Thermodynamics and Statistical Physics

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Abstract

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1 Basic Law of Thermodynamics

1.1 Equation of State

Definition 1.1. The **thermal expansion coefficient** α, the **pressure coefficient** β and the **isothermal compressibility** κ_T are defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V, \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{1.1}$$

By $f(p, V, T) = 0$ we have

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1, \quad \alpha = \kappa_T \beta p \tag{1.2}$$

To more accurately describe the state of real gases, we have the following equations of state.

Proposition 1.2 (Van der Waals Equation)**.**

$$\left(p + a\frac{n^2}{V^2}\right)(V - nb) = nRT \tag{1.3}$$

where a, b are determined by experiments.

Proposition 1.3 (Onnes Equation)**.**

$$p = \frac{nRT}{V}\left(1 + \frac{n}{V}B(T) + \frac{n^2}{V^2}C(T) + \cdots\right) \tag{1.4}$$

1.2 The First Law

Proposition 1.4 (First Law of Thermodynamics)**.**

$$\mathrm{d}U = đQ + đW \tag{1.5}$$

1.3 Heat Capacity and Enthalpy

Definition 1.5. The **heat capacity** C, **molar heat capacity** C_m and **specific heat capacity** c are defined as

$$C = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} = \frac{đQ}{\mathrm{d}T}, \quad C_m = \frac{C}{n}, \quad c = \frac{C}{m}. \tag{1.6}$$

The heat capacity at constant volume C_V and at constant pressure C_p are defined as

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p. \tag{1.7}$$

Definition 1.6. The **enthalpy** H is defined as

$$H = U + pV \tag{1.8}$$

Then, we have

$$C_p = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} = \lim_{\Delta T \to 0} \frac{\Delta U + p\Delta V}{\Delta T} = C_V + p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p. \tag{1.9}$$

1.4 Internal Energy of Ideal Gas

Proposition 1.7 (Joule's Law)**.** *The internal energy of an ideal gas is determined solely by its temperature and independent of volume, i.e.* $U = U(T)$.

By Joule's law and assuming constant heat capacity, we have

$$U = U_0 + \int \mathrm{d}U = U_0 + \int C_V \mathrm{d}T = U_0 + C_V T. \tag{1.10}$$

Similarly, for enthalpy we have

$$H = H_0 + \int C_p \mathrm{d}T = H_0 + C_p T. \tag{1.11}$$

By $pV = nRT$, we have

$$C_p - C_V = nR, \quad \gamma = \frac{C_p}{C_V}. \tag{1.12}$$

Therefore,

$$C_V = \frac{nR}{\gamma - 1}, \quad C_p = \frac{\gamma nR}{\gamma - 1}. \tag{1.13}$$

1.5 Adiabatic Process of Ideal Gas

For an adiabatic process, we have $đQ = 0$, thus

$$\mathrm{d}U - đW = C_V \mathrm{d}T + p\mathrm{d}V = \frac{nR}{\gamma - 1}\mathrm{d}T + p\mathrm{d}V = \frac{1}{\gamma - 1}\left(\gamma p \mathrm{d}V + V \mathrm{d}p\right) = 0.$$

Integrating the above equation gives

$$pV^\gamma = \text{const}, \quad TV^{\gamma-1} = \text{const}, \quad \frac{T^\gamma}{p^{\gamma-1}} = \text{const}. \tag{1.14}$$

1.6 Carnot Cycle of Ideal Gas

Definition 1.8. The **efficiency** η of a heat engine is defined as

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} \tag{1.15}$$

where Q_1 is the heat absorbed from the hot reservoir, Q_2 is the heat released to the cold reservoir, and W is the work done by the engine. And the **coefficient of performance** ε of a refrigerator is defined as

$$\varepsilon = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \tag{1.16}$$

For a Carnot cycle, we consider the following four processes:

(1) Isothermal expansion at T_1: $pV = nRT_1$, $V_1 \to V_2$, $Q_1 = -W_1 = \int_{V_A}^{V_B} p\mathrm{d}V = nRT_1 \ln \frac{V_2}{V_1}$.

(2) Adiabatic expansion: $Q = 0$.

(3) Isothermal compression at T_2: $pV = nRT_2$, $V_3 \to V_4$, $Q_2 = nRT_2 \ln \frac{V_3}{V_4}$, $W_3 = -Q_2$.

(4) Adiabatic compression: $Q = 0$.

By $TV^{\gamma-1} = \text{const}$, we have

$$\eta = 1 - \frac{T_2}{T_1} < 1. \tag{1.17}$$

Similarly, for a Carnot refrigerator, we have

$$\varepsilon = \frac{T_2}{T_1 - T_2}. \tag{1.18}$$

1.7 The Second Law

The second law of thermodynamics can be stated in two equivalent ways.

Proposition 1.9 (Kelvin's Statement)**.** *It is impossible to construct a device that operates in a cycle and produces no effect other than the extraction of heat from a single reservoir and the performance of an equivalent amount of work.*

Proposition 1.10 (Clausius' Statement)**.** *It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.*

1.8 Carnot Theorem

Theorem 1.11 (Carnot Theorem)**.** *No engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between the same reservoirs.*

All Carnot engines operating between the same two heat reservoirs have the same efficiency.

1.9 Temperature Scale

The efficiency of a Carnot engine depends only on the temperatures of the two reservoirs and so does the heat, then we have

$$\frac{Q_2}{Q_1} = F(\theta_1, \theta_2),$$

where θ is the temperature measured by a certain scale.

Assume there is another Carnot engine operating between θ_3 and θ_1, then we have

$$\frac{Q_1}{Q_3} = F(\theta_3, \theta_1).$$

By combining the two engines, we have

$$\frac{Q_2}{Q_3} = F(\theta_3, \theta_2), \quad F(\theta_1, \theta_2) = \frac{F(\theta_3, \theta_2)}{F(\theta_3, \theta_1)}.$$

Since θ_3 is arbitrary, we can write $F(\theta_1, \theta_2) = \frac{f(\theta_2)}{f(\theta_1)}$. And we choose a temperature scale such that $f(T^*) \propto T^*$, then we have $\frac{Q_2}{Q_1} = \frac{T_2^*}{T_1^*}$. This temperature scale is called the **absolute temperature scale**.

1.10 Clausius' Theorem

Theorem 1.12 (Clausius's Theorem)**.** *For any cyclic process, we have*

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}\leqslant 0,\quad \sum_{i=1}^{n}\frac{Q_i}{T_i}\leqslant 0. \tag{1.19}$$

In other words,

$$\oint\frac{đQ}{T}\leqslant 0. \tag{1.20}$$

The equality holds if and only if the process is reversible.

Proof.

$$\eta=1-\frac{Q_2}{Q_1}\leqslant 1-\frac{T_2}{T_1}\Longrightarrow\frac{Q_1}{T_1}+\frac{Q_2}{T_2}\leqslant 0.$$

□

1.11 Entropy

By Clausius's theorem, $\int_A^B\frac{đQ}{T}$ is independent of the path from A to B.

Definition 1.13. The **entropy** S is defined as

$$S(B)-S(A)=\int_A^B\frac{đQ}{T}. \tag{1.21}$$

Then we have the fundamental thermodynamic equation

$$\mathrm{d}S=\frac{\mathrm{d}U+p\mathrm{d}V}{T},\quad \mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V,\quad \mathrm{d}U=T\mathrm{d}S+\sum_i Y_i\mathrm{d}y_i. \tag{1.22}$$

For an ideal gas, we have

$$\mathrm{d}S=\frac{\mathrm{d}U+p\mathrm{d}V}{T}=\frac{C_V}{T}\mathrm{d}T+\frac{nR}{V}\mathrm{d}V,\quad S=C_V\ln T+nR\ln V+S_0. \tag{1.23}$$

Similarly, we have

$$S=C_p\ln T-nR\ln p+S_0. \tag{1.24}$$

From a microscopic point of view, we have

$$S=k\ln W, \tag{1.25}$$

where W is the number of microstates corresponding to the macrostate.

By Clausius's theorem $\int_B^A\frac{đQ_r}{T}+\int_A^B\frac{đQ}{T}\leqslant 0$, we have

$$S_B-S_A=\int_A^B\frac{đQ_r}{T}\geqslant\int_A^B\frac{đQ}{T}.$$

By $\mathrm{d}S\geqslant\frac{đQ}{T}$, we have

$$\mathrm{d}U\leqslant T\mathrm{d}S-p\mathrm{d}V.$$

Theorem 1.14 (Principle of Entropy Increase)**.** *For an isolated system, we have*

$$S_B - S_A \geqslant 0. \tag{1.26}$$

The equality holds if and only if the process is reversible.

Proof. For equilibrium states A and B, we have $Q = 0$, we have

$$S_B - S_A \geqslant \int_A^B \frac{đQ}{T} = 0.$$

For general cases, we can divide the system into n subsystems, each of which is isolated and goes from equilibrium state A_k to B_k. Then we have

$$\int_A^B \frac{đQ}{T} + \sum_{k=1}^{n} \int_{A_k}^{B_k} \frac{đQ_r}{T} < 0 \Longrightarrow \sum_{k=1}^{n} S_{B_k} - \sum_{k=1}^{n} S_{A_k} > \int_A^B \frac{đQ}{T} \Longrightarrow S_B - S_A \geqslant 0.$$

□

1.12 Free Energy and Gibbs Function

Definition 1.15. The **free energy** F is defined as

$$F = U - TS. \tag{1.27}$$

By $\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \leqslant -S\mathrm{d}T + đW$, we have the maximum work principle.

Proposition 1.16 (Maximum Work Principle)**.** *For a system at constant temperature, the maximum work obtainable from the system is equal to the decrease in its free energy.*

Proposition 1.17 (Free Energy Criterion)**.** *For a system at constant temperature and volume, the free energy never increases and always decreases for irreversible processes. The equilibrium state is the state of minimum free energy.*

Definition 1.18. The **Gibbs function** G is defined as

$$G = F + pV = U - TS + pV. \tag{1.28}$$

Hence, we have $\mathrm{d}G = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T + V\mathrm{d}p + p\mathrm{d}V \leqslant -S\mathrm{d}T + V\mathrm{d}p$. For a system at constant temperature and pressure, we have $\mathrm{G} \leqslant 0$.

Proposition 1.19 (Gibbs Function Criterion)**.** *For a system at constant temperature and pressure, the Gibbs function never increases and always decreases for irreversible processes. The equilibrium state is the state of minimum Gibbs function.*

2 Homogeneous Substances

2.1 Internal Energy, Enthalpy, Free Energy and Gibbs Function

Since $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$, we have

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \quad p = -\left(\frac{\partial U}{\partial V}\right)_S \Longrightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V. \tag{2.1}$$

Since $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$, we have

$$T = \left(\frac{\partial H}{\partial S}\right)_p, \quad V = \left(\frac{\partial H}{\partial p}\right)_S \Longrightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p. \tag{2.2}$$

Since $\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$, we have

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad p = -\left(\frac{\partial F}{\partial V}\right)_T \Longrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V. \tag{2.3}$$

Since $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$, we have

$$S = -\left(\frac{\partial G}{\partial T}\right)_p, \quad V = \left(\frac{\partial G}{\partial p}\right)_T \Longrightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p. \tag{2.4}$$

These four equations are called the **Maxwell relations**.

2.2 Simple Applications of Maxwell Relations

Proposition 2.1.

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = TpV\alpha\beta = \frac{TV\alpha^2}{\kappa_T}. \tag{2.5}$$

Proof. Since $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ and $\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$, we have

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V, \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p. \tag{2.6}$$

Since $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$, we have

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p, \quad \left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_p. \tag{2.7}$$

Therefore,

$$C_p - C_V = T\left(\left(\frac{\partial S}{\partial T}\right)_p - \left(\frac{\partial S}{\partial T}\right)_V\right) = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = TpV\alpha\beta = \frac{TV\alpha^2}{\kappa_T}.$$

□

For ideal gases, we have $C_p - C_V = nR$.

2.3 Joule-Thomson Process

Consider a steady flow of gas through a porous plug from a region of high pressure p_1 to a region of low pressure p_2. Assume the process is adiabatic, then we have

$$U_2 - U_1 = p_1V_1 - p_2V_2 \Longrightarrow H_1 = H_2. \tag{2.8}$$

Definition 2.2. The **Joule-Thomson coefficient** μ is defined as

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H. \tag{2.9}$$

Proposition 2.3. *In a Joule-Thomson process, we have*

$$\mu = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = \frac{1}{C_p}\left(T\left(\frac{\partial V}{\partial T}\right)_p - V\right) = \frac{V}{C_p}(T\alpha - 1). \tag{2.10}$$

For ideal gases, $T = \frac{1}{\alpha}$ and $\mu = 0$. For real gases, μ is positive if $T < \frac{1}{\alpha}$ and negative if $T > \frac{1}{\alpha}$. The curve $\alpha = \frac{1}{T}$ is called the **inversion curve** and $\frac{1}{\alpha}$ is called the **inversion temperature**.

For Onnes equation $p = \frac{nRT}{V}\left(1 + \frac{n}{V}B(T)\right)$, where $\frac{n}{V}B(T) \ll 1$, by substituting $\frac{n}{V} = \frac{p}{RT}$, we have

$$V = n\left(\frac{RT}{p} + B(T)\right) \Longrightarrow \mu = \frac{n}{C_p}\left(T\frac{\mathrm{d}B}{\mathrm{d}T} - B\right). \tag{2.11}$$

Consider the adiabatic expansion of the gas. If the process is quasi-static, then we have $\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p = 0$, hence we have

$$\mu_S = \left(\frac{\partial T}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p = \frac{VT\alpha}{C_p} > 0. \tag{2.12}$$

2.4 Basic Thermodynamical Functions

Taking T and V as state variables, we have

$$U = \int\left(C_V\mathrm{d}T + \left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right)\mathrm{d}V\right) + U_0, \quad S = \int\left(\frac{C_V}{T}\mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V\right) + S_0. \tag{2.13}$$

Proposition 2.4. *If we know C_V^0 at some volume, then we can calculate C_V at any volume by*

$$C_V = C_V^0 + T\int_{V_0}^{V}\left(\frac{\partial^2 p}{\partial T^2}\right)_V \mathrm{d}V. \tag{2.14}$$

Proof. Since $C_V = T\left(\frac{\partial C_V}{V}\right)_V$, we have

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial T}{\partial V}\right)_T\left(\frac{\partial C_V}{\partial T}\right)_V + T\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T = T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

□

Taking T and p as state variables, we have

$$H = \int \left(C_p \mathrm{d}T + \left(V - T \left(\frac{\partial V}{\partial T} \right)_p \right) \mathrm{d}p \right) + H_0, \quad S = \int \left(\frac{C_p}{T} \mathrm{d}T - \left(\frac{\partial V}{\partial T} \right)_p \mathrm{d}p \right) + S_0. \tag{2.15}$$

And U can be obtained by $U = H - pV$.

Proposition 2.5. *If we know C_p^0 at some pressure, then we can calculate C_p at any pressure by*

$$C_p = C_p^0 - T \int_{p_0}^{p} \left(\frac{\partial^2 V}{\partial T^2} \right)_p \mathrm{d}p. \tag{2.16}$$

Proof. Since $C_p = T \left(\frac{\partial S}{\partial T} \right)_p$, we have

$$\left(\frac{\partial C_p}{\partial p} \right)_T = \left(\frac{\partial T}{\partial p} \right)_T \left(\frac{\partial C_p}{\partial T} \right)_p + T \left(\frac{\partial}{\partial p} \left(\frac{\partial S}{\partial T} \right)_p \right)_T = T \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial p} \right)_T \right)_p = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_p$$

□

2.5 Characteristic Functions

Theorem 2.6 (Massieu)**.** *Taking independent variables properly, from one thermodynamical function, we can derive all the thermodynamical functions by partial differentiation.*

Definition 2.7. Thermodynamical functions in Theorem 2.6 are called **characteristic functions**, including $U(S,V)$, $H(S,p)$, $S(U,V)$, $F(T,V)$ and $G(T,p)$.

Proposition 2.8. ***Gibbs-Helmholtz equation*** *is given by*

$$S = -\frac{\partial F}{\partial T} \Longrightarrow U = F - T\frac{\partial F}{\partial T}, \quad H = G - T\frac{\partial G}{\partial T}. \tag{2.17}$$

2.6 Thermodynamics of Magnetic Medium

Denote the magnetization by $\mathscr{M}$ and the magnetic field intensity by $\mathscr{H}$, then $m = \mathscr{M}V$ is the total magnetic moment.

Proposition 2.9 (Curie Law)**.** *For a paramagnetic substance, we have*

$$m = \frac{CV}{T}\mathscr{H}. \tag{2.18}$$

where C is the Curie constant.

If the system does not contain magnetic fields and volume work, then we have

$$đW = \mu_0 V \mathscr{H} \mathrm{d}m.$$

By substituting $p \to \mu_0 \mathscr{H}$ and $V \to m$, we have

$$\mathrm{d}U = T\mathrm{d}S + \mu_0 \mathscr{H} \mathrm{d}m \Longrightarrow \left(\frac{\partial T}{\partial m} \right)_S = \mu_0 \left(\frac{\partial \mathscr{H}}{\partial S} \right)_m. \tag{2.19}$$

Similarly, we have the following Maxwell relations:

$$\mathrm{d}H = T\mathrm{d}S + -m\mu_0\mathrm{d}\mathscr{H} \Longrightarrow \left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\mu_0\left(\frac{\partial m}{\partial S}\right)_{\mathscr{H}}, \tag{2.20}$$

$$\mathrm{d}F = -S\mathrm{d}T + \mu_0\mathscr{H}\mathrm{d}m \Longrightarrow \left(\frac{\partial S}{\partial m}\right)_T = -\mu_0\left(\frac{\partial \mathscr{H}}{\partial T}\right)_m. \tag{2.21}$$

$$\mathrm{d}U = -S\mathrm{d}T + -\mu_0 m\mathrm{d}\mathscr{H} \Longrightarrow \left(\frac{\partial S}{\partial \mathscr{H}}\right)_T = \mu_0\left(\frac{\partial m}{\partial T}\right)_{\mathscr{H}}. \tag{2.22}$$

Fixing the magnetic field, we have the capacity of magnetic medium

$$C_{\mathscr{H}} = T\left(\frac{\partial S}{\partial T}\right)_{\mathscr{H}}. \tag{2.23}$$

Then we have

$$\left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\left(\frac{\partial S}{\partial \mathscr{H}}\right)_T\left(\frac{\partial T}{\partial S}\right)_{\mathscr{H}} \Longrightarrow \left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\frac{\mu_0 T}{C_{\mathscr{H}}}\left(\frac{\partial m}{\partial T}\right)_{\mathscr{H}}. \tag{2.24}$$

Proposition 2.10 (Magnetocaloric Effect)**.** *When the magnetic field is decreased adiabatically, the temperature of a paramagnetic substance decreases.*

Proof. Supppose that the magnetic media follows the Curie law $m = \frac{CV}{T}\mathscr{H}$, then we have

$$\left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\frac{\mu_0 T}{C_{\mathscr{H}}}\left(\frac{\partial m}{\partial T}\right)_{\mathscr{H}} = \frac{CV}{C_{\mathscr{H}}T}\mu_0\mathscr{H} > 0.$$

□

Proposition 2.11. *If we consider the change of volume, then we have*

$$\left(\frac{\partial V}{\partial \mathscr{H}}\right)_{T,p} = -\mu_0\left(\frac{\partial m}{\partial p}\right)_{T,\mathscr{H}}. \tag{2.25}$$

This Maxwell relation describes the relationship between magnetostriction and the pressure dependence of magnetization.

Proof.

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p - \mu_0\mathscr{H}\mathrm{d}m \Longrightarrow V = \left(\frac{\partial G}{\partial p}\right)_{T,\mathscr{H}}, \quad -\mu_0 m = \left(\frac{\partial G}{\partial \mathscr{H}}\right)_{T,p}.$$

□

3 Phase Transition of One Component Systems

3.1 Equilibrium Criterion

Consider the Taylor expansion of U:

$$\Delta U = \frac{\mathrm{d}U}{\mathrm{d}x}\delta x + \frac{1}{2}\frac{\mathrm{d}^2U}{\mathrm{d}x^2}\delta x^2 + \cdots .$$

The equilibrium condition is given by $\frac{\mathrm{d}U}{\mathrm{d}x} = 0$. The stability condition is given by

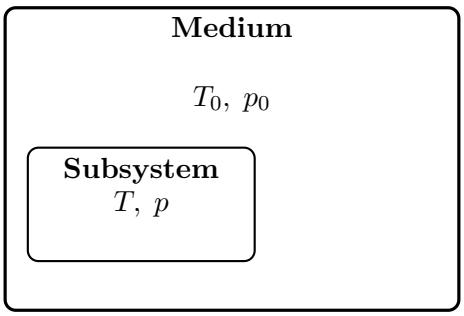
- $\frac{\mathrm{d}^2U}{\mathrm{d}x^2} > 0 \Longrightarrow$ stable or metastable equilibrium
- $\frac{\mathrm{d}^2U}{\mathrm{d}x^2} < 0 \Longrightarrow$ unstable equilibrium;
- $\frac{\mathrm{d}^2U}{\mathrm{d}x^2} = 0 \Longrightarrow$ neutral equilibrium.

Proposition 3.1. *By the stability condition of U, we have stability conditions of other thermodynamical functions:*

$$\delta^2 S < 0, \quad \delta^2 F > 0, \quad \delta^2 G > 0, \quad \delta^2 U > 0, \quad \delta^2 H > 0. \tag{3.1}$$

For an isolated homogeneous system, consider any small part of the system as the subsystem and the rest as the medium,

$$\begin{cases} U + U_0 = \text{ constant} \\ V + V_0 = \text{ constant} \end{cases} \Longrightarrow \begin{cases} \delta U + \delta U_0 = 0 \\ \delta V + \delta V_0 = 0 \end{cases} . \tag{3.2}$$



Proposition 3.2. *The equilibrium conditions are given by*

$$T = T_0, \quad p = p_0. \tag{3.3}$$

Proof. The change of entropy is given by

$$\Delta S = \delta S + \frac{1}{2}\delta S^2, \quad \Delta S_0 = \delta S_0 + \frac{1}{2}\delta S_0^2.$$

By the equilibrium condition, the entropy should reach maximum at equilibrium, hence $\delta S + \delta S_0 = 0$. Then we have

$$\delta S + \delta S_0 = \frac{\delta U + p\delta V}{T} + \frac{\delta U_0 + p_0\delta V_0}{T_0} = \left(\frac{1}{T} - \frac{1}{T_0}\right)\delta U + \left(\frac{p_0}{T_0} - \frac{p}{T}\right)\delta V = 0.$$

Since δU and δV are independent, we have

$$T = T_0, \quad p = p_0.$$

□

Proposition 3.3. *The stability conditions are given by*

$$C_V > 0, \quad \left(\frac{\partial p}{\partial V}\right)_T < 0. \tag{3.4}$$

Proof. Since the subsystem is much smaller than the medium, the maximum entropy condition requires

$$\delta^2 S + \delta^2 S_0 \approx \delta^2 S = \left(\frac{\partial^2 S}{\partial U^2}\right)\delta U^2 + \left(\frac{\partial^2 S}{\partial V^2}\right)\delta V^2 + 2\left(\frac{\partial^2 S}{\partial U \partial V}\right)\delta U \delta V < 0.$$

Since $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$ and $\left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T}$, we have

$$\begin{aligned}
\delta S^2 &= \left(\frac{\partial}{\partial U}\left(\frac{1}{T}\right)\delta U + \frac{\partial}{\partial V}\left(\frac{1}{T}\right)\delta V\right)\delta U + \left(\frac{\partial}{\partial U}\left(\frac{p}{T}\right)\delta U + \frac{\partial}{\partial V}\left(\frac{p}{T}\right)\delta V\right)\delta V \\
&= \left(\delta\left(\frac{1}{T}\right)\right)\delta U + \left(\delta\left(\frac{p}{T}\right)\right)\delta V = -\frac{1}{T^2}\delta T\left(C_V \delta T + \left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right)\delta V\right) \\
&+ \left(\left(\frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V - \frac{p}{T^2}\right)\delta T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)T\delta V\right)\delta V = -\frac{C_V}{T^2}\delta T^2 + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T \delta V^2 < 0
\end{aligned}$$

□

3.2 Thermodynamic Fundamental Equations of Open Systems

Definition 3.4. A **one component system** is a thermodynamical system consisting of only one chemical substance. A **multiphase system** is a thermodynamical system which is not homogeneous, but consists of several homogeneous parts.

For an open system, the amount of substance is changing, then we have

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu \mathrm{d}n, \tag{3.5}$$

where μ is the **chemical potential** defined by

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p}. \tag{3.6}$$

Since $G(T, p, n) = nG_m(T, p)$, we have

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = G_m. \tag{3.7}$$

Proposition 3.5.

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

$$\left(\frac{\partial S}{\partial p}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{p,n}, \quad \left(\frac{\partial S}{\partial n}\right)_{T,p} = -\left(\frac{\partial \mu}{\partial T}\right)_{p,n}, \quad \left(\frac{\partial V}{\partial n}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,n}. \tag{3.8}$$

Definition 3.6. The **grand potential** J is defined as

$$J(T, V, \mu) = F - \mu. \tag{3.9}$$

Then we have

$$\mathrm{d}J = -S\mathrm{d}T - p\mathrm{d}V - n\mathrm{d}\mu. \tag{3.10}$$

Proposition 3.7.

$$S = -\left(\frac{\partial J}{\partial T}\right)_{V,\mu}, \quad p = -\left(\frac{\partial J}{\partial V}\right)_{T,\mu}, \quad n = -\left(\frac{\partial J}{\partial \mu}\right)_{T,V}.$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,\mu} = \left(\frac{\partial p}{\partial T}\right)_{V,\mu}, \quad \left(\frac{\partial S}{\partial \mu}\right)_{T,V} = \left(\frac{\partial n}{\partial T}\right)_{V,\mu}, \quad \left(\frac{\partial p}{\partial \mu}\right)_{T,V} = \left(\frac{\partial n}{\partial V}\right)_{T,\mu}. \tag{3.11}$$

3.3 Multiphase Equilibrium Condition of One Component Systems

Consider an isolated one component system consisting of two phases α and β.

Proposition 3.8. *The equilibrium conditions are given by*

$$T^\alpha = T^\beta, \quad p^\alpha = p^\beta, \quad \mu^\alpha = \mu^\beta. \tag{3.12}$$

Proof.

$$\begin{cases} U^\alpha + U^\beta = \text{ constant} \\ V^\alpha + V^\beta = \text{ constant} \\ n^\alpha + n^\beta = \text{ constant} \end{cases}, \quad \begin{cases} \delta U^\alpha + \delta U^\beta = 0 \\ \delta V^\alpha + \delta V^\beta = 0 \\ \delta n^\alpha + \delta n^\beta = 0 \end{cases}, \quad \begin{cases} \delta S^\alpha = \frac{\delta U^\alpha + p^\alpha \delta V^\alpha - \mu^\alpha \delta n^\alpha}{T^\alpha} \\ \delta S^\beta = \frac{\delta U^\beta + p^\beta \delta V^\beta - \mu^\beta \delta n^\beta}{T^\beta} \end{cases}.$$

By the equilibrium condition, we have $\delta S^\alpha + \delta S^\beta = 0$. Hence we have the conclusion. □

If the equilibrium conditions are not satisfied, then the system will spontaneously evolve towards the direction that increases the total entropy.

- $T^\alpha \neq T^\beta \Longrightarrow$ heat transfer from high temperature phase to low temperature phase;
- $p^\alpha \neq p^\beta \Longrightarrow$ volume of high pressure phase will increase while that of low pressure phase will decrease;
- $\mu^\alpha \neq \mu^\beta \Longrightarrow$ substance transfer from high chemical potential phase to low chemical potential phase.

3.4 Equilibrium Properties of One Component Multiphase Systems

Given T and p, the stable phase is the one with the lowest μ.

If two phases coexist at equilibrium, then they have the same μ, T and p. Only one of T, p is independent along the coexistence curve of two phases. Since $\mu^\alpha = \mu^\beta$, two phases can coexist at any amount ratio and the Gibbs function will not change, hence the system is in a neutral equilibrium state.

Proposition 3.9 (Clapeyron Equation)**.** *For a one component two-phase system at equilibrium, we have*

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T(V_m^\beta - V_m^\alpha)}, \quad L = T(S_m^\beta - S_m^\alpha). \tag{3.13}$$

Proof. Suppose (T, p) and $(T + \mathrm{d}T, p + \mathrm{d}p)$ are two equilibrium states of the system, then we have

$$\mu^\alpha(T,p) = \mu^\beta(T,p), \quad \mu^\alpha(T+\mathrm{d}T, p+\mathrm{d}p) = \mu^\beta(T+\mathrm{d}T, p+\mathrm{d}p) \Longrightarrow \mathrm{d}\mu^\alpha = \mathrm{d}\mu^\beta.$$

Since $\mathrm{d}\mu = -S_m \mathrm{d}T + V_m \mathrm{d}p$, we have

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_m^\beta - S_m^\alpha}{V_m^\beta - V_m^\alpha} = \frac{L}{T(V_m^\beta - V_m^\alpha)},$$

where L is the latent heat per mole of the phase transition from phase α to phase β. □

While evaporation and sublimation, we have $L > 0$ and $V_m^\beta > V_m^\alpha$, hence $\frac{\mathrm{d}p}{\mathrm{d}T} > 0$. Most substances expand, i.e. $\frac{\mathrm{d}p}{\mathrm{T}} > 0$, when they melt. However, water is an exception.

Example 3.10. Saturated vapor is in equilibrium with its liquid. Denote α as the liquid phase and β as the vapor phase, then we have $V_m^\beta \gg V_m^\alpha$ and $pV_m^\beta = RT$. Hence, the Clapeyron equation reduces to

$$\frac{1}{p}\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{RT^2} \Longrightarrow \ln p = -\frac{L}{RT} + A, \quad p = p_0 e^{-\frac{L}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)}.$$

3.5 Critical Points and Gas-Liquid Phase Transition

At a high temperature, the isotherm is similar to that of ideal gases. At a low temperature, the isotherm has a part parallel to the volume axis. At a **certain temperature** T_c, the parallel part shrinks to a point, corresponding to critical pressure p_c.

On the isotherm,

$$\mathrm{d}\mu = -S_m \mathrm{d}T + V_m \mathrm{d}p \Longrightarrow \mu - \mu_0 = \int_{p_0}^{p} V_m \mathrm{d}p.$$

Proposition 3.11.

$$V_{mc} = 3b, \quad T_c = \frac{8a}{27Rb}, \quad p_c = \frac{a}{27b^2}. \tag{3.14}$$

Proof. At the critical point, since $\left(\frac{\partial p}{\partial V_m}\right)_T = 0$ and $\left(\frac{\partial^2 p}{\partial V_m^2}\right)_T = 0$, we have

$$\left(\frac{\partial p}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0, \quad \left(\frac{\partial^2 p}{\partial V_m^2}\right)_T = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} = 0.$$

By the Van der Waals equation, we have

$$V_{mc} = 3b, \quad T_c = \frac{8a}{27Rb}, \quad p_c = \frac{a}{27b^2}.$$

□

3.6 Classification of Phase Transition

The phase transition of water from liquid to vapor increases the volume. We call this kind of phase transition as first-order phase transition.

Definition 3.12. A **first-order phase transition** is a phase transition satisfies

$$\begin{cases} \mu^{(1)}(T,p) = \mu^{(2)}(T,p) \\ \frac{\partial \mu^{(1)}}{\partial T} \neq \frac{\partial \mu^{(2)}}{\partial T}, \quad \frac{\partial \mu^{(1)}}{\partial p} \neq \frac{\partial \mu^{(2)}}{\partial p} \end{cases}. \tag{3.15}$$

Definition 3.13. A **second-order phase transition** is a phase transition satisfies

$$\begin{cases} \mu^{(1)}(T,p) = \mu^{(2)}(T,p) \\ \frac{\partial \mu^{(1)}}{\partial T} = \frac{\partial \mu^{(2)}}{\partial T}, \quad \frac{\partial \mu^{(1)}}{\partial p} = \frac{\partial \mu^{(2)}}{\partial p} \\ \frac{\partial^2 \mu^{(1)}}{\partial T^2} \neq \frac{\partial^2 \mu^{(2)}}{\partial T^2}, \quad \frac{\partial^2 \mu^{(1)}}{\partial p^2} \neq \frac{\partial^2 \mu^{(2)}}{\partial p^2} \end{cases}. \tag{3.16}$$

For two sides of the isotherm, there exists latent heat and volume change. At the critical point, the latent heat and volume change both vanish.

Theorem 3.14 (Ehrenfest Equations)**.** *For a second-order phase transition, we have*

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{c_p^{(2)} - c_p^{(1)}}{Tv(\alpha^{(2)} - \alpha^{(1)})} = \frac{\alpha^{(2)} - \alpha^{(1)}}{\kappa_T^{(2)} - \kappa_T^{(1)}}. \tag{3.17}$$

3.7 Critical Phenomenon and Critical Exponents

Ferromagnetic materials have a critical temperature T_c. When $T < T_c$, the material is ferromagnetic. When $T > T_c$, the material is paramagnetic.

Definition 3.15. The magnetization of ferromagnetic materials is non-zero even without external magnetic field and this magnetization is called **spontaneous magnetization** $\mathscr{M}(T)$.

The spontaneous magnetization of paramagnetic materials is zero.

Proposition 3.16. *We have the following experiment results.*

1. $$\mathscr{M}(T) \propto (-t)^{\beta}, \quad t \to -0, \quad \beta \approx \frac{1}{3}. \tag{3.18}$$

2. *Magnetic susceptibility* $\chi = \left(\frac{\partial \mathscr{M}}{\partial \mathscr{H}}\right)_T$ *is divergent when* $t \to \pm 0$*, and*

$$\begin{cases} \chi \propto t^{-\gamma}, \quad t \to +0, \quad 1.2 \leqslant \gamma \leqslant 1.4 \\ \chi \propto (-t)^{-\gamma'}, \quad t \to -0, \quad 1.0 \leqslant \gamma' \leqslant 1.2 \end{cases}. \tag{3.19}$$

3. *When* $t = 0$ *or the magnetic field is very weak, we have*

$$\mathscr{M} \propto \mathscr{H}^{1/\delta}, \quad 4.2 \leqslant \delta \leqslant 4.8. \tag{3.20}$$

4. *The heat capacity at zero magnetic field* $c_{\mathscr{H}}(\mathscr{H} = 0)$ *follows*

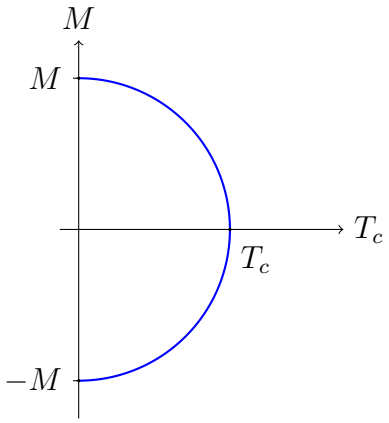
$$\begin{cases} c_{\mathscr{H}} \propto t^{-\alpha}, \quad t \to +0, \quad 0 \leqslant \alpha \leqslant 0.2 \\ c_{\mathscr{H}} \propto (-t)^{-\alpha'}, \quad t \to -0, \quad 0 \leqslant \alpha' \leqslant 0.2 \end{cases}. \tag{3.21}$$

Actually, this is similar with the liquid-gas fluid system. We have the following correspondence:

$$\rho_f - \rho_g \longleftrightarrow \mathscr{M}, \quad \kappa_T \longleftrightarrow \chi, \quad p - p_c \longleftrightarrow \mathscr{H}.$$

3.8 Landau Theory of Phase Transition

In 1937, Landau proposed the concept of **order parameter**. The characteristic of continuous phase transition is the change of symmetry. The order parameter is zero in the high symmetry phase and non-zero in the low symmetry phase. For the three-dimensional homogeneous ferromagnetic system, atoms has fixed magnetic moments and the interaction energy is lower when the magnetic moments of two adjacent atoms are parallel.



Since at low temperature the system is well ordered while at high temperature the system is disordered, we can choose the order parameter as the magnetization $\mathscr{M}$. Near the critical temperature T_c, the free energy per unit volume can be expanded as

$$F(T,\mathscr{M}) = F_0(T) + \frac{1}{2}a(T)\mathscr{M}^2 + \frac{1}{4}b(T)\mathscr{M}^4 + \cdots . \tag{3.22}$$

Since F is an even function of $\mathscr{M}$, only even order terms appear in the expansion.

At a stable equilibrium, F reaches minimum, hence we have

$$\frac{\partial F}{\partial \mathscr{M}} = \mathscr{M}(a + b\mathscr{M}^2) = 0, \quad \frac{\partial^2 F}{\partial \mathscr{M}^2} = a + 3b\mathscr{M}^2 > 0 \Longrightarrow \mathscr{M} = 0, \pm\sqrt{-\frac{a}{b}}. \tag{3.23}$$

$\mathscr{M} = 0$ represents the disordered state

Landau theory is adapted to system with one-dimensional order parameter. Landau theory is a theory of mean field approximation, neglecting the fluctuation.

4 Equilibrium of Many Component Systems

4.1 Thermodynamic of Many Component Systems

A many component system contains at least two chemical substances.
First, we recall Euler's theorem.

Theorem 4.1 (Euler's Theorem)**.** *If a function $f(x_1, x_2, \cdots, x_n)$ is a homogeneous function of degree m, then we have*

$$\sum_{i=1}^{n} x_i \left(\frac{\partial f}{\partial x_i}\right) = mf. \tag{4.1}$$

Proof.

$$f(\lambda x_1, \lambda x_2, \cdots, \lambda x_n) = \lambda^m f(x_1, x_2, \cdots, x_n).$$

Differentiate both sides with respect to λ and let $\lambda = 1$, we have the conclusion. □

Consider a many component system with k components. To describe the system, we introduce the quantity of substance $n_1, n_2, \cdots, n_k$ as state variables.

$$\begin{cases} V = V(T, p, n_1, n_2, \cdots, n_k) \\ U = U(T, p, n_1, n_2, \cdots, n_k) \\ S = S(T, p, n_1, n_2, \cdots, n_k) \end{cases} \Longrightarrow \begin{cases} V = \sum_i n_i \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j} = \sum_i n_i v_i \\ U = \sum_i n_i \left(\frac{\partial U}{\partial n_i}\right)_{T,p,n_j} = \sum_i n_i u_i \\ S = \sum_i n_i \left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_j} = \sum_i n_i s_i \end{cases}, \tag{4.2}$$

where v_i, u_i, s_i are the molar volume, molar internal energy and molar entropy of component i respectively.

Consider the Gibbs function, we have

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,n_i} \mathrm{d}p + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \mathrm{d}n_i = -S\mathrm{d}T + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i, \tag{4.3}$$

By $U = G + TS - pV$, we have

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i. \tag{4.4}$$

4.2 Equilibrium Conditions of Many Component Multiphase Systems

Suppose the system contains φ phases. Consider $\delta n_i^1, \delta n_i^2, \cdots, \delta n_i^\varphi$ as the changes of the amount of substance i in each phase, then we have

$$\sum_{\alpha=1}^{\varphi} \delta n_i^\alpha = 0, \quad i = 1, 2, \cdots, k. \tag{4.5}$$

The change of Gibbs function when temperature and pressure are fixed is given by

$$\delta G^\alpha = \sum_i \mu_i^\alpha \delta n_i^\alpha \Longrightarrow \delta G = \sum_{\alpha=1}^{\varphi} \delta G^\alpha = \sum_{i=1}^{k} \sum_{\alpha=1}^{\varphi} \mu_i^\alpha \delta n_i^\alpha. \tag{4.6}$$

4.3 Gibbs Phase Rule

For water, equilibrium of three phases only exists at the triple point with $T = 0.01°C$, $p = 611.657\text{Pa}$.

Suppose that the system contains k components and φ phases and there is no chemical reaction. Replace n_i^φ by $x_i^\alpha = n_i^\alpha / n_i$, then we have

$$\sum_{i=1}^{k} x_i^\alpha = 1, \quad \alpha = 1, 2, \cdots, \varphi. \tag{4.7}$$

There are $k-1$ independent x_i^α in each phase, hence there are totally $\varphi(k-1)$ independent x_i^α.

$$f = (k+1)\varphi - (k+2)(\varphi - 1) = k - \varphi + 2. \tag{4.8}$$

4.4 Third Law

Theorem 4.2 (Nernst)**.** *As $T \to 0$, the entropy change of any isothermal process approaches zero, i.e.*

$$\lim_{T\to 0} (\Delta S)_T = 0. \tag{4.9}$$

By Maxwell relations, we have

$$\lim_{T\to 0} \alpha = \lim_{T\to 0} \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \lim_{T\to 0} -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_T = 0, \quad \lim_{T\to 0} \beta = \tag{4.10}$$

Let y be the state variable. Then by Nernst theorem, we have

$$S(0, y_B) - S(0, y_A) = 0.$$

$$C_y = T\left(\frac{\partial S}{\partial T}\right)_y = \left(\frac{\partial S}{\partial \ln T}\right)_y \Longrightarrow \lim_{T\to 0} C_y = 0. \tag{4.11}$$

$$S(T, y) = S(0, y) + \int_0^T \frac{C_y}{T} \mathrm{d}T.$$

Definition 4.3. Take $S(0, y) = 0$, then we have the **absolute entropy**:

$$S(T, y) = \int_0^T \frac{C_y}{T} \mathrm{d}T. \tag{4.12}$$

5 Most Probable Distribution of Nearly Independent Particles

5.1 Classical Description of Particle Motion

A classical particle with a degree of freedom r has generalized coordinate $q_1, q_2, \cdots, q_r$ and generalized momentum $p_1, p_2, \cdots, p_r$. The space formed by $(q_1, q_2, \cdots, q_r; p_1, p_2, \cdots, p_r)$ is called the ***μ* space** of the particle. A point in μ space represents a state of the particle and the trajectory of the point represents the evolution of the state.

Here we introduce some examples.

A free particle moving in one-dimensional space has one degree of freedom. The μ space is two-dimensional, with generalized coordinate x and generalized momentum $p = p_x = m\dot{x}$. The energy of the particle is given by

$$\varepsilon = \frac{p^2}{2m}.$$

The equal-energy surface is given by $p = \pm\sqrt{2m\varepsilon}$, which is two lines. The phase volume below the enegy ε is given by

$$\omega = 2L\sqrt{2m\varepsilon}.$$

A free particle moving in three-dimensional space has three degrees of freedom. The μ space is six-dimensional, with generalized coordinates x, y, z and generalized momenta p_x, p_y, p_z. The energy and equal-energy surface are given by

$$\varepsilon = \frac{p_x^2 + p_y^2 + p_z^2}{2m}, \quad p_x^2 + p_y^2 + p_z^2 = 2m\varepsilon,$$

which is a sphere in the three-dimensional momentum space. The phase volume below the energy ε is given by

$$\omega = \int\int\int \mathrm{d}x\mathrm{d}y\mathrm{d}z \int\int\int \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z = \frac{4}{3}\pi V(2m\varepsilon)^{3/2}.$$

A linear oscillator has one degree of freedom. The μ space is two-dimensional, with generalized coordinate $q = x$ and generalized momentum p. The energy and equal-energy surface are given by

$$\varepsilon = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2, \quad \frac{p^2}{2m\varepsilon} + \frac{x^2}{\frac{2\varepsilon}{m\omega^2}} = 1,$$

which is an ellipse in the μ space. The phase volume below the energy ε is given by

$$\omega = \int\int \mathrm{d}x\mathrm{d}p = \pi\frac{2\varepsilon}{\omega}.$$

A rigid rotator has two degrees of freedom. The μ space is four-dimensional, with generalized coordinates θ, φ and generalized momenta p_θ, p_φ. The energy is given by

$$\varepsilon = \frac{1}{2}m\left(r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\varphi}^2\right) = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right), \quad I = mr^2.$$

If there is no external force, the angular momentum $\boldsymbol{L}$ is conserved and we choose the z-axis along $\boldsymbol{L}$. Then we have

$$\theta = \frac{\pi}{2}, \quad p_\theta = 0 \Longrightarrow \varepsilon = \frac{p_\varphi^2}{2I} = \frac{L^2}{2I}.$$

5.2 Quantum Description of Particle Motion

Here we introduce some examples.

Electrons have intrinsic angular momentum (spin) and an intrinsic magnetic moment, which satisfied

$$\boldsymbol{\mu} = -\frac{e}{m}\boldsymbol{S}, \quad \mu_z = -\frac{e}{m}S_z, \quad S_z = m_s\hbar, \quad m_s = \pm\frac{1}{2}.$$

Definition 5.1. m_s is called the **spin quantum number**.

The energy of an electron in a external magnetic field is given by

$$\varepsilon = -\boldsymbol{\mu}\cdot\boldsymbol{B} = \pm\frac{e\hbar}{2m}B.$$

A rotator has quantized energy $\varepsilon = \frac{L^2}{2I}$ with $L^2 = l(l+1)\hbar^2$ and $M_z = m\hbar$ with **magnetic quantum number** $m = -l, -l+1, \cdots, l-1, l$.

A free particle in a one-dimensional room with length L satisfies

$$L = |n_x|\lambda, \quad k_x = \frac{2\pi}{L}n_x, \quad p_x = \frac{2\pi\hbar}{L}n_x, \quad \varepsilon_{n_x} = \frac{2\pi^2\hbar^2}{mL^2}n_x^2, \quad n_x = 0, \pm1, \pm2, \cdots. \tag{5.1}$$

In volume V, possible quantum states number of a free particle with energy between ε and $\varepsilon + \mathrm{d}\varepsilon$ is given by

$$D(\varepsilon)\mathrm{d}\varepsilon = \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2}\mathrm{d}\varepsilon. \tag{5.2}$$

5.3 Description of Microscopic States of Systems

For a system consisting of N nearly independent particles, the interaction between particles is negligible. The total energy of the system is given by

$$E = \sum_{i=1}^{N}\varepsilon_i.$$

There are two kinds of microscopic particles, bosons and fermions. A compound particle consisting of even number of fermions is a boson, otherwise it is a fermion and a compound particle consisting of bosons is a boson.

A system consisting of fermions is called a **Fermi system** and follows the Pauli exclusion principle. A system consisting of bosons is called a **Bose system** and does not follow the Pauli exclusion principle. A **Boltzmann system** is a system consisting of classical particles, which are distinguishable.

5.4 Principle of Equal Probability

Principle of equal probability is the basis of statistical physics.

Proposition 5.2 (Principle of Equal Probability)**.** *For an isolated system in equilibrium, all accessible microscopic states are equally probable.*

5.5 Distributions and Microscopic States

Consider a system consisting of N nearly independent particles with given E and V. Denote the energy level as ε_l and the degeneracy of the energy level as ω_l. Suppose that there are a_l particles occupying the energy level ε_l, then we denote a distribution as $\{a_l\}$, which satisfies

$$\sum_l a_l = N, \quad \sum_l a_l \varepsilon_l = E. \tag{5.3}$$

For a Boltzmann, Bose and Fermi system, the number of microscopic states corresponding to the distribution $\{a_l\}$ are given by

$$\Omega_{\text{M.B.}} = \frac{N!}{\prod_l a_l!} \prod_l \omega_l^{a_l}, \quad \Omega_{\text{B.E.}} = \prod_l \frac{(\omega_l + a_l - 1)!}{a_l!(\omega_l - 1)!}, \quad \Omega_{\text{F.D.}} = \prod_l \frac{\omega_l!}{a_l!(\omega_l - a_l)!}. \tag{5.4}$$

For a Bose or Fermi system, if we have the **classical limit condition** (**non degeneracy condition**) $\omega_l \gg a_l$, then

$$\Omega_{\text{B.E.}} = \prod_l \frac{(\omega_l + a_l - 1)(\omega_l + a_l - 2) \cdots \omega_l}{a_l!} \approx \prod_l \frac{\omega_l^{a_l}}{a_l!} = \frac{\Omega_{\text{M.B.}}}{N!}, \tag{5.5}$$

$$\Omega_{\text{F.D.}} = \prod_l \frac{\omega_l(\omega_l - 1) \cdots (\omega_l - a_l + 1)}{a_l!} \approx \prod_l \frac{\omega_l^{a_l}}{a_l!} = \frac{\Omega_{\text{M.B.}}}{N!}. \tag{5.6}$$

5.6 Boltzmann Distribution

Definition 5.3. The distribution consisting of the most microscopic states, is called the **most probable distribution**.

Proposition 5.4 (Sterling's Formula)**.** *For $m \gg 1$, we have*

$$\ln m! \approx m(\ln m - 1). \tag{5.7}$$

Proposition 5.5. *For a Boltzmann system, the most probable distribution is given by*

$$a_l = \omega_l e^{-\alpha - \beta\varepsilon_l}. \tag{5.8}$$

Proof. For a Boltzmann system, we have

$$\ln \Omega = \ln N! - \sum_l \ln a_l! + \sum_l a_l \ln \omega_l \approx N \ln N - \sum_l a_l \ln a_l + \sum_l a_l \ln \omega_l$$

$$\implies \delta\Omega = -\sum_l \ln a_l \delta a_l - \sum_l \delta a_l + \sum_l \delta a_l \ln \omega_l = -\sum_l \ln\left(\frac{a_l}{\omega_l}\right) \delta a_l = 0.$$

$\{\delta a_l\}$ satisfies $\delta N = \sum_l \delta a_l = 0$ and $\delta E = \sum_l \varepsilon_l \delta a_l = 0$. By Lagrange multiplier method, we have

$$\delta \ln \Omega - \alpha \delta N - \beta \delta E = -\sum_l \left(\ln\left(\frac{a_l}{\omega_l}\right) + \alpha + \beta\varepsilon_l\right) \delta a_l = 0 \implies a_l = \omega_l e^{-\alpha - \beta\varepsilon_l}.$$

α, β are determined by N and E. □

Actually, later we will see that $\beta = \frac{1}{k_B T}$ and $\alpha = -\frac{\mu}{k_B T}$.

5.7 Bose Distribution and Fermi Distribution

Proposition 5.6. *For a Bose system, the most probable distribution, called* ***Bose-Einstein distribution****, is given by*

$$a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} - 1}. \tag{5.9}$$

Proposition 5.7. *For a Fermi system, the most probable distribution, called* ***Fermi-Dirac distribution****, is given by*

$$a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} + 1}. \tag{5.10}$$

5.8 Relationships between Three Distributions

If $e^\alpha \gg 1$, then both Bose-Einstein distribution and Fermi-Dirac distribution reduce to Boltzmann distribution. Since

$$\frac{a_l}{\omega_l} \ll 1 \Longleftrightarrow e^\alpha \gg 1,$$

e^α is also called the classical limit condition or the non-degeneracy condition.

6 Boltzmann Statistics

6.1 Statistical Expressions of Thermodynamic Quantities

Definition 6.1. The **partition function** of a single particle is defined as

$$Z_1 = \sum_l \omega_l e^{-\beta\varepsilon_l}. \tag{6.1}$$

$$N = e^{-\alpha} Z_1, \quad U = e^{-\alpha} \sum_l \varepsilon_l \omega_l e^{-\beta\varepsilon_l} = e^{-\alpha} \left(-\frac{\partial}{\partial\beta}\right) Z_1 = -N \frac{\partial}{\partial\beta} \ln Z_1. \tag{6.2}$$

Suppose when external parameters change, the force acting on a particle of energy level ε_l is given by $\frac{\partial\varepsilon_l}{\partial y}$, then the generalized force is given by

$$Y = \sum_l a_l \frac{\partial\varepsilon_l}{\partial y} = \sum_l \omega_l e^{-\alpha-\beta\varepsilon_l} \frac{\partial\varepsilon_l}{\partial y} = e^{-\alpha} \left(-\frac{1}{\beta}\frac{\partial}{\partial y}\right) \sum_l \omega_l e^{-\beta\varepsilon_l} = -\frac{N}{\beta}\frac{\partial}{\partial y} \ln Z_1. \tag{6.3}$$

An example of generalized force is pressure

$$p = \frac{N}{\beta}\frac{\partial}{\partial V} \ln Z_1.$$

External work is given by

$$Y \mathrm{d}y = \mathrm{d}y \sum_l a_l \frac{\partial\varepsilon_l}{\partial y} = \sum_l a_l \mathrm{d}\varepsilon_l.$$

$$\mathrm{d}U = \sum_l \varepsilon_l \mathrm{d}a_l + \sum_l a_l \mathrm{d}\varepsilon_l \Longrightarrow đQ = \mathrm{d}U - Y\mathrm{d}y = \sum_l \varepsilon_l \mathrm{d}a_l.$$

Since $\mathrm{d}\ln Z_1 = \frac{\partial \ln Z_1}{\partial\beta}\mathrm{d}\beta + \frac{\partial \ln Z_1}{\partial y}\mathrm{d}y$, the entropy is given by

$$\mathrm{d}S = \frac{đQ}{T} = \frac{1}{T}\left(-N\mathrm{d}\left(\frac{\partial \ln Z_1}{\partial\beta}\right) + \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial y}\mathrm{d}y\right) = \frac{N}{\beta T}\mathrm{d}\left(\ln Z_1 - \beta\frac{\partial \ln Z_1}{\partial\beta}\right) \tag{6.4}$$

Proposition 6.2. ***Boltzmann relation*** *holds:*

$$S = k \ln \Omega = k\left(N \ln N + \sum_l a_l \ln \omega_l - \sum_l a_l \ln a_l\right). \tag{6.5}$$

Proof. □

6.2 State Equation of Ideal Gas

We consider single atom ideal gas, whose energy is given by $\varepsilon = \frac{p_x^2+p_y^2+p_z^2}{2m}$. The number of microscopic states in $\mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$ is given by

$$\frac{\mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z}{h^3} \Longrightarrow Z_1 = \frac{1}{h^3}\int\cdots\int e^{-\frac{\beta}{2m}\left(p_x^2+p_y^2+p_z^2\right)}\mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z.$$

$$Z_1 = \frac{1}{h^3}\int\int\int \mathrm{d}x\mathrm{d}y\mathrm{d}z \int e^{-\frac{\beta}{2m}p_x^2}\mathrm{d}p_x \int e^{-\frac{\beta}{2m}p_y^2}\mathrm{d}p_y \int e^{-\frac{\beta}{2m}p_z^2}\mathrm{d}p_z = V\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}. \tag{6.6}$$

Hence, the pressure is given by

$$p = \frac{N}{\beta}\frac{\partial}{\partial V}\ln Z_1 = \frac{N}{\beta V} = \frac{Nk_BT}{V}. \tag{6.7}$$

Notice that, generally, gas satisfies the classical limit condition

$$e^{\alpha} = \frac{Z_1}{N} = \frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \gg 1.$$

The average energy per particle is approximated as $\varepsilon = \pi kT \Longrightarrow \lambda = \frac{h}{p} = \frac{h}{\sqrt{2m\varepsilon}} = \frac{h}{\sqrt{2\pi m k_B T}}$. Then

$$e^{\alpha} \gg 1 \Longleftrightarrow n\lambda^3 \ll 1.$$

6.3 Maxwell Distribution of Velocity

In general, gas satisfies the classical limit condition. Hence, gas particles follow Boltzmann distribution. In volume V, the particle number with momentum in $\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$ is given by

$$\frac{V}{h^3}e^{-\alpha-\frac{1}{2mkT}\left(p_x^2+p_y^2+p_z^2\right)}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z.$$

$$\frac{V}{h^3}\iiint e^{-\alpha-\frac{1}{2mkT}\left(p_x^2+p_y^2+p_z^2\right)}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z = N \Longrightarrow e^{-\alpha} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}.$$

Hence, the particle number with velocity in $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ is given by

$$N\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-\frac{m}{2kT}\left(v_x^2+v_y^2+v_z^2\right)}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z.$$

Definition 6.3. The **Maxwell distribution** of velocity is given by

$$f(v_x,v_y,v_z)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z = \left(\frac{m}{2\pi kT}\right)^{3/2}e^{-\frac{m}{2kT}\left(v_x^2+v_y^2+v_z^2\right)}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z. \tag{6.8}$$

The particle number with speed in $\mathrm{d}v$ is given by

$$4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-\frac{mv^2}{2kT}}v^2\mathrm{d}v.$$

Definition 6.4. The **Maxwell distribution** of speed is given by

$$f(v)\mathrm{d}v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-\frac{mv^2}{2kT}}v^2\mathrm{d}v. \tag{6.9}$$

Definition 6.5. The **most probable speed**, **average speed** and **root-mean-square speed** are given by

$$\left.\frac{\mathrm{d}f}{\mathrm{d}v}\right|_{v=v_p} = 0 \Longrightarrow v_p = \sqrt{\frac{2kT}{m}},\quad \overline{v} = \sqrt{\frac{8kT}{\pi m}},\quad v_s = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}. \tag{6.10}$$

Hence

$$v_p < \overline{v} < v_s.$$

6.4 Energy Equipartition Theorem

Theorem 6.6 (Energy Equipartition Theorem)**.** *In thermal equilibrium at temperature T, the average energy associated with each quadratic degree of freedom of the particles is $\frac{1}{2}kT$.*

Proof. ε is the sum of kinetic energy ε_p and potential energy ε_q, where

$$\varepsilon_p = \frac{1}{2}\sum_{i=1}^{r} a_i p_i^2, \quad \varepsilon_q = \frac{1}{2}\sum_{i=1}^{r'} b_i q_i^2 + \varepsilon_q'\left(q_{r'+1}, \cdots, q_r\right).$$

$$\overline{\frac{1}{2}a_1 p_1^2} = \frac{1}{N}\int \frac{1}{2}a_1 p_1^2 e^{-\alpha-\beta\varepsilon}\frac{\mathrm{d}q_1\cdots\mathrm{d}q_r\mathrm{d}p_1\cdots\mathrm{d}p_r}{h_0^r} = \frac{1}{Z_1}\int \frac{1}{2}a_1 p_1^2 e^{-\beta\varepsilon}\frac{\mathrm{d}q_1\cdots\mathrm{d}q_r\mathrm{d}p_1\cdots\mathrm{d}p_r}{h_0^r}.$$

$$\int_{-\infty}^{+\infty}\frac{1}{2}a_1 p_1^2 e^{-\frac{\beta}{2}a_1 p_1^2}\mathrm{d}p_1 = \left(-\frac{p_1}{2\beta}e^{-\frac{\beta}{2}a_1 p_1^2}\right)\Bigg|_{-\infty}^{+\infty} + \int_{-\infty}^{+\infty}\frac{1}{2\beta}e^{-\frac{\beta}{2}a_1 p_1^2}\mathrm{d}p_1 \Longrightarrow$$

$$\overline{\frac{1}{2}a_1 p_1^2} = \frac{1}{2\beta Z_1}\int e^{-\beta\varepsilon}\frac{\mathrm{d}q_1\cdots\mathrm{d}q_r\mathrm{d}p_1\cdots\mathrm{d}p_r}{h_0^r} = \frac{1}{2}kT, \text{ similarly, } \overline{\frac{1}{2}b_1 q_1^2} = \frac{1}{2}kT.$$

□

For a molecule with two atoms, the evergy is given by

$$\varepsilon = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + \frac{1}{2I}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right) + \frac{1}{2m_\mu}p_r^2 + u(r).$$

Atoms in a solid vibrate about their equilibrium positions. The energy of each atom is given by

$$\varepsilon = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 q^2 \Longrightarrow \overline{\varepsilon} = 3kT, \quad U = 3NkT, \quad C_V = 3Nk.$$

Hence, every ideal solid has the same molar heat capacity, which is the same as the results by Dulong and Petit's experiment in 1819. However, at low temperature, the molar heat capacity of solid decreases rapidly to zero, which cannot be explained by classical Boltzmann statistics.

6.5 Internal Energy and Heat Capacity of Ideal Gas

The energy of a double atom ideal gas particle is given by

$$\varepsilon = \varepsilon^t + \varepsilon^r + \varepsilon^v.$$

The partition function is given by

$$Z_1 = \sum_l \omega_l e^{-\beta\varepsilon_l} = \sum_{t,v,r}\omega_t\omega_v\omega_r e^{-\beta(\varepsilon_t+\varepsilon_v+\varepsilon_r)} = Z_1^t Z_1^v Z_1^r.$$

The energy level of a linear oscillator is given by

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \cdots \Longrightarrow$$

$$Z_1^v = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}, \quad U^v = -N\frac{\partial}{\partial\beta}\ln Z_1^v = N\hbar\omega\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}\right).$$

The first term is the zero-point energy, which is independent of temperature. The second term is the excited energy at temperature T. The heat capacity contributed by vibration is given by

$$C_V^v = Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}}-1\right)^2}. \tag{6.11}$$

Definition 6.7. The **characteristic temperature** of vibration θ_v is defined as

$$k\theta_v = \hbar\omega. \tag{6.12}$$

Hence, we have

$$U^v = Nk\theta_v\left(\frac{1}{2}+\frac{1}{e^{\frac{\theta_v}{T}}-1}\right), \quad C_V^v = Nk\left(\frac{\theta_v}{T}\right)^2 \frac{e^{\frac{\theta_v}{T}}}{\left(e^{\frac{\theta_v}{T}}-1\right)^2}. \tag{6.13}$$

When $T \ll \theta_v$,

$$U^v \approx \frac{Nk\theta_v}{2} + Nk\theta_v e^{-\frac{\theta_v}{T}} \approx \frac{Nk\theta_v}{2}, \quad C_V^v \approx Nk\left(\frac{\theta_v}{T}\right)^2 e^{-\frac{\theta_v}{T}} \approx 0.$$

When $T \gg \theta_v$,

$$U^v \approx \frac{Nk\theta_v}{2} + NkT \approx NkT, \quad C_V^v \approx Nk.$$

This is the same as the prediction by classical limit condition.

The rotation energy levels of a double atom molecule, which has different nuclears, are given by

$$\varepsilon^r = \frac{l(l+1)\hbar^2}{2I}\hbar^2, \quad l = 0,1,2,\cdots \Longrightarrow Z_1^r = \sum_{l=0}^{\infty}(2l+1)e^{-\beta\frac{l(l+1)\hbar^2}{2I}}.$$

Similarly, we define the **characteristic temperature** of rotation θ_r as

$$k\theta_r = \frac{\hbar^2}{2I} \Longrightarrow Z_1^r = \sum_{l=0}^{\infty}(2l+1)e^{-\frac{\theta_r}{T}l(l+1)}.$$

For room temperature, $\theta_r \ll T$, then $x = l(l+1)\frac{\theta_r}{T}$ can be viewed as a continuous variable. Hence, we have

$$\mathrm{d}x = (2l+1)\frac{\theta_r}{T}\mathrm{d}l \Longrightarrow Z_1^r = \frac{T}{\theta_r}\int_0^{\infty} e^{-x}\mathrm{d}x = \frac{T}{\theta_r} = \frac{2I}{\beta\hbar^2}.$$

Then, the rotational internal energy and heat capacity are given by

$$U^r = NkT, \quad C_V^r = Nk.$$

Now we discuss the electron's contribution to heat capacity of gas. For most molecules, thermal motion energy is much smaller than the energy difference between the ground state and the first excited state of electron. Hence, most electrons stay in the ground state and do not contribute to heat capacity of gas.