Statistical Mechanics Notes

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Contents

1 Fundamentals of Statistical Mechanics

1.1 Micro Canonical Ensemble (NVU Ensemble)

Consider two systems in contact with fixed total energy and fixed individul particle number, the probability density function is:

$$P(\mathcal{H}) \sim \delta(E - \mathcal{H}(p, q))$$

We have the following expression for the total multiplicity:

$$\Omega = \sum_{U_1 + U_2 = U} \Omega_1(U_1)\Omega_2(U_2)$$

We now want to find when thermal equilibrium is reached, a.k.a. the most probable state. Since the particle numbers are held constant, we only differentiate with respect to the energies:

$$\mathrm{d}\Omega = \Omega_2 \frac{\partial \Omega_1}{\partial U_1} \, \mathrm{d}U_1 + \Omega_1 \frac{\partial \Omega_2}{\partial U_2} \, \mathrm{d}U_2 = 0$$

dividing both sides by $\Omega_1\Omega_2$, and applying $\mathrm{d}U_1 + \mathrm{d}U_2 = 0$, we get:

$$\frac{\partial \ln \Omega_1}{\partial U_1} = \frac{\partial \ln \Omega_2}{\partial U_2}$$

from which we arrive at the definition of entropy and temperature.

Definition 1.1. Entropy and Temperature

$$S := k \ln \Omega \,, \quad \frac{1}{T} := \left(\frac{\partial S}{\partial U} \right)_{N,V}$$

Consider an ensemble of possible quantum states labeled i, particles in this system have probability p_i of being in the i th state, then

$$\ln \Omega = \ln \left(\frac{N!}{\prod_i N_i!} \right) = -\sum_i \frac{N_i}{N} \ln \left(\frac{N_i}{N} \right) = -\sum_i p_i \ln p_i$$

thus

Formula 1.1. Gibbs Entropy

$$S = -k \sum_i p_i \ln p_i$$

For a more rigorous and generalized approach, we take the logarithm at the first step:

$$\ln \Omega = \ln \Omega_1 + \ln \Omega_2 + \ldots$$

which shows that entropy is additive, using the Lagrange multipliers we obtain the zeroth law of thermodynamics.

Law 1.1. Zeroth Law of Thermodynamics
Under thermal equilibrium:

$$\sum \left(\frac{\partial \ln \Omega_i}{\partial U_i} - \beta \right) \mathrm{d}U_i = 0 \,, \quad \beta = \frac{1}{kT}$$

1.2 Canonical Ensemble (NVT Ensemble)

Fixing the total energy of a system in contact with an environment is unrealistic, we thus need a different approach. Consider a closed two state system $\mathcal{S}$ in contact with a large reservoir $\mathcal{R}$, the two state system can either be in excited state with energy E or in ground state. The total energy of the reservoir and the two state system is $U(\gg E)$. The total multiplicity of the excited state is:

$$\ln \Omega = \ln \Omega_{\mathcal{R}}(U - E) + \ln \Omega_{\mathcal{S}}(E)$$
$$= \ln \Omega_{\mathcal{R}}(U) - \frac{\partial \ln \Omega_{\mathcal{R}}}{\partial U} E + \ln g(E)$$
$$= \ln \Omega_{\mathcal{R}}(U) - \beta E + \ln g(E)$$

this is the Boltzmann distribution:

$$P(E) \sim \exp(-\beta E)$$

Definition 1.2. Partition Function
The partition function is defined as the sum of all possibilities of the states:

$$Z := \sum_{\text{quantum state}} e^{-\beta E_{\text{state}}} = \sum_{n} g(E_n) \exp(-\beta E_n)$$

where $g(E_n)$ is the degeneracy of the nth energy eigenstate.
The partition function is relatively easy to evaluate, from which other physical quantities can be obtained.

Formula 1.2. Internal Energy
The total internal energy is:

$$U = \frac{\sum E_n P(E_n)}{\sum P(E_n)} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

Formula 1.3. Helmholtz Free Energy
We perform Legendre transformation on U and substitute β for T

$$U := F + TS = F - T \frac{\partial F}{\partial T} = F + \beta \frac{\partial F}{\partial \beta} = \frac{\partial}{\partial \beta}(\beta F)$$

sub in $U = -\dfrac{\partial \ln Z}{\partial \beta}$, we have:

$$F = -kT(\ln Z + \text{const.})$$

since $S = -\dfrac{\partial F}{\partial T} = k(\ln Z + \text{const.})$, and when $T \to 0$, $S \to 0$, the constant is 0. Thus:

$$F = -kT \ln Z$$

1.3 Macro Canonical Ensemble (μVT Ensemble)

Now we consider the most generalized case in which the particle number also fluctuates. Take a small system $\mathcal{S}$ and a large reservoir $\mathcal{R}$, this time they can exchange not only energy but also particles. The total multiplicity is therefore:

$$\ln \Omega = \ln \Omega_{\mathcal{R}}(U - E_{\mathcal{S}}, N - N_{\mathcal{S}}) + \ln \Omega_{\mathcal{S}}(E_{\mathcal{S}}, N_{\mathcal{S}})$$
$$= \ln \Omega_{\mathcal{R}}(U, N) - \frac{\partial \ln \Omega_{\mathcal{R}}}{\partial U} E_{\mathcal{S}} - \frac{\partial \ln \Omega_{\mathcal{R}}}{\partial N} N_{\mathcal{S}} + \ln g(E_{\mathcal{S}}, N_{\mathcal{S}})$$
$$= \ln \Omega_{\mathcal{R}}(U, N) - \beta E_{\mathcal{S}} + \alpha N_{\mathcal{S}} + \ln g(E_{\mathcal{S}}, N_{\mathcal{S}})$$

Recall the identity:

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

Referring back to classical thermodynamics we have: $\left(\frac{\partial U}{\partial N}\right)_S = \mu$, thus:

$$-\left(\frac{\partial S}{\partial N}\right)_U = \left(\frac{\partial S}{\partial U}\right)_N \left(\frac{\partial U}{\partial N}\right)_S = \frac{\mu}{T} \Rightarrow \alpha = \frac{\mu}{kT} = \beta \mu$$

subbing in α we arrive at the grand canonical distribution:

$$P(E, N) \sim \exp(-\beta(E - \mu N))$$

Definition 1.3. Grand Partition Function

$$\mathcal{Z} = \sum_{\text{states}} \exp(-\beta(E - \mu N)) = \sum_{n,m} g(E_n, N_m) \exp(-\beta(E_n - \mu N_m))$$

where n, m denotes levels with these quantum numbers, naturally

Formula 1.4.

$$U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \;,\; \langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

1.4 Minimal Information Principle

An alternative approach to obtain the different ensembles is to assume that natural opts for the distribution that carries the least information, that is, it maximized the Gibbs entropy. Assumptions we make on systems can be introduced by imposing constraint via Lagrange multipliers when maximizing the entropy.

Example 1.1. Macro Canonical Ensemble
Entropy:

$$S_G = -k \sum_{\text{states}} p \ln p$$

Constraints:

$$\langle E \rangle = \sum_{\text{states}} P(\text{states}) E(\text{states}) \;,\; \langle N \rangle = \sum_{\text{states}} P(\text{states}) N(\text{states}) \;,$$

2   Distributions

Different assumptions on the properties of particles will produce different distribution functions.

2.1   Maxwell Boltzmann Distribution

Distribution of distinguishable classical ideal gas particles follow:

$$f_{\mathrm{MB}} = e^{-\beta(E-\mu)}$$

The total multiplicity is:

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

with homogeneous constraints:

$$\sum_i n_i = N \ , \ \ \sum_i n_i E_i = U$$

apply Lagrange multipliers to find the distribution when entropy is maximized:

$$\frac{\partial \ln \Omega}{\partial n_i} + \alpha - \beta E_i = 0$$

$$\Rightarrow \frac{g_i}{n_i} = \exp(-\alpha + \beta E_i)$$

$$\Rightarrow n_i = g_i \exp(-\beta(E_i - \mu))$$

2.2   Bose Einstein Distribution

Bosons can occupy the same state, thus they follow the distribution function:

$$f_{\mathrm{BE}}(E) = \frac{1}{e^{\beta(E-\mu)} - 1}$$

Using micro canonical ensemble, the total multiplicity is:

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

with homogeneous constraints:

$$\sum_i n_i = N \ , \ \ \sum_i n_i E_i = U$$

Differentiate the multiplicity with respect to n_i:

$$\ln \Omega = \sum_i \ln(n_i + g_i - 1)! - \ln n_i! - \ln(g_i - 1)!$$

$$\mathrm{d} \ln \Omega \approx \sum_i \frac{\partial}{\partial n_i} \left((n_i + g_i - 1) \ln(n_i + g_i - 1) - n_i \ln n_i \right) \mathrm{d} n_i$$

$$\approx \sum_i \ln \left(\frac{g_i}{n_1} + 1 \right) \mathrm{d} n_i$$

then apply Lagrange multipliers to find the distribution when entropy is maximized:

$$\frac{\partial \ln \Omega}{\partial n_i} + \alpha - \beta E_i = 0$$

$$\Rightarrow \frac{g_i}{n_i} + 1 = \exp(-\alpha + \beta E_i)$$

$$\Rightarrow n_i = \frac{g_i}{\exp(\beta E_i - \alpha) - 1} = \frac{g_i}{\exp(\beta(E_i - \mu)) - 1}$$

2.3 Fermi Dirac Distribution

Fermions obey Pauli's exclusion principle, thus they follow the distribution function:

$$f_{\text{FD}}(E) = \frac{1}{e^{\beta(E-\mu)} + 1}$$

Using micro canonical ensemble, the total multiplicity is:

$$\Omega = \prod_i C_{n_i}^{g_i} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$$

with homogeneous constraints:

$$\sum_i n_i = N , \quad \sum_i n_i E_i = U$$

Differentiate the multiplicity with respect to n_i:

$$\ln \Omega = \sum_i \ln g_i! - \ln n_i! - \ln(g_i - n_i)!$$

$$\mathrm{d}\ln \Omega \approx \sum_i \frac{\partial}{\partial n_i} \left(-n_i \ln n_i - (g_i - n_i) \ln(g_i - n_i) \right) \mathrm{d}n_i$$

$$= \sum_i \ln \left(\frac{g_i}{n_i} - 1 \right) \mathrm{d}n_i$$

then apply Lagrange multipliers to find the distribution when entropy is maximized:

$$\frac{\partial \ln \Omega}{\partial n_i} + \alpha - \beta E_i = 0$$

$$\Rightarrow \frac{g_i}{n_i} - 1 = \exp(-\alpha + \beta E_i)$$

$$\Rightarrow n_i = \frac{g_i}{\exp(\beta E_i - \alpha) + 1} = \frac{g_i}{\exp(\beta(E_i - \mu)) + 1}$$

2.4 Quantum Mechanical Ensemble Theory

I don't wanna.

3 Kinetic Theory of Ideal Gases

Kinetic Theory is the connection between the micro and macro world.

3.1 Maxwell-Boltzmann Distribution

According to Boltzmann distribution, the probability of a particle with velocity $(v_x, v_y, v_z) \sim (v_x + \mathrm{d}v_x, v_y + \mathrm{d}v_y, v_z + \mathrm{d}v_z)$ can be written as:

$$f(v_x, v_y, v_z)\, \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z \sim \exp\left(-\frac{1}{2}\beta m v_x^2\right) \exp\left(-\frac{1}{2}\beta m v_y^2\right) \exp\left(-\frac{1}{2}\beta m v_z^2\right) \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z$$

its speed is $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$, therefore the probability of the particle being at speed $v \sim v + \mathrm{d}v$ is:

$$
\begin{aligned}
f(v)\, \mathrm{d}v &= \left(\int_{-\infty}^{\infty} \exp\left(-\frac{m v_i^2}{2kT}\right) \mathrm{d}v_i\right)^{-3} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right) \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z \\
&= \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m v^2}{2kT}\right) v^2 \sin\theta\, \mathrm{d}v\, \mathrm{d}\theta\, \mathrm{d}\phi \\
&= \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m v^2}{2kT}\right) 4\pi v^2\, \mathrm{d}v \quad \text{(integrated over the solid angle)}
\end{aligned}
$$

The root mean square velocity is:

$$\sqrt{\langle v^2 \rangle} := v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}}$$

the mean speed is:

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

the speed of maximum probability is:

$$v_{\mathrm{mp}} = \sqrt{\frac{2kT}{m}}$$

3.2 Equal Partition Theorem

There is energy $\frac{1}{2}kT$ for every degree of freedom with energy of the form: $E \propto x^2$, where x is either the generalized coordinate or the generalized momentum.

proof.

$$E = \alpha x^2 \Rightarrow P(x)\, \mathrm{d}x \propto \exp\left(-\beta \alpha x^2\right) \mathrm{d}x$$

Thus:

$$\langle E \rangle = \frac{\int \alpha x^2 \exp\left(-\beta \alpha x^2\right) \mathrm{d}x}{\int \exp\left(-\beta \alpha x^2\right) \mathrm{d}x} = \frac{1}{2\beta} = \frac{1}{2}kT$$

One example is:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3}v^2$$

3.3 Pressure

Consider container with volume V, in which are N gas particles of mass m and temperature T, the pressure can be obtained by calculating the difference of the gas particles' momenta:

$$p = \frac{1}{A}\frac{\Delta|\mathbf{p}|}{\Delta t} = \frac{1}{A} \cdot \frac{NAv\cos\theta\Delta t}{2V} \cdot \frac{2mv\cos\theta}{\Delta t} = \frac{Nm\left\langle v^2\right\rangle}{3V} = \frac{1}{3}\nu m\left\langle v^2\right\rangle$$

where ν is defined to be the number density of the gas molecules.

We thus have a relation between the translational internal energy and the pressure:

$$U_T = \frac{1}{2}Nmv^2 = \frac{3}{2}pV$$

as well as the rms velocity from MB distribution, from which we conclude:

$$pV = NkT = nRT$$

which is the ideal gas law.

3.4 Frequency of Collision

The frequency of collision f is defined as the number of particles that hit a surface per unit time per unit area:

$$f = \frac{1}{A}\frac{\mathrm{d}N}{\mathrm{d}t}$$

Consider the number of particles in the infinitesimal volume that hits the surface:

$$\mathrm{d}N = \nu A\left\langle v_z\right\rangle\bigg|_{v_z>0}\mathrm{d}t$$

then convert this expression into an integral in $\mathbf{v}$ space:

$$\mathrm{d}N = \nu A\,\mathrm{d}t\int_0^{2\pi}\int_0^{\pi/2}\int_0^{\infty}v\cos\theta\cdot\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)v^2\sin\theta\,\mathrm{d}v\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= \nu A\,\mathrm{d}t\cdot 2\pi\cdot\frac{1}{2}\cdot\frac{1}{4\pi}\int_0^{\infty}vf(v)\,\mathrm{d}v$$

$$\Rightarrow f = \frac{1}{A}\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{1}{4}\nu\left\langle v\right\rangle$$

3.5 Mean Free Path

The probability of a particle not colliding satisfies:

$$P(t+\mathrm{d}t) = P(t) - n\sigma v\,\mathrm{d}t \Rightarrow P(t) = P(0)\exp(-n\sigma vt) = \exp(-n\sigma vt)$$

Thus, the mean time period between collisions is:

$$\tau = \frac{\int_0^{\infty}tP(t)\,\mathrm{d}t}{\int_0^{\infty}P(t)\,\mathrm{d}t} = \frac{1}{n\sigma v}$$

where σ is the collision cross section.

3.6 Transport Properties

4   Classical Thermodynamics

Classical thermodynamics studies the empirical relationships between macroscopic observables such as pressure and volume.

4.1   Equations of State

Ideal Gas Law

By analyzing various previously obtained results, the ideal gas law can be obtained:

$$pV = nRT = NkT$$

Most gases obey this law, especially at low density and high temperature. However, the ideal gas law cannot describe phase transitions, making it less realistic and less powerful under certain situations.

Van der Waals Equation

Van der Waals equation adds on the a term that represents interaction and the b term that represents the effective volume of a particle to the ideal gas equation.

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

The critical point of gas liquid transition is:

$$p_C = \frac{a}{27b^2} \ , \quad V_C = 3nb \ , \quad T_C = \frac{8a}{27bR}$$

4.2   Zeroth Law of Thermodynamics

Law 4.1. Zeroth Law
The zeroth law of thermodynamics is an equivalence relation between states. If A and B are in thermal equilibrium and B and C are in thermal equilibrium, A and C must be in thermal equilibrium.

4.3   Transfer of Heat

Heat capacity related the temperature difference and heat applied:

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T}$$

Law 4.2. Fourier Law of Conduction
The heat transferred per unit time into a volume V can be expressed as:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\oint_{\partial V} \kappa \boldsymbol{\nabla} T \cdot \mathrm{d}\mathbf{a}$$

In one dimension, it can be expressed as:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\kappa A \frac{\mathrm{d}T}{\mathrm{d}x}$$

Here, κ is the thermal conductivity, and A is the cross-sectional area.

Law 4.3. Law of Radiation

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -Ae\sigma T^4$$

4.4   First Law of Thermodynamics

The first law of thermodynamics is an expression of energy conservation.

Law 4.4. First Law of Thermodynamics

$$\mathrm{d}Q = \mathrm{d}U + \mathrm{d}W$$

Here, $\mathrm{d}Q$ is the heat absorbed, $\mathrm{d}U$ is the increase in internal energy, and $\mathrm{d}W$ is the work done by the system on the surroundings. In general, $T\,\mathrm{d}S \geq \mathrm{d}Q$ and $\mathrm{d}W \geq p\,\mathrm{d}V$, in a quasi-static process, $\mathrm{d}W = p\,\mathrm{d}V$, in a reversible process, $\mathrm{d}Q = T\,\mathrm{d}S$, $\mathrm{d}W = p\,\mathrm{d}V$.

4.5   Second Law of Thermodynamics

In classical thermodynamics, entropy is defined as:

$$\Delta S = \int_{T_i}^{T_f} \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}$$

the subscript rev meaning we integrate over a reversible process. For example, for an ideal gas, we have:

$$\mathrm{d}S = \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} = \frac{nC_V\,\mathrm{d}T + p\,\mathrm{d}V}{T} = nC_V \frac{\mathrm{d}T}{T} + nR\frac{\mathrm{d}V}{V}$$

Therefore:

$$\Delta S = nC_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

Law 4.5. Second Law of Thermodynamics
Planck's Statement：
For any thermodynamic process, the total entropy of an isolated system must increase:

$$\int \mathrm{d}S \geq 0$$

This indicates that thermodynamic processes are generally irreversible. For reversible processes:

$$\int \mathrm{d}S = 0$$

4.6   Thermodynamics Potentials

Definition 4.1. Helmholtz Free Energy

$$F := U - TS \ , \ \ \mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$$

Definition 4.2. Enthalpy

$$H := U + pV \ , \ \ \mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p$$

Definition 4.3. Gibbs Free Energy

$$G := H - TS \ , \ \ \mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T$$

Definition 4.4. Chemical Potential

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

The differentials of the Potentials are modified:

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$$
$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$$
$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N$$
$$\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T + \mu\,\mathrm{d}N$$

By considering extensive and intensive variables we get:

$$G = N\mu$$

4.7   Maxwell Relations

Maxwell relations relate various thermodynamics variables by their partial derivatives.

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(-\frac{\partial p}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V} \ , \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V}$$
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p = \frac{\partial^2 H}{\partial S \partial p} \ , \qquad \left(\frac{\partial V}{\partial T}\right)_p = \left(-\frac{\partial S}{\partial p}\right)_T = \frac{\partial^2 G}{\partial T \partial p}$$

4.8   (Reversible) Thermodynamic Processes

Constant Volume

From the first law:

$$\mathrm{d}Q = \mathrm{d}U + p\,\mathrm{d}V = \mathrm{d}U$$

Define the molar heat capacity at constant volume:

$$C_V := \frac{1}{n}\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_V = \frac{1}{n}\left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)_V$$

and since $U = \frac{3}{2}nRT = \frac{3}{2}Nk_BT$ for monatomic ideal gas,

$$C_V = \frac{3}{2}R$$

thus:

$$\Delta Q = \Delta U = \frac{3}{2}nR(T_f - T_i)$$

Constant Pressure

$$dQ = dU + p\,dV = nC_V\,dT + p\,dV \quad \text{(for ideal gas } = n(C_V + R)\,dT)$$

$$C_p := \frac{1}{n}\left(\frac{dU}{dT}\right)_p = \text{(for ideal gas } = C_V + R)$$

Isothermal

$$dQ = dU + p\,dV = \frac{nRT}{V}\,dV$$

$$\Delta Q = W = nRT\ln\left(\frac{V_2}{V_1}\right)$$

Adiabatic/Isentropic

$$PV^\gamma = \text{const.}, \quad TV^{\gamma-1} = \text{const.}$$

5   Special Gas and Statistics

5.1   Photon Gas (Ultrarelativistic Identical Bosons)

Photon gas follows the dispersion relation $E = |\mathbf{p}|c$, from kinetic theory we have:

$$p = \frac{1}{3}\frac{N}{V}\langle \mathbf{p} \cdot \mathbf{v} \rangle = \frac{1}{3}\frac{N}{V}|\langle \mathbf{p} \rangle| c = \frac{1}{3}u$$

in addition, it obeys BE statistics, therefore:

$$u = \int_0^\infty u_\omega \, \mathrm{d}\omega = \int_0^\infty \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\beta\hbar\omega} - 1}\, \mathrm{d}\omega = \frac{\pi^2 k^4}{15\hbar^3 c^3}T^4 \ , \ \ U = uV$$

these are the equations of states of photon gas, often times abbreviated:

$$p = \frac{1}{3}u \ , \ u = aT^4$$

5.2   Phonons

5.3   Free Electron Fermi Gas

6 Phase Transition

6.1 Landau Theory of Phase Transition

The Landau theory of phase transition is a phenomenological model based on observations. The free energy of a system near equilibrium can be modeled using the order parameter m and temperature T:

$$F(m,T) = F_0(T) + \alpha(T)m + \beta(T)m^2 + \gamma(T)m^3 + \delta(T)m^4 \ldots$$

In a system with space inversion symmetry, the odd power terms vanish, the remaining terms in the free energy are:

$$F(T,m) = F_0(T) + \beta(T)m^2 + \delta(T)m^4$$

when equilibrium is reached, the free energy is minimized:

$$\frac{\partial F}{\partial m} = 0 \Rightarrow 2\beta m + 4\delta m^3 = 0 \Rightarrow m = 0 \ \text{ or } \ \pm\sqrt{-\frac{\beta}{2\delta}}$$

assume $\beta \approx \beta_0(T - T_C)$ and $\delta \approx \delta_0$, where T_C is the critical temperature, we have:

$$T < T_C \Rightarrow m = \pm\sqrt{\frac{\beta_0}{2\delta_0}}(T_C - T)^{1/2}$$

$$T > T_C \Rightarrow m = 0$$

The above is know as second order phase transition, it shows spontaneous symmetry breaking at low temperatures.