

Thermodynamics & Statistical Physics

Review

Yuan-Chuan Zou
zouyc@hust.edu.cn

School of Physics, Huazhong University of Science and Technology

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1. Basic Laws in Thermodynamics

- 0th law of thermodynamics: Exists the T , that any two contacting systems with the same T stay in thermal equilibrium.
- 1st law of thermodynamics: $dU = \delta Q + \delta W$.
- 2nd law of thermodynamics: $dS \geq \frac{\delta Q}{T}$.
- 3rd law of thermodynamics: $T = 0\text{K}$ is unreachable.

Basic Laws in Thermodynamics

- Coefficient of cubical expansion: $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$.
- Pressure coefficient: $\beta = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V$.
- Isothermal compressibility: $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$.

Thermal capacity

- Thermal capacity (heat capacity): $C \equiv \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T}$.
- Isochoric (constant-volume) process:
 $\Delta Q = \Delta U - \Delta W = \Delta U$.
 $\therefore C_V = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta U}{\Delta T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$.
- Isobaric (constant pressure) process:
 $C_p = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta U + p\Delta V}{\Delta T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p$.

Thermodynamical functions

- Internal energy: U .
- Enthalpy: $H \equiv U + pV$.
- Entropy: $dS \equiv \frac{\delta Q}{T}$.
- Free energy: $F \equiv U - TS$.
- Gibbs function: $G \equiv F + pV (= U - TS + pV)$.
- Grand thermal potential: $J \equiv F - G = -pV$.

2. Thermodynamical properties of uniform medium

- $dU = TdS - pdV$;
- $dH = TdS + Vdp$;
- $dF = -SdT - pdV$;
- $dG = -SdT + Vdp$.
- Maxwell relations:
- $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V}$;
- $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p = \frac{\partial^2 H}{\partial S \partial p}$;
- $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial V \partial T}$;
- $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial^2 G}{\partial p \partial T}$.

Basic thermodynamical functions – Example

- Eg: Derive H, S, G of ideal gas as function of (T, p) .
- Ans: EOS: $pV_m = RT$,
 $\Rightarrow \left(\frac{\partial V_m}{\partial T}\right)_p = \frac{R}{p}$,
 $\Rightarrow V_m - T \left(\frac{\partial V_m}{\partial T}\right)_p = 0$.
- $H_m = \int \left\{ C_{p,m} dT + \left[V_m - T \left(\frac{\partial V_m}{\partial T}\right)_p \right] dp \right\} + H_{m,0}$
 $= \int C_{p,m} dT + H_{m,0}$.
- $S_m = \int \left[\frac{C_{p,m}}{T} dT - \left(\frac{\partial V_m}{\partial T}\right)_p dp \right] + S_{m,0}$
 $= \int \frac{C_{p,m}}{T} dT - \int \left(\frac{\partial V_m}{\partial T}\right)_p dp + S_{m,0}$
 $= \int \frac{C_{p,m}}{T} dT - R \ln p + S_{m,0}$.

3. Phase transition of single-component system

- Criterion of thermal equilibrium: for adiabatic system, virtual variation $\Delta S \leq 0$.
- Equilibrium condition for multi-phase system:
 $T^\alpha = T^\beta$ (thermodynamics), $p^\alpha = p^\beta$ (mechanics),
 $\mu^\alpha = \mu^\beta$ (phase).
- Classification of the phase transition:
1st order (1st order of partial differential of μ not continuous $d\mu = -S_m dT + V_m dp$);
Non-1st order – continuous phase transition.

Basics equations with chemical potential

- Open system:
- chemical potential: $\mu \equiv \frac{G}{n} = G_m = u - Ts + pv.$
- $dU = TdS - pdV + \mu dn,$
 $dH = TdS + Vdp + \mu dn,$
 $dF = -SdT - pdV + \mu dn,$
 $dG = -SdT + Vdp + \mu dn,$
 $dJ = -SdT - pdV - nd\mu.$

4. Equilibrium of multi-component system

- Description of multi-component system:
 (T, p, n_1, \dots, n_k) .
- $U(T, p, n_1, \dots, n_k) = \sum n_i u_i$.
- Equilibrium condition for multi-phase multi-component system: $T^\alpha = T^\beta$ (thermodynamics), $p^\alpha = p^\beta$ (mechanics), $\mu_i^\alpha = \mu_i^\beta$ (phase).

5. Thermodynamics of irreversible processes

- 5.1 Local equilibrium, entropy flux density and production rate.
- 5.2 Linear and nonlinear processes, Onsager relation.

6. The most probable distribution of nearly independent particles

- The principle of equal a priori probabilities.
- Object: nearly independent identical particles.
- Constraints: N, E, V .
- Aim: count the number of micro-states.

energy level	$\varepsilon_1, \varepsilon_2, \dots, \varepsilon_l, \dots$
degeneracy	$\omega_1, \omega_2, \dots, \omega_l, \dots$
particle number	$a_1, a_2, \dots, a_l, \dots$

- $\{a_l\}$ represents one kind of distribution (contains multiple micro-state), obeys: $\sum a_l = N, \sum a_l \varepsilon_l = E$.

Boltzmann, Bose and Fermi distributions

$$\bullet \Omega_M = \frac{N!}{\prod a_l!} \prod \omega_l^{a_l}, \quad \Omega_B = \prod \frac{(\omega_l + a_l - 1)!}{a_l! (\omega_l - 1)!},$$

$$\Omega_F = \prod \frac{\omega_l!}{a_l! (\omega_l - a_l)!}.$$

In the case $\frac{a_l}{\omega_l} \ll 1$, $\Omega_B \simeq \frac{\omega_l^{a_l}}{\prod a_l!}$, $\Omega_F \simeq \frac{\omega_l^{a_l}}{\prod a_l!}$.

$$\therefore \Omega_B \simeq \Omega_F \simeq \frac{\Omega_M}{N!}.$$

- Boltzmann distribution: $a_l = \frac{\omega_l}{e^{\alpha + \beta \varepsilon_l}}.$
- Fermi/Bose distribution: $a_l = \frac{\omega_l}{e^{\alpha + \beta \varepsilon_l} \pm 1}.$
- If $\alpha + \beta \varepsilon_l \gg 1$, i.e., $\frac{a_l}{\omega_l} \ll 1$, three distributions merge.
Called non-degenerate condition.

7. Boltzmann Statistics

- Partition function: $Z_1 = \sum \omega_l e^{-\beta \varepsilon_l}$.
For classical particle system, $\omega_l \rightarrow \frac{d\omega}{h_0^r}$.
- $N = e^{-\alpha} Z_1$.
- $U = -N \frac{\partial}{\partial \beta} \ln Z_1$.
- $Y = -\frac{N}{\beta} \frac{\partial \ln Z_1}{\partial y}$.
- $S = Nk(\ln Z_1 - \beta \frac{\partial \ln Z_1}{\partial \beta})$.
- $S = k \ln \Omega_M$.
- Maxwell velocity distribution:
$$f(v_x, v_y, v_z) = n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z.$$
- Maxwell speed distribution:
$$f(v)dv = 4\pi n \left(\frac{m}{2kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT}v^2} v^2 dv.$$
- Energy equipartition theorem.

8. Bose statistics and Fermi statistics

- Grand partition function for Fermion/Boson system:

$$\mathcal{Z} = \prod \mathcal{Z}_l = \prod (1 \pm e^{-\alpha - \beta \epsilon_l})^{\pm \omega_l}.$$

$$\ln \mathcal{Z} = \pm \sum \omega_l \ln(1 \pm e^{-\alpha - \beta \epsilon_l}).$$

- $N = -\frac{\partial}{\partial \alpha} \ln \mathcal{Z}.$

- $U = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}.$

- $Y = -\frac{1}{\beta} \frac{\partial}{\partial y} \ln \mathcal{Z}.$

- $S = Nk(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}).$

- $S = k \ln \Omega.$

- $J = -kT \ln \mathcal{Z}$

- Method for Bose(Fermi) statistics:

$$\{\epsilon_l\}, \{\omega_l\} \rightarrow \ln \mathcal{Z}(\alpha, \beta, y)$$

\rightarrow Other thermal variables ($N, U, S \dots$).

9. Ensemble theory

- The microcanonical ensemble:
isolated system.
- The principle of equal a priori probabilities.
- Canonical ensemble:
contact with thermal reservoir.
- Partition function: $Z = \sum_s e^{-\beta E_s}$.
- $U = -\frac{\partial}{\partial \beta} \ln Z$.
- $Y = -\frac{1}{\beta} \frac{\partial}{\partial y} \ln Z$.
- $S = k(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z)$.
- $F = -kT \ln Z$.

Grand canonical ensemble

- Grand canonical ensemble: open system with reservoir.
- The grand partition function: $\mathcal{Z} = \sum_{N=0}^{\infty} \sum_s e^{-\alpha N - \beta E_s}$.
- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}$.
- $U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$.
- $Y = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial y}$.
- $S = k(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta})$.
- $J = -kT \ln \mathcal{Z}$.

10. Fluctuation

- $W \propto e^{-\frac{C_V}{2kT^2}(\Delta T)^2 + \frac{1}{2kT}(\frac{\partial p}{\partial V})_T(\Delta V)^2}$.
- The probability for the system with deviation ΔT and ΔV : $\overline{(\Delta T)^2} = \frac{kT^2}{C_V}$, $\overline{(\Delta V)^2} = -kT(\frac{\partial V}{\partial p})_T = kTV\kappa_T$.
- Brownian motion:
- Langevin's equation: $m\frac{d^2x}{dt^2} = -\alpha\frac{dx}{dt} + F(t) + \mathcal{F}(t)$.
- $t \gg \tau$, $\overline{x^2} \simeq \frac{2kT}{\alpha}t \propto t$.

11. Statistical mechanics for non-equilibrium processes

- Relaxation time approximation of Boltzmann's equation:

$$\frac{\partial f}{\partial t} = -\left(v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z}\right) - \frac{f - f^{(0)}}{\tau_0}.$$

- Boltzmann integro-differential equation:

$$\begin{aligned} \frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} \\ = \iint (f' f'_1 - f f_1) d\omega_1 \Lambda d\Omega. \end{aligned}$$

- H theorem: $\frac{dH}{dt} \leq 0$,
 $f f_1 = f' f'_1$ for detailed balance.

Clues for the applications

- Applications:

- 1 Ideal gas

- 2 Blackbody radiation

- 3 Magnetized material

App 1: Ideal gas – Thermodynamics

- Ideal gas EOS: $pV = nRT$.
- Real gas: van der Waals approximation:

$$(p + \frac{an^2}{V^2})(V - nb) = nRT.$$
- Internal energy (ideal gas): $U(T, V) \rightarrow U(T)$.

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT}; C_p = \frac{dH}{dT} = C_V + nR; \gamma \equiv \frac{C_p}{C_V}.$$
- Adiabatic process of the ideal gas: $pV^\gamma = \text{Const.}$
- Carnot cycle in the ideal gas:
 - 1 Isothermal expansion: absorb heat $Q_1 = RT_1 \ln \frac{V_2}{V_1}$;
 - 2 Adiabatic expansion: $Q = 0$;
 - 3 Isothermal compression: release heat $Q_2 = RT_2 \ln \frac{V_3}{V_4}$;
 - 4 Adiabatic compression: $Q = 0$.

App 1: Ideal gas – Thermodynamics

- Entropy of ideal gas:

$$S_m = C_{V,m} \ln T + R \ln V_m + S_{m,0}, \text{ or}$$

$$S_m = \int \frac{C_{p,m}}{T} dT - R \ln p + S_{m,0} \text{ if } C_{p,m} \text{ is not a constant.}$$

- $H_m = \int C_{p,m} dT + H_{m,0}.$

- $G_m =$
 $\int C_{p,m} dT - T \int \frac{C_{p,m}}{T} dT + TR \ln p + H_{m,0} - TS_{m,0}.$

App 1: Ideal gas. – In Boltzmann statistics.

- Equation of state of ideal gas: a simple application of Boltzmann statistics.
- Object: ideal gas with monatomic molecule, nearly independent.
- Energy of each particle: $\varepsilon = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$.
- Micro-states number: $\frac{dx dy dz dp_x dp_y dp_z}{h^3}$.
- Partition function:

$$\begin{aligned}
 Z_1 &= \frac{1}{h^3} \int \dots \int e^{-\beta \varepsilon_l} dx dy dz dp_x dp_y dp_z \\
 &= \frac{1}{h^3} \iiint dx dy dz \iiint e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)} dp_x dp_y dp_z \\
 &= \frac{V}{h^3} \int_{-\infty}^{+\infty} e^{-\frac{\beta}{2m}p_x^2} dp_x \int_{-\infty}^{+\infty} e^{-\frac{\beta}{2m}p_y^2} dp_y \int_{-\infty}^{+\infty} e^{-\frac{\beta}{2m}p_z^2} dp_z \\
 &= \left(\frac{2\pi m}{h^2 \beta}\right)^{\frac{3}{2}} V.
 \end{aligned}$$

App 1: Ideal gas. – In Boltzmann statistics.

- $p = \frac{N}{\beta} \frac{\partial \ln Z_1}{\partial y} = \frac{N}{\beta} \frac{\partial \ln Z_1}{\partial V} = \frac{N}{\beta} \frac{\partial \ln[(\frac{2\pi m}{h^2 \beta})^{\frac{3}{2}} V]}{\partial V} = \frac{N}{\beta} \frac{1}{V} = \frac{NkT}{V}.$
- Comparing with $pV = nRT$, $k = \frac{n}{N}R$ is determined.
- $f(v_x, v_y, v_z)dv_x dv_y dv_z$
 $= n(\frac{m}{2\pi kT})^{\frac{3}{2}} e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z.$
 $f(v_x, v_y, v_z)$ is the Maxwell velocity distribution.
 Obeys $\iiint f(v_x, v_y, v_z)dv_x dv_y dv_z = n.$
- Speed distribution: $f(v)dv = 4\pi n(\frac{m}{2kT})^{\frac{3}{2}} e^{-\frac{m}{2kT}v^2} v^2 dv.$
- Internal energy (monatomic):
 $U = -N \frac{\partial}{\partial \beta} \ln Z_1 = \frac{3}{2} NkT.$
- Entropy: $S = Nk(\ln Z_1 - \beta \frac{\partial}{\partial \beta} \ln Z_1) - k \ln N!$
 $= \frac{3}{2} Nk \ln T + Nk \ln \frac{V}{N} + \frac{3}{2} Nk [\frac{5}{3} + \ln \frac{2\pi mk}{h^2}].$

App 1: Ideal gas. – In microcanonical ensemble theory

- $d\Omega = dq_1 \dots dq_f dp_1 \dots dp_f$
 $= dq_{11} dq_{12} dq_{13} \dots dq_{N3} dp_1 \dots dp_f,$
 $\therefore \Omega = \frac{1}{N!} \frac{1}{h^{Nr}} \int d\Omega = CV^N, C \text{ does not depend on } q.$
- $\frac{p}{kT} = \gamma = \frac{\partial \ln \Omega}{\partial V} = \frac{\partial \ln V^N}{\partial V} = \frac{N}{V}. \Rightarrow pV = NkT.$
- Hamiltonian: $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}.$
- $\Omega(N, E, V) = \frac{1}{N! h^{3N}} \int_{(E, E+\Delta E)} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}$
 $= \frac{1}{N! h^{3N}} \left(\int_{H \leq E+\Delta E} d\Omega - \int_{H \leq E} d\Omega \right).$ Provable:
 $\int_{H \leq E} d\Omega = V^N \int_{H \leq E} dp_1 \dots dp_{3N} = V^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{(\frac{3}{2}N)!};$

App 1: Ideal gas. – In microcanonical ensemble theory

- $$\Omega(N, E, V) = \left(\frac{V}{h^3}\right)^N \cdot \frac{(2\pi m)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!} \left[(E + \Delta E)^{\frac{3}{2}N} - E^{\frac{3}{2}N} \right]$$

$$\simeq \frac{3}{2}N \cdot \left(\frac{V}{h^3}\right)^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!} \frac{\Delta E}{E}.$$
- Entropy:** $S = k \ln \Omega \simeq Nk \ln \left[\left(\frac{V}{h^3 N}\right) \left(\frac{4\pi m E}{3N}\right)^{\frac{3}{2}} \right] + \frac{5}{2}Nk.$
- $$\Rightarrow E(N, S, V) = \frac{3h^2 N^{\frac{5}{3}}}{4\pi m V^{\frac{2}{3}}} e^{\left(\frac{2S}{3Nk} - \frac{5}{3}\right)}.$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V} = \frac{2}{3} \frac{E}{Nk}, \Rightarrow E = \frac{3}{2}NkT.$$

$$p = -\left(\frac{\partial E}{\partial V}\right)_{N,S} = \frac{2}{3} \frac{E}{V}.$$
- $$\Rightarrow pV = NkT, S = Nk \ln \left[\frac{V}{N} \left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} \right] + \frac{5}{2}Nk.$$

Same as eq. (7.6.2).

App 1: Ideal gas. – Real gas in ensemble theory

- 1st step: partition function:

$$Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N};$$

- 2nd step: thermal quantities: $p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z$.
- E (kinetic energy and potential energy):

$$E = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i < j} \phi(\vec{r}_{ij}).$$

- Kinetic term of E : $\int e^{-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}} dp_1 \dots dp_{3N}$

$$= \int e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}} dp_1 \dots dp_{3N} = \prod_{i=1}^{3N} \int e^{-\beta \frac{p_i^2}{2m}} dp_i = \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}N}.$$

- Potential part: $Q \equiv \int e^{-\beta \sum_{i < j} \phi(\vec{r}_{ij})} dq_1 \dots dq_{3N}.$

App 1: Ideal gas. – Real gas in ensemble theory

- Then the partition function: $Z = \frac{1}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}N} Q$.
- If the interacting is weak, i.e., $\phi(\vec{r}_{ij}) \rightarrow 0$, then $f_{ij} \rightarrow 0$. Only keep the first two terms:

$$Q = \int (1 + \sum_{i < j} f_{ij}) d\tau_1 \dots d\tau_N.$$
- Semi-empirical formula: $\phi(r) = \phi_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right]$.
 Approximation: $\phi(r) \rightarrow \infty$ if $r < r_0$; $\phi(r) = -\phi_0 \left(\frac{r_0}{r} \right)^6$ if $r > r_0$.
- $p = \frac{1}{\beta} \frac{\partial}{\partial \beta} \ln Z = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Q = \frac{NkT}{V-nb} - \frac{n^2 a}{V^2}$, where
 $b = \frac{2}{3} \pi N_A r_0^3$, $a = \frac{2}{3} \pi N_A^2 \phi_0 r_0^3$.
 Or $(p + \frac{n^2 a}{V^2})(V - nb) = NkT$.
 van der Waals equation (3.5.2).

App 2: Blackbody radiation – Thermodynamics

- Thermodynamical function for the equilibrium radiation inside the cavity.
- State parameter: (p, V, T) . EOS: $p = u/3$.
- Uniform $\rightarrow U(T, V) = u(T)V$,
- as $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p, \Rightarrow u = \frac{T}{3} \frac{du}{dT} - \frac{u}{3},$
 $\Rightarrow T \frac{du}{dT} = 4u, \Rightarrow u = aT^4$, where a is the integration constant.
- Entropy S : $dS = \frac{dU + pdV}{T} \Rightarrow S = \frac{4}{3}aT^3V$.
- In adiabatic process, $dS = 0 \Rightarrow VT^3 = \text{const.}$
- Gibbs function G : $G = U - TS + pV = 0$.
- $J_u = \frac{1}{4}cu$: energy from unit area in unit time.

App 2: Blackbody radiation – Photon gas in Bose statistics

- Number of quantum states: $2 \cdot \frac{V4\pi p^2 dp}{h^3} = \frac{8\pi V p^2 dp}{h^3}$,
where 2 is because of the polarization.
- Convert to frequency $\hbar\omega = \varepsilon = pc, \Rightarrow p = \frac{\hbar\omega}{c}$,

$$D(\omega)d\omega = \frac{8\pi V (\frac{\hbar\omega}{c})^2 d(\frac{\hbar\omega}{c})}{h^3} = \frac{V}{\pi^2 c^3} \omega^2 d\omega.$$
- Number of photons at $(\omega, \omega + d\omega)$:

$$a(\omega)d\omega = \frac{V}{\pi^2 c^3} \frac{\omega^2 d\omega}{e^{\frac{\hbar\omega}{kT}} - 1}.$$
- Internal energy: $U(\omega, T)d\omega = \frac{V}{\pi^2 c^3} \frac{\hbar\omega^3 d\omega}{e^{\frac{\hbar\omega}{kT}} - 1}.$
- Total internal energy: $U = \int_0^\infty U(\omega, T)d\omega$

$$= \int_0^\infty \frac{V}{\pi^2 c^3} \frac{\hbar\omega^3 d\omega}{e^{\frac{\hbar\omega}{kT}} - 1} = \frac{\pi^2 k^4}{15c^3 \hbar^3} T^4 V = aT^4 V. \quad (a = \frac{\pi^2 k^4}{15c^3 \hbar^3}).$$

App 2: Blackbody radiation – Photon gas in Bose statistics

- Grand partition function for the photons:

$$\ln \mathcal{Z} = - \sum \omega_l \ln(1 - e^{-\alpha - \beta \varepsilon_l}) = \frac{\pi^2 V}{45 c^3} \frac{1}{(\beta \hbar)^3}.$$

- Internal energy:

$$U = - \frac{\partial}{\partial \beta} \ln \mathcal{Z} = - \frac{\pi^2 V}{45 c^3} \frac{1}{\hbar^3} \frac{-3}{\beta^4} = \frac{\pi^2 k^4}{15 c^3 \hbar^3} T^4 V.$$

- Pressure:

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln \mathcal{Z} = \frac{1}{\beta} \frac{\pi^2}{45 c^3} \frac{1}{(\beta \hbar)^3} = \frac{\pi^2 k^4}{45 c^3 \hbar^3} T^4 V = \frac{1}{3} \frac{U}{V}.$$

- Entropy:

$$\begin{aligned} S &= k \left(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta} \right) = k \left(\ln \mathcal{Z} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta} \right) \\ &= k \left[\frac{\pi^2 V}{45 c^3} \frac{1}{(\beta \hbar)^3} + \beta \frac{\pi^2 k^4}{15 c^3 \hbar^3} T^4 V \right] \\ &= k \left(\frac{\pi^2 V}{45 c^3} \frac{k^3 T^3}{\hbar^3} + \frac{\pi^2 V}{15 c^3} \frac{k^3 T^3}{\hbar^3} \right) = \frac{4}{45} \frac{\pi^2 k^4 V}{c^3 \hbar^3} T^3. \end{aligned}$$

App 3: Magnetized material – Thermodynamics

- Object: paramagnetic material.
- Start from $\delta W = V d(\frac{\mu_0}{2} \mathcal{H}^2) + \mu_0 V \mathcal{H} dM - p dV$.
- For magnetic medium, neglecting the small volume change, $\delta W = \mu_0 V \mathcal{H} dM$,
setting the total magnetic momentum $m = MV$,
 $\delta W = \mu_0 \mathcal{H} dm$; $-p \rightarrow \mu_0 \mathcal{H}$, $V \rightarrow m$.
- $G = U - TS - \mu_0 \mathcal{H} m$, $dG = -S dT - \mu_0 m d\mathcal{H}$.
 $-S = (\frac{\partial G}{\partial T})_{\mathcal{H}}$, $-\mu_0 m = (\frac{\partial G}{\partial \mathcal{H}})_T$, $\frac{\partial^2 G}{\partial T \partial \mathcal{H}} = \frac{\partial^2 G}{\partial \mathcal{H} \partial T}$.
 $\Rightarrow (\frac{\partial S}{\partial \mathcal{H}})_T = \mu_0 (\frac{\partial m}{\partial T})_{\mathcal{H}}$, Maxwell's relation for magnetic medium.
- Thermal capacity: $C_{\mathcal{H}} = T (\frac{\partial S}{\partial T})_{\mathcal{H}}$.
- EOS (Cruie's law): $m = \frac{CV}{T} \mathcal{H}$.

App 3: Magnetized material – In Boltzmann statistics

- Object: paramagnetic particles fixed on the crystal lattice.
- Simplification: Magnetic quantum number $\frac{1}{2}$.
- In the external magnetic field B , only two choices of quantum number $\pm\frac{1}{2}$ (parallel or anti-parallel to B).
- Energy level: $\pm\mu B$. (μ is the magnetic momentum.)
- Partition function: $Z_1 = \sum \omega_l e^{-\beta \epsilon_l} = e^{\beta \mu B} + e^{-\beta \mu B}$.
- Remind e.q.(2.7.19), $\text{d}W = -\mu_0 m \text{d}\mathcal{H}$. ($-\mu_0 m$ generalized force, \mathcal{H} generalized displacement.)
e.q.(7.1.6), $Y = -\frac{N}{\beta} \frac{\partial}{\partial y} \ln Z_1$.
 $\therefore -\mu_0 m = -\frac{N}{\beta} \frac{\partial}{\partial \mathcal{H}} \ln Z_1$.

App 3: Magnetized material – In Boltzmann statistics

- $-\mu_0 \frac{m}{V} = -\frac{N}{V\beta} \frac{\partial}{\partial \mathcal{H}} \ln Z_1$
 $\Rightarrow M = \frac{n}{\beta} \frac{\partial}{\partial (\mu_0 \mathcal{H})} \ln Z_1 = n\mu \frac{e^{\frac{2\mu B}{kT}} - 1}{e^{\frac{2\mu B}{kT}} + 1}.$
- $\frac{\mu B}{kT} \ll 1$, $M \simeq n\mu \frac{2\mu B}{2} = \frac{n\mu^2}{kT} B$, Curie's law.
- $\frac{\mu B}{kT} \gg 1$, $M \simeq n\mu$, saturation.
- Internal energy density: $u = -n \frac{\partial}{\partial \beta} \ln Z_1 = -MB$, potential energy in the external field.
- Entropy density: $s = nk(\ln Z_1 - \beta \frac{\partial}{\partial \beta} \ln Z_1)$
 $= nk \left[\ln(e^{\frac{2\mu B}{kT}} + 1) - \frac{\mu B}{kT} \frac{2e^{\frac{2\mu B}{kT}}}{e^{\frac{2\mu B}{kT}} + 1} \right].$
- $\frac{\mu B}{kT} \ll 1$, $s = nk \ln 2 = k \ln 2^n$, states: 2^n .
- $\frac{\mu B}{kT} \gg 1$, $s \simeq 0$, only one micro-state.

App 3: Magnetized material – In Ensemble theory

- Ising Model – Ferromagnet.
- Potential energy between two magnetic momenta: $J_1 \vec{\mu}_1 \cdot \vec{\mu}_2$, where J_1 is a coefficient depending on position.
- $J_1 \vec{\mu}_1 \cdot \vec{\mu}_2 = J_2 \sigma_1 \sigma_2$.
- Ising model: Similar form for the total interacting energy between two lattice points: $-J \sigma_1 \sigma_2$, where J is a constant for neighbours, 0 for others.
- Total interacting energy: $-J \sum'_{i,j} \sigma_i \sigma_j$, where $\sum'_{i,j}$ means the summation only exerts on the neighbours.

App 3: Magnetized material – In Ensemble theory

- In external magnetic field, the total energy:

$$E\{\sigma_i\} = -J \sum'_{i,j} \sigma_i \sigma_j - \mu B \sum_i \sigma_i.$$

- The partition function: $Z = \sum_s e^{-\beta E_s} = \sum_{\{\sigma_i\}} e^{-\beta E\{\sigma_i\}}$

$$= \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \cdots \sum_{\sigma_N=\pm 1} e^{-\beta E\{\sigma_i\}}.$$

- Important subject to solve it.
- An approximation solution: mean field approximation.
- Rewrite the total energy:

$$E\{\sigma_i\} = -\frac{1}{2} \sum_{i,j} J_{ij} \sigma_i \sigma_j - \mu B \sum_i \sigma_i, \text{ where } J_{ij} = J \text{ for } i \text{ and } j \text{ being neighbours, } 0 \text{ for other.}$$

App 3: Magnetized material – In Ensemble theory

- The total energy is then: $E = -\mu \bar{B} \sum_i \sigma_i$.
- The partition function: $Z = \prod_i \sum_{\sigma_i} e^{\beta \mu \bar{B} \sigma_i}$
 $= \prod_i (e^{\beta \mu \bar{B}} + e^{-\beta \mu \bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta \mu \bar{B}} + e^{-\beta \mu \bar{B}}$.
- $\bar{m} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \bar{B}} = \frac{N}{\beta} \frac{\partial \ln Z_1}{\partial \bar{B}} = N \mu \frac{e^{\beta \mu \bar{B}} - e^{-\beta \mu \bar{B}}}{e^{\beta \mu \bar{B}} + e^{-\beta \mu \bar{B}}}$.
- On the other hand, $\bar{m} = N \mu \bar{\sigma}$. $\Rightarrow \bar{\sigma} = \frac{e^{\beta \mu \bar{B}} - e^{-\beta \mu \bar{B}}}{e^{\beta \mu \bar{B}} + e^{-\beta \mu \bar{B}}}$.
- Without external field, $\bar{B} = \frac{1}{\mu} J z \bar{\sigma}$. $\rightarrow \beta \mu \bar{B} = \beta J z \bar{\sigma}$.
 $Z_1 = e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}$.
- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N k T_c \bar{\sigma}^2$.
- Phase transition at $(\beta J z = 1)$: $T_c = \frac{J z}{k}$.