0.536(3)	1.60	0.451	0.733(8)	0.230
	3	1	0.73	0.813(9)	1.25	0.73	0.584(5)	0.12
	4 ⁺	1	-1	1	1	2	$\frac{1}{2}$	0
Conserved directed percolation (Manna, or "local linear interface")	1	1		0.28(1)		0.14(1)	1.11(2) ^[1]	0.34(2) ^[1]
	2	1		0.64(1)	1.59(3)	0.50(5)	1.29(8)	0.29(5)
	3	1		0.84(2)	1.23(4)	0.90(3)	1.12(8)	0.16(5)
	4 ⁺	1		1	1	1	1	0
Protected percolation	2	1		$5/41^{[2]}$	$86/41^{[2]}$			
	3	1		0.28871(15) ^[2]	1.3066(19) ^[2]			
Ising	2	\mathbb{Z}_2	0	$\frac{1}{8}$	$\frac{7}{4}$	15	1	$\frac{1}{4}$
	3	\mathbb{Z}_2	0.11008(1)	0.326419(3)	1.237075(10)	4.78984(1)	0.629971(4)	0.036298(2)
XY	3	$O(2)$	-0.01526(30)	0.34869(7)	1.3179(2)	4.77937(25)	0.67175(10)	0.038176(44)
Heisenberg	3	$O(3)$	-0.12(1)	0.366(2)	1.395(5)		0.707(3)	0.035(2)
Mean field	all	any	0	$\frac{1}{2}$	1	3	$\frac{1}{2}$	0
Molecular beam Epitaxy								
Gaussian Field								

Table 7: Universal Critical Exponents

B.1 Polylogarithm Functions and Chemical Potential

In thermodynamics, the extensive function of energy can be written in the following form, where ω_s is the spin degeneracy

$$\bar{Q} = \omega_s \sum_i Q(\varepsilon_i) n(\varepsilon_i) = \omega_s \int_0^\infty Q(\varepsilon) g(\varepsilon) n(\varepsilon) d\varepsilon \quad (\text{B.1})$$

which involves an integral

$$\int_0^\infty \varepsilon^n n(\varepsilon) d\varepsilon = \int_0^\infty \frac{\varepsilon^n d\varepsilon}{e^{(\varepsilon-\mu)/kT} + a} = (kT)^{n+1} \int_0^\infty \frac{x^n dx}{e^x z^{-1} + a} \quad (\text{B.2})$$

where the fugacity is $z = \exp(\beta\mu)$, $a = 0, \pm 1$, the integral can be transformed into the form of Gamma functions and polylogarithm functions

$$\begin{aligned} \int_0^\infty \frac{x^{s-1}}{e^x z^{-1} + 1} dx &= -\Gamma(s) \text{Li}_s(-z) \\ \int_0^\infty \frac{x^{s-1}}{e^x z^{-1} - 1} dx &= \Gamma(s) \text{Li}_s(z) \\ \int_0^\infty \frac{x^{s-1}}{e^x z^{-1}} dx &= \Gamma(s) z \end{aligned} \quad (\text{B.3})$$

Substituting the specific form of $n(\varepsilon)$, we get

$$\begin{aligned} \int_0^\infty \frac{\varepsilon^n d\varepsilon}{e^{(\varepsilon-\mu)/kT} + 1} &= -(kT)^{n+1} \Gamma(n+1) \text{Li}_{n+1}(-e^{\mu/kT}) \\ \int_0^\infty \frac{\varepsilon^n d\varepsilon}{e^{(\varepsilon-\mu)/kT} - 1} &= +(kT)^{n+1} \Gamma(n+1) \text{Li}_{n+1}(+e^{\mu/kT}) \\ \int_0^\infty \frac{\varepsilon^n d\varepsilon}{e^{(\varepsilon-\mu)/kT}} &= +(kT)^{n+1} \Gamma(n+1) e^{\mu/kT} \end{aligned} \quad (\text{B.4})$$

For the quantum wave vector k_q , the corresponding quantum energy is

$$\varepsilon_q = \hbar^2 k_q^2 / 2m \quad (\text{B.5})$$

In one, two, and three dimensions, the quantum energy is

$$\begin{aligned} \varepsilon_q &= \frac{\hbar^2}{2m} \left(\frac{\pi}{\omega_s} \frac{N}{L} \right)^2 \quad 1d \\ &= \frac{\hbar^2}{2m} \left(\frac{4\pi}{\omega_s} \frac{N}{A} \right)^{2/2} \quad 2d \\ &= \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{\omega_s} \frac{N}{V} \right)^{2/3} \quad 3d \end{aligned} \quad (\text{B.6})$$

The density of states in one, two, and three dimensions is

$$\begin{aligned} g(\varepsilon) &= \frac{1}{2} \frac{N}{\omega_s} \frac{1}{(\varepsilon \varepsilon_q)^{1/2}} \quad 1d \\ &= \frac{N}{\omega_s} \frac{1}{\varepsilon_q} \quad 2d \\ &= \frac{3}{2} \frac{N}{\omega_s} \frac{\varepsilon^{1/2}}{\varepsilon_q^{3/2}} \quad 3d \end{aligned} \quad (\text{B.7})$$

We integrate the density of states to get the relationship with dimension d

$$g(\varepsilon) = \frac{d}{2} \frac{N}{\omega_s} \varepsilon^{(d-2)/2} / \varepsilon_q^{d/2} \quad (\text{B.8})$$

Integrating the following equation gives the total number of particles in the system

$$N = \omega_s \int_0^\infty g(\varepsilon) n(\varepsilon) d\varepsilon \quad (\text{B.9})$$

We obtain the expression of quantum energy in terms of chemical potential and temperature

$$\varepsilon_q^{d/2} = \frac{d}{2} \int_0^\infty \varepsilon^{(d-2)/2} n(\varepsilon) d\varepsilon \quad (\text{B.10})$$

The specific expression is given by

$$\begin{aligned} \varepsilon_q^{d/2} &= (kT)^{d/2} \Gamma(1 + d/2) e^{\mu/kT} && \text{Maxwell} \\ &= -(kT)^{d/2} \Gamma(1 + d/2) \text{Li}_{d/2}(-e^{\mu/kT}) && \text{Fermi} \\ &= (kT)^{d/2} \Gamma(1 + d/2) \text{Li}_{d/2}(e^{\mu/kT}) && \text{Bose} \end{aligned} \quad (\text{B.11})$$

Define the reduced chemical potential and reduced temperature

$$\mu^* = \mu/\varepsilon_q, \quad \tau = kT/\varepsilon_q \quad (\text{B.12})$$

The fugacity is re-expressed as

$$z(\tau) = e^{\mu^*(\tau)/\tau} \quad (\text{B.13})$$

Equation Eq. B.11 becomes

$$\begin{aligned} \tau^{-d/2} &= \Gamma(1 + d/2) z(\tau) && \text{Maxwell} \\ &= -\Gamma(1 + d/2) \text{Li}_{d/2}(-z(\tau)) && \text{Fermi} \\ &= \Gamma(1 + d/2) \text{Li}_{d/2}(z(\tau)) && \text{Bose.} \end{aligned} \quad (\text{B.14})$$

Solving for the reduced chemical potential, we get

$$\mu^*(\tau) = \tau \ln \left\{ \frac{1}{\Gamma(1 + d/2)} \tau^{-d/2} \right\} \quad (\text{B.15a})$$

$$= \tau \ln \left\{ -\text{Li}_{d/2}^{-1} \left[\frac{-1}{\Gamma(1 + d/2)} \tau^{-d/2} \right] \right\} \quad (\text{B.15b})$$

$$= \tau \ln \left\{ +\text{Li}_{d/2}^{-1} \left[\frac{1}{\Gamma(1 + d/2)} \tau^{-d/2} \right] \right\} \quad (\text{B.15c})$$

We discuss the one-dimensional case as an example, observing the change in chemical potential for these three cases, taking $d = 1$, Maxwellon satisfies

$$\begin{aligned} \mu_{M1}^*(\tau) &= \tau \log \left(\frac{2}{\sqrt{\pi}} \tau^{-1/2} \right) \\ z_{M1}(\tau) &= \frac{2}{\sqrt{\pi}} \tau^{-1/2} \end{aligned} \quad (\text{B.16})$$

Fermion satisfies

$$\begin{aligned}\mu_{F1}^*(\tau) &= \tau \ln \left\{ -\text{Li}_{1/2}^{-1} \left[-\frac{2}{\sqrt{\pi}} \tau^{-1/2} \right] \right\} \\ z_{F1}(\tau) &= -\text{Li}_{1/2}^{-1} \left[-\frac{2}{\sqrt{\pi}} \tau^{-1/2} \right]\end{aligned}\quad (\text{B.17})$$

Low-temperature expansion of chemical potential

$$\mu_{F1}^*(\tau) = 1 + \frac{\pi^2}{12} \tau^2 + \frac{\pi^4}{36} \tau^4 + \frac{7\pi^6}{144} \tau^6 + \dots \quad (\text{B.18})$$

High-temperature expansion of chemical potential

$$\mu_{F1}^*(\tau) = \tau \log \left(\frac{2}{\sqrt{\pi}} \tau^{-1/2} \right) + \sqrt{\frac{2}{\pi}} \tau^{1/2} + \frac{(9 - 4\sqrt{3})}{3\pi} + \frac{4(5\sqrt{2} - 4\sqrt{6} + 3)}{3\pi^{3/2}} \frac{1}{\tau^{1/2}} - \frac{(12\sqrt{2} - 48\sqrt{3} + 71)}{3\pi^2} \frac{1}{\tau} + \dots \quad (\text{B.19})$$

Fugacity can also be expanded at low temperatures, yielding $\tau \rightarrow 0$, $z_{F1}(\tau) \sim e^{1/\tau}$

$$z_{F1}(\tau) = e^{1/\tau} \left\{ 1 + \frac{\pi^2}{12} \tau + \frac{\pi^4}{288} \tau^2 + \frac{(288\pi^4 + \pi^6)}{10368} \tau^3 + \dots \right\} \quad (\text{B.20})$$

High-temperature expansion of fugacity, the first term is the Maxwell fugacity

$$z_{F1}(\tau) = \frac{2}{\sqrt{\pi}} \frac{1}{\tau^{1/2}} + \frac{2\sqrt{2}}{\pi} \frac{1}{\tau} + \frac{8(3 - \sqrt{3})}{3\pi^{3/2}} \frac{1}{\tau^{3/2}} + \frac{4(15\sqrt{2} - 10\sqrt{6} + 6)}{3\pi^2} \frac{1}{\tau^2} + \dots \quad (\text{B.21})$$

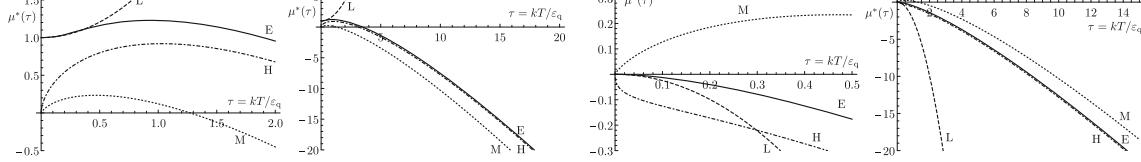


Fig. 67: One-dimensional Fermi/Bose chemical potential, E represents the exact solution, L, H, M represent low-temperature, high-temperature, Maxwell chemical potential

Boson satisfies

$$\begin{aligned}\mu_{B1}^*(\tau) &= \tau \ln \left\{ \text{Li}_{1/2}^{-1} \left[\frac{2}{\sqrt{\pi}} \tau^{-1/2} \right] \right\}, \\ z_{B1}(\tau) &= \text{Li}_{1/2}^{-1} \left[\frac{2}{\sqrt{\pi}} \tau^{-1/2} \right].\end{aligned}\quad (\text{B.22})$$

Low-temperature expansion of chemical potential

$$\mu_{B1}^*(\tau) = -\frac{1}{4}\pi^2 \tau^2 - \frac{1}{4}\pi^{5/2} \zeta \left(\frac{1}{2} \right) \tau^{5/2} - \frac{3}{16} \zeta \left(\frac{1}{2} \right)^2 \pi^3 \tau^3 + \frac{1}{16} \pi^{7/2} \left(\pi \zeta \left(-\frac{1}{2} \right) - 2\zeta \left(\frac{1}{2} \right)^3 \right) \tau^{7/2} + \dots \quad (\text{B.23})$$

High-temperature expansion of chemical potential

$$\mu_{B1}^*(\tau) = \tau \log \left(\frac{2}{\sqrt{\pi}} \tau^{-1/2} \right) - \sqrt{\frac{2}{\pi}} \tau^{1/2} + \frac{(9 - 4\sqrt{3})}{3\pi} - \frac{4(5\sqrt{2} - 4\sqrt{6} + 3)}{3\pi^{3/2}} \frac{1}{\tau^{1/2}} - \frac{(12\sqrt{2} - 48\sqrt{3} + 71)}{3\pi^2} \frac{1}{\tau} + \dots \quad (\text{B.24})$$

where the first term is the Maxwell chemical potential.

Low-temperature expansion of fugacity

$$z_{\text{B}1}(\tau) = 1 - \frac{\pi^2}{4}\tau - \frac{\pi^{5/2}}{4}\zeta\left(\frac{1}{2}\right)\tau^{3/2} - \frac{1}{32}\left(6\pi^3\zeta\left(\frac{1}{2}\right)^2 - 4\pi^4\right)\tau^2 + \dots \quad (\text{B.25})$$

High-temperature expansion of fugacity

$$z_{\text{B}1}(\tau) = \frac{2}{\sqrt{\pi}}\frac{1}{\tau^{1/2}} - \frac{2\sqrt{2}}{\pi}\frac{1}{\tau} + \frac{8(3 - \sqrt{3})}{3\pi^{3/2}}\frac{1}{\tau^{3/2}} - \frac{4(15\sqrt{2} - 10\sqrt{6} + 6)}{3\pi^2}\frac{1}{\tau^2} + \dots \quad (\text{B.26})$$

For more detailed discussions on two-dimensional and three-dimensional cases, refer to the paper by Brian Cowan. On the Chemical Potential of Ideal Fermi and Bose Gases¹. *Journal of Low Temperature Physics*. 2019

¹<https://doi.org/10.1007/s10909-019-02228-0>

B.2 Sound Waves/Shock Waves

1. Sound Waves

Sound waves are mechanical waves that transmit energy through the motion of atoms/molecules. Sound waves propagate through liquids in a longitudinal manner (longitudinal waves, where particle motion is parallel to the direction of wave propagation), in contrast to electromagnetic waves that propagate transversely (transverse waves, where particles move perpendicular to the direction of wave propagation).

According to the continuity equation of fluid

$$\int_S \rho \mathbf{u} \cdot d\mathbf{S} = -\frac{\partial}{\partial t} \int_V \rho dV. \quad (\text{B.27})$$

The differential form is given by

$$\nabla \cdot (\rho \mathbf{u}) = -\frac{\partial \rho}{\partial t} \quad (\text{B.28})$$

Considering the pressure gradient equation, the above equation is modified to the Euler equation

$$-\frac{1}{\rho} \nabla p = \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \quad (\text{B.29})$$

For one-dimensional fluid

$$\frac{\partial(\rho u)}{\partial x} = u \frac{\partial \rho}{\partial x} + \rho \frac{\partial u}{\partial x} = -\frac{\partial \rho}{\partial t} \quad (\text{B.30})$$

Let $s = \delta \rho / \rho$, then the equation is written as

$$u \frac{\partial s}{\partial x} + \frac{\partial u}{\partial x} = -\frac{\partial s}{\partial t} \quad (\text{B.31})$$

For low-amplitude sound waves, small terms can be ignored

$$\frac{\partial u}{\partial x} = -\frac{\partial s}{\partial t} \quad (\text{B.32})$$

The wave equation for s is obtained, where the bulk modulus is defined by Eq. B.35

$$\frac{\partial^2 s}{\partial x^2} = \frac{\omega}{k} = \frac{\rho}{B} \frac{\partial^2 s}{\partial t^2} \quad (\text{B.33})$$

The propagation of sound waves can be described by the Newton-Laplace equation (where B is the bulk modulus, ρ is the density)

$$v_s = \sqrt{\frac{B}{\rho}} \quad (\text{B.34})$$

The expression for the bulk modulus can be given (using $\rho = m/V$)

$$B = -V \frac{\partial p}{\partial V} = \rho \frac{\partial p}{\partial \rho} \quad (\text{B.35})$$

(1) Under isothermal conditions, the speed of sound is

$$B_T = -V \left(\frac{\partial p}{\partial V} \right)_T = p \quad (\text{B.36})$$

The speed of sound can be obtained from formula Eq. 4.167

$$v_s = \sqrt{\frac{B_T}{\rho}} = \sqrt{\frac{p}{\rho}} = \sqrt{\frac{\frac{1}{3}nm \langle v^2 \rangle}{\rho}} = \sqrt{\frac{\langle v^2 \rangle}{3}} \quad (\text{B.37})$$

(2) Under adiabatic conditions, due to the adiabatic condition

$$p \propto V^{-\gamma}, \quad \frac{dp}{p} = -\gamma \frac{dV}{V} \quad (\text{B.38})$$

The bulk modulus is obtained

$$B_S = -V \left(\frac{\partial p}{\partial V} \right)_S = \gamma p \quad (\text{B.39})$$

The speed of sound is

$$v_s = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{\gamma \langle v^2 \rangle}{3}} \quad (\text{B.40})$$

To determine whether the sound wave is adiabatic or isothermal, the relationship between wavelength and skin depth needs to be measured. Since the wavelength of the sound wave is

$$\lambda = \frac{2\pi v_s}{\omega} \quad (\text{B.41})$$

The skin depth is determined by the diffusion coefficient D (given by Eq. 7.32) and the angular frequency $\omega = 2\pi/T$

$$\delta^2 = \frac{2D}{\omega} = \frac{DT}{\pi} \quad (\text{B.42})$$

When the wavelength is much greater than the skin depth, the sound wave is adiabatic, otherwise, it is isothermal.

2. Shock Waves

When a disturbance propagates through a medium at a speed faster than the speed of sound in that medium, a shock wave occurs. The Mach number M of a disturbance is defined as the ratio of the speed w of the disturbance through the medium to the speed of sound v_s in that medium

$$M = \frac{w}{v_s} \quad (\text{B.43})$$

When $M > 1$, such a disturbance is called a shock front, and the speed of propagation of the disturbance is supersonic. The evolution of the shock wave is shown in the right figure, which shows the wavefront produced by a moving point source. A point source moving at speed w emits many circular wavefronts, and when $w > v_s$, i.e., when $M \geq 1$, these wavefronts coherently overlap to form a single conical wavefront. The half-angle of the cone decreases as M increases, and the half-angle α is given by

$$\sin \alpha = \frac{1}{M} \quad (\text{B.44}) \quad M = 0.8, 1, 1.2, 1.4$$

The mechanism of shock waves can be explained as follows (see the figure below): In two reference frames, the undisturbed gas stationary reference frame and the shock front stationary reference frame (shock frame), the speed of the undisturbed gas (unshocked gas, undisturbed gas) and the shocked gas relative to the shock front (gray rectangle) is discussed.

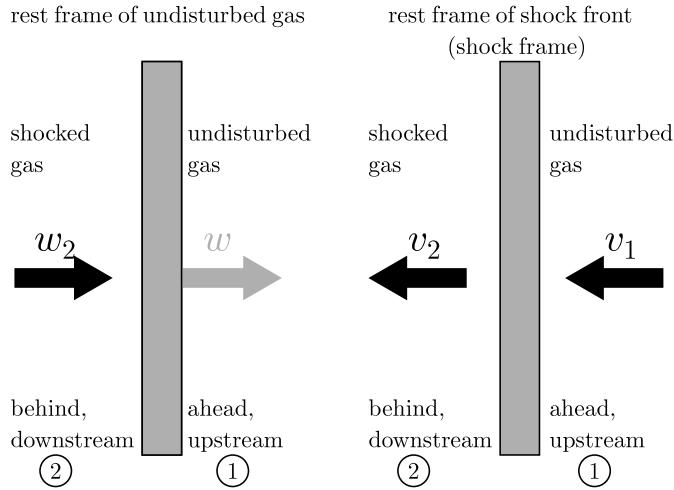


Fig. 69: Shock front in the undisturbed gas stationary reference frame and shock front stationary reference frame

In the undisturbed gas stationary reference frame, the shock front moves at speed w , while the gas that has passed through the shock moves at speed w_2 ($w_2 < w$). A shock occurs because the shock front propagates at speed $w > v_{s1}$, where v_{s1} is the speed of sound in the undisturbed gas. If $w \gg v_{s1}$, it is called a strong shock; if w is only slightly greater than v_{s1} , it is called a weak shock.

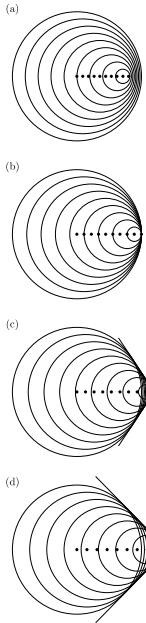


Fig. 68: Mach number
 $M = 0.8, 1, 1.2, 1.4$

In the shock frame, the gas in the region that has passed through the shock moves away from the shock at speed v_2 , while the undisturbed gas moves towards the shock at speed v_1 . Therefore, $v_1 = w$, which is the speed at which the undisturbed gas enters the shock front. In the same reference frame, the speed of the shocked gas leaving the back of the shock is given by:

$$v_2 = w - w_2 \quad (\text{B.45})$$

Below are the conservation laws for shock waves

(1) Mass conservation law: The mass flux of gas passing through the shock front per unit time is equal

$$\rho_2 v_2 = \rho_1 v_1 = \Phi_m \quad (\text{B.46})$$

(2) Momentum conservation law: The sum of the pressure and the rate of momentum transfer through a unit area is equal

$$p_2 + \rho_2 v_2^2 = p_1 + \rho_1 v_1^2 \quad (\text{B.47})$$

(3) Energy conservation law: The rate of work done by gas pressure on a unit area (given by $p v$) plus the rate of transfer of internal energy and kinetic energy per unit area $\left(\rho \tilde{u} + \frac{1}{2} \rho v^2\right) v$ (where \tilde{u} is the internal energy per unit mass) is a constant, giving the relationship:

$$p_2 v_2 + \left(\rho_2 \tilde{u}_2 + \frac{1}{2} \rho_2 v_2^2\right) v_2 = p_1 v_1 + \left(\rho_1 \tilde{u}_1 + \frac{1}{2} \rho_1 v_1^2\right) v_1 \quad (\text{B.48})$$

The internal energy per unit mass can be given by the internal energy expressed by the adiabatic index Eq. 1.39 (since $\tilde{u} = U/M$)

$$\tilde{u} = \frac{p}{\rho(\gamma - 1)} \quad (\text{B.49})$$

Rearranging this equation gives $p = (\gamma - 1)\rho\tilde{u}$, substituting it into the energy conservation equation Eq. B.48 gives

$$\gamma \rho_2 v_2 \tilde{u}_2 + \frac{1}{2} \rho_2 v_2^3 = \gamma \rho_1 v_1 \tilde{u}_1 + \frac{1}{2} \rho_1 v_1^3 \quad (\text{B.50})$$

Using the mass conservation equation Eq. B.46, dividing the left side by $\rho_2 v_2$ and the right side by $\rho_1 v_1$ gives

$$\frac{\gamma p_2}{(\gamma - 1)\rho_2} + \frac{1}{2} v_2^2 = \frac{\gamma p_1}{(\gamma - 1)\rho_1} + \frac{1}{2} v_1^2 \quad (\text{B.51})$$

Based on $v_1^2 - v_2^2 = (p_2 - p_1)(\rho_1^{-1} + \rho_2^{-1})$ and multiplying by $\gamma - 1$, the above equation can be rearranged to obtain

$$2\gamma(p_1\rho_1^{-1} - p_2\rho_2^{-1}) + (\gamma - 1)(p_2 - p_1)(\rho_1^{-1} + \rho_2^{-1}) = 0 \quad (\text{B.52})$$

Therefore, we can obtain

$$\frac{\rho_2^{-1}}{\rho_1^{-1}} = \frac{(\gamma + 1)p_1 + (\gamma - 1)p_2}{(\gamma - 1)p_1 + (\gamma + 1)p_2} \quad (\text{B.53})$$

Substituting this equation into $\Phi_m^2 = (p_2 - p_1) / (\rho_1^{-1} - \rho_2^{-1})$, we have

$$\Phi_m^2 = \frac{p_2 - p_1}{\rho_1^{-1} [1 - \rho_2^{-1}/\rho_1^{-1}]} = \frac{1}{2} \rho_1 [(\gamma - 1)p_1 + (\gamma + 1)p_2] \quad (\text{B.54})$$

Thus, the first flow velocity

$$v_1^2 = \Phi_m^2 \rho_1^{-2} = \frac{1}{2} \rho_1^{-1} [(\gamma - 1)p_1 + (\gamma + 1)p_2] \quad (B.55)$$

All quantities can be expressed in terms of the Mach number M_1 of the shock wave, based on $M_1 = v_1/v_{s1}$ and $v_{s1} = \sqrt{\gamma p_1/\rho_1}$, we have $M_1^2 = \frac{\rho_1 v_1^2}{\gamma p_1}$ (B.56)

Substituting into equation Eq. B.54 gives

$$\rho_1 v_1^2 = M_1^2 \gamma p_1 = \frac{1}{2} [(\gamma - 1)p_1 + (\gamma + 1)p_2] \quad (B.57)$$

Or the pressure on both sides of the shock front can be related, i.e.,

$$\frac{p_2}{p_1} = \frac{2\gamma M_1^2 - (\gamma - 1)}{\gamma + 1} \quad (B.58)$$

The above two equations are called the Rankine-Hugoniot conditions, describing the physical properties of the material on both sides of the shock front, and the results are shown in the figure below.

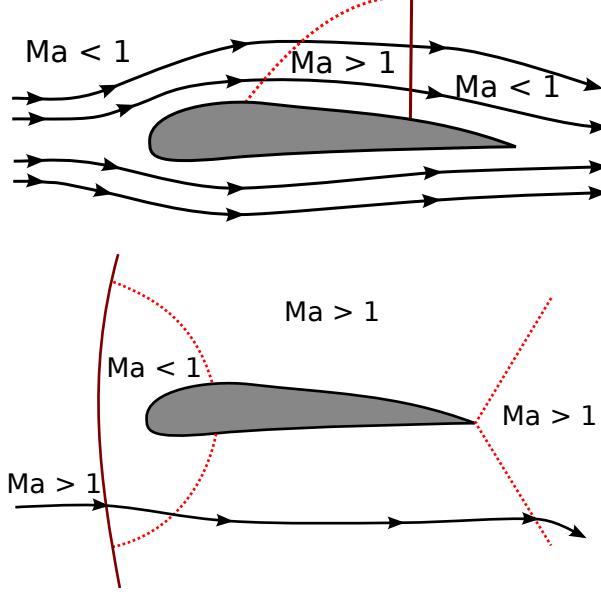


Fig. 70: Mach number of airflow around an airfoil near transonic speeds as speed gradually increases

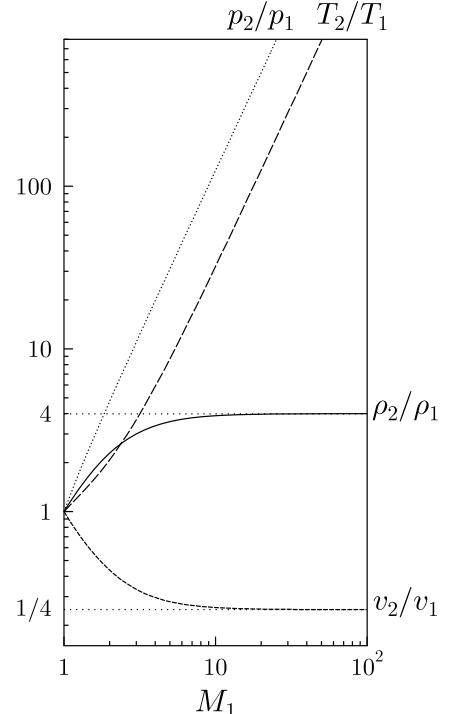


Fig. 71: Rankine-Hugoniot conditions at the shock front, assuming non-relativistic monatomic gas $\gamma = \frac{5}{3}$

Domain	Subsonic	Transonic	Sonic	Supersonic	Hypersonic	High-speed
Mach	< 0.8	0.8 – 1.2	1.0	1.2 – 5.0	5.0 – 10.0	> 8.8

Table 8: Speeds at different Mach numbers