Thermodynamics & Statistical Physics

Chapter 9. Ensemble theory

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- For the system, to describe the micro-state, using the **phase-space point**:

  $(q_{11}, ...q_{1r}, ...q_{N1}, ...q_{Nr}; p_{11}, ...p_{1r}, ...p_{N1}, ...p_{Nr})$

Phase space and Liouville's theorem

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- The variance of the number comes from the flowing in and out through the surfaces of the volume element.

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$$\Rightarrow \frac{\partial\rho}{\partial t}=-\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]$$
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Or $\frac{\partial\rho}{\partial t}=-\sum(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i}-\frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i})$.

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  The assumption goes to (equal probability principle):

$$\rho(q,p) = \begin{cases} \text{const.}, & E \leq H \leq E + \Delta E, \\ 0, & \text{others.} \end{cases}$$

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- "The most probable distribution" is different from the ensemble average, in concept. But if the fluctuation is small, $\frac{\bar{B}^2-(\bar{B})^2}{(\bar{B})^2} \ll 1$, both are equal.

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- Obviously, $N^{(0)} = N_1 + N_2$, $E^{(0)} = E_1 + E_2$, $V^{(0)} = V_1 + V_2$, and $\Omega^{(0)} = \Omega_1 \cdot \Omega_2$.
- Keep (N_1, N_2, V_1, V_2), let (E_1, E_2) vary, to see the condition to get equilibrium: $\frac{\partial \Omega^{(0)}}{\partial E_1} = 0$, i.e., with the choosing of (E_1, E_2), number of states has maximum because of the equal probability principle.

Thermodynamics in microcanonical ensemble theory

- $\dfrac{\partial \Omega^{(0)}}{\partial E_1}$

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial \Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1 \Omega_2)}{\partial E_1}$

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial \Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1 \Omega_2)}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial E_1}$

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- More complete:
  $\left(\frac{\partial\ln\Omega_1(N_1,E_1,V_1)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial\ln\Omega_2(N_2,E_2,V_2)}{\partial E_2}\right)_{N_2,V_2}.$

Thermodynamics in microcanonical ensemble theory

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  Set $\beta = (\frac{\partial\ln\Omega(N,E,V)}{\partial E})_{N,V}$, $\beta_1 = \beta_2$.

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial\Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1\Omega_2)}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$
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- As $\frac{1}{T} = k\beta$, $S = k \ln \Omega$.

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- The condition for equilibrium: $T_1 = T_2$, $p_1 = p_2$, $\mu_1 = \mu_2$; also showed the meaning of α, β, and γ.

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- First: $p_i = \sqrt{2mE}x_i \Rightarrow \sigma(E) = (2mE)^{\frac{3}{2}N} \int\limits_{\sum x_i^2\leq 1} \mathrm{d}x_1 ... \mathrm{d}x_{3N} \equiv K(2mE)^{\frac{3}{2}N}$...(a)

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- Second, calculate $A \equiv \int_{-\infty}^{+\infty} e^{-\beta H} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$.

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- First: $p_i = \sqrt{2mE}x_i \Rightarrow \sigma(E) = (2mE)^{\frac{3}{2}N} \int\limits_{\sum x_i^2\leq 1} \mathrm{d}x_1 ... \mathrm{d}x_{3N} \equiv K(2mE)^{\frac{3}{2}N}$...(a)
- Second, calculate $A \equiv \int_{-\infty}^{+\infty} e^{-\beta H} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$.
- Method 1. $A = \int_{-\infty}^{+\infty} e^{-\beta \sum \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$

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$= (\frac{2\pi m}{\beta})^{\frac{3}{2}N}$...(b)

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \ldots \text{(b)}}$,

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  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \frac{1}{\beta} \left(- \int_0^{\infty} E^{\frac{3}{2}N-1} \mathrm{d}e^{-\beta E} \right)$

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$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot (\frac{3}{2}N - 1) \cdot \frac{1}{\beta} \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-2} \mathrm{d}E$

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \text{...(b)}}$,

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$= K \cdot (\frac{2m}{\beta})^{\frac{3}{2}N} (\frac{3}{2}N)! \ldots$(c)

Application: monatomic ideal gas. $\boxed{A=(\frac{2\pi m}{\beta})^{\frac{3}{2}N}...\text{(b)}}$,

$$\boxed{\sigma(E)\equiv\int_{H\le E}\mathrm{d}p_1...\mathrm{d}p_{3N}=K(2mE)^{\frac{3}{2}N}...\text{(a)}}$$

- Method 2. $A\equiv\int_{-\infty}^{+\infty}e^{-\beta E}\mathrm{d}p_1...\mathrm{d}p_{3N}=\int e^{-\beta E}\mathrm{d}\sigma(E)$
  $=\int_0^{+\infty}e^{-\beta E}\frac{\mathrm{d}\sigma(E)}{\mathrm{d}E}\mathrm{d}E$
  $=K\cdot(2m)^{\frac{3}{2}N}\cdot\frac{3}{2}N\cdot\int_0^{\infty}e^{-\beta E}E^{\frac{3}{2}N-1}\mathrm{d}E$
  $=K\cdot(2m)^{\frac{3}{2}N}\cdot\frac{3}{2}N\cdot\frac{1}{\beta}\left(-\int_0^{\infty}E^{\frac{3}{2}N-1}\mathrm{d}e^{-\beta E}\right)$
  $=K\cdot(2m)^{\frac{3}{2}N}\cdot\frac{3}{2}N\cdot(\frac{3}{2}N-1)\cdot\frac{1}{\beta}\int_0^{\infty}e^{-\beta E}E^{\frac{3}{2}N-2}\mathrm{d}E$ ...
  $=K\cdot(\frac{2m}{\beta})^{\frac{3}{2}N}(\frac{3}{2}N)!...\text{(c)}$
- (b)=(c) $\Rightarrow K=\frac{\pi^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$,

Application: monatomic ideal gas. $\boxed{A = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}N} \text{...(b)}}$,

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$= K \cdot \left(\frac{2m}{\beta}\right)^{\frac{3}{2}N} (\frac{3}{2}N)! \text{...(c)}$
- (b)=(c) $\Rightarrow K = \frac{\pi^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$,
- $\therefore \sigma(E) = \frac{(2\pi m E)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$. $\square$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot \left(\frac{V}{h^3}\right)^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

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- Entropy: $S = k \ln \Omega$

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- Entropy: $S = k\ln\Omega = k\ln[(\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N-1)!}\frac{\Delta E}{E}]$

Application: monatomic ideal gas.

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$\simeq Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[\ln N! + \ln(\frac{3}{2}N)!] + k\ln\frac{\Delta E}{E}$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot \left(\frac{V}{h^3}\right)^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

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$= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[N(\ln N - 1) +$
$\frac{3}{2}N(\ln\frac{3}{2}N - 1)] + k\ln\frac{\Delta E}{E}$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot (\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

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Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot (\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

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  $= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - Nk\ln N + Nk -$
  $\frac{3}{2}Nk\ln(\frac{3}{2}N) + \frac{3}{2}Nk + k\ln\frac{\Delta E}{E}$
  $= Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk + k\ln\frac{\Delta E}{E}$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot (\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

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  $= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - Nk\ln N + Nk - \frac{3}{2}Nk\ln(\frac{3}{2}N) + \frac{3}{2}Nk + k\ln\frac{\Delta E}{E}$
  $= Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk + k\ln\frac{\Delta E}{E}$
  $\simeq Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk.$

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.
  $T = (\frac{\partial E}{\partial S})_{N,V} = \frac{2}{3}\frac{E}{Nk}$

Application: monatomic ideal gas.

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

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.
  $T = (\frac{\partial E}{\partial S})_{N,V} = \frac{2}{3}\frac{E}{Nk} \Rightarrow E = \frac{3}{2}NkT$
  $p = -(\frac{\partial E}{\partial V})_{N,S} = \frac{2}{3}\frac{E}{V}$

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.
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- $\Rightarrow pV = NkT$,

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.
  $T = (\frac{\partial E}{\partial S})_{N,V} = \frac{2}{3}\frac{E}{Nk} \Rightarrow E = \frac{3}{2}NkT$
  $p = -(\frac{\partial E}{\partial V})_{N,S} = \frac{2}{3}\frac{E}{V}$
- $\Rightarrow pV = NkT$,
  $S = Nk\ln[\frac{V}{N}(\frac{2\pi mkT}{h^2})^{\frac{3}{2}}] + \frac{5}{2}Nk$. Same as eq. (7.6.2).

Table of contents

9.4 Canonical ensemble

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- Consider the probability for the system at state s.

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- As state s, there exists energy E_s. Reservoir can be any state with energy $E_r = E^{(0)} - E_s$. Total number of these states: $\Omega_r(E^{(0)} - E_s)$. For the combined system being isolated system, obeys microcanonical ensemble's the principle of equal a priori probabilities.

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  $= \ln \Omega_r(E^{(0)}) - \beta E_s$. Notice (9.3.5).
- $\therefore \rho_s \propto e^{\ln \Omega_r(E^{(0)}) - \beta E_s} \propto e^{-\beta E_s}$,
  where $\ln \Omega_r(E^{(0)}) = $ Const.

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- For continuous (classical) case:
  $\rho(q,p) \mathrm{d}\Omega = \frac{1}{N! h^{Nr}} \frac{e^{-\beta E(q,p)}}{Z} \mathrm{d}\Omega$,
  where $Z = \frac{1}{N! h^{Nr}} \int e^{-\beta E(q,p)} \mathrm{d}\Omega$.

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  $= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2}$

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  $= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$

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- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta}$

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- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T}$

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- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} = kT^2 \frac{\partial U}{\partial T}$

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$= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2)$;
- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V$.
- Relative fluctuation: $\frac{\overline{(E-\bar{E})^2}}{\bar{E}^2} = \frac{kT^2 C_V}{\bar{E}^2}$

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  $= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
  $= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$
- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V.$
- Relative fluctuation: $\frac{\overline{(E-\bar{E})^2}}{\bar{E}^2} = \frac{kT^2 C_V}{\bar{E}^2} \propto \frac{1}{N}.$

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  For $N \gg 1$, the relative fluctuation $\to 0$; back to microcanonical ensemble (equivalent).

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- 2nd step: thermal quantities, like $p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z$.
- E (kinetic energy and potential energy): $E = \sum_{i=1}^{N} \frac{\vec{p_i}^2}{2m} + \sum_{i<j} \phi(\overrightarrow{r_{ij}})$.

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EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms:
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- Simplify, at high temperature, molecule's kinetic energy can be greater than the potential energy ϕ_0, i.e., $\phi_0 \ll kT$, then $e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} \simeq 1 + \frac{\phi_0}{kT}(\frac{r_0}{r})^6$.

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- $\therefore B \simeq 2\pi N_A(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT})$.

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- $\therefore B \simeq 2\pi N_A(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT})$.
- Define $b = \frac{2}{3}\pi N_A r_0^3$, $a = \frac{2}{3}\pi N_A^2 \phi_0 r_0^3$, then $B = b - \frac{a}{N_A kT}$.

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- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions), with dispersion relations: $\omega = c_l k$, $\omega = c_t k$, where c is the speed of sound. For low frequencies, ω_i can be taken as continuous.
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$$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}, \boxed{\omega_D^3 = \frac{9N}{B}}, \boxed{y_D = \frac{\hbar\omega_D}{kT}}$$

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  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D} \frac{y^3}{e^y-1}\mathrm{d}y$

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- $U=U_0+B\int_0^{\frac{\hbar\omega_D}{kT}}\frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
$=U_0+B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
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  $C_V = 3nk\frac{4\pi^4}{5}(\frac{T}{\theta_D})^3 \propto T^3$. Source of (8.5.20).

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- In single-axis ferromagnet, only 2 choices for each magnetic momentum ($\sigma = \pm 1$).

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- Total interacting energy: $-J\sum_{i,j}{}'\sigma_i\sigma_j$, where $\sum_{i,j}{}'$ means the summation only exerts on the neighbors. At absolute 0K, all directions being the same can get lowest total energy. Get macroscopic magnetic field, spontaneous magnetization.

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- Rewrite the total energy: $E\{\sigma_i\} = -\frac{1}{2} \sum_{i,j} J_{ij} \sigma_i \sigma_j - \mu B \sum_i \sigma_i$, where $J_{ij} = J$ for i and j being neighbors, 0 for other.

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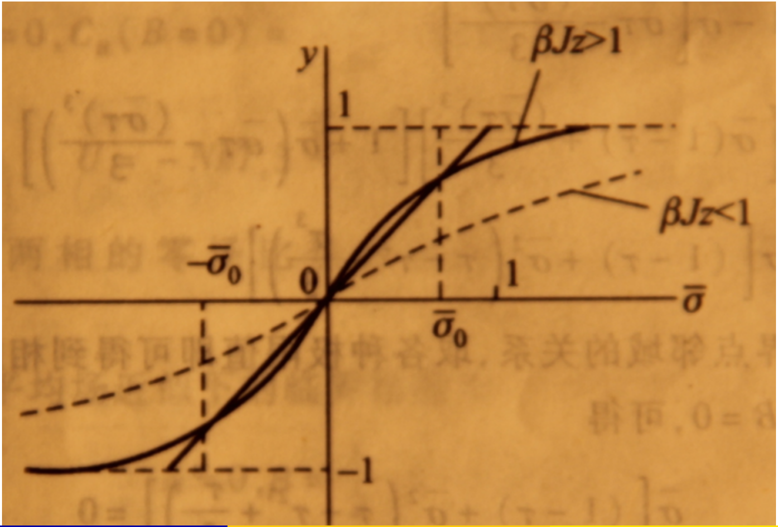
The critical temperature ($\beta J z = 1$): $T_c = \frac{Jz}{k}$.



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$= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$
$= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}.$
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- $$\Rightarrow \overline{(N - \overline{N})^2} = -(\frac{\partial \overline{N}}{\partial \alpha})_{\beta, y} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}.$$

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

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Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

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  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$
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  $\Rightarrow (\frac{\partial \mu}{\partial v})_T = v(\frac{\partial p}{\partial v})_T$, and
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$$= \frac{1}{\mathcal{Z}_s} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s}$$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\mathrm{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\mathrm{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$
\begin{aligned}
f_s = \overline{a}_s &= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}} \\
&= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} \\
&= \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \prod_{s'} \sum_{a_{s'}} a_s^{\overset{1}{?}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} \\
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&= \frac{1}{\mathcal{Z}_s} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} = \frac{1}{\mathcal{Z}_s}\left(-\frac{\partial}{\partial\alpha}\right)\mathcal{Z}_s
\end{aligned}
$$

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Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

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  $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l}\pm 1} = \overline{a}_l\left(1 \mp \frac{1}{e^{\alpha+\beta\varepsilon_l}\pm 1}\right)$

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- $\overline{(a_l-\overline{a}_l)(a_m-\overline{a}_m)} = \overline{a_l a_m} - \overline{a}_l\overline{a}_m = 0$, no correlation.

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