partition function in Quantum case

$$Z = \sum_{n_1 n_2 \cdots n_N} e^{-\beta \sum_j \hbar\omega_j (n_j + \frac{1}{2})} = \prod_{j=1}^{N} \sum_{n_j=0}^{\infty} e^{-\beta\hbar\omega_j n_j} e^{-\beta\frac{\hbar\omega_j}{2}}$$

Date

$$= \prod_{j=1}^{N} \frac{1}{1-e^{-\beta\hbar\omega_j}} e^{-\beta\frac{\hbar\omega_j}{2}}$$

$\hbar \to 0$ approach classical result of $\prod_j \frac{1}{\beta\hbar\omega_j}$

$$F = +k_B T \sum_{j=1}^{N} \left[\ln\left(1-e^{-\beta\hbar\omega_j}\right) + \frac{1}{2}\beta\hbar\omega_j \right]$$

$\ln(1+x) = x$

$$S = -\frac{\partial F}{\partial T} = -k_B \sum_{j=1}^{N} \left[\ln\left(1-e^{-\beta\hbar\omega_j}\right) + \frac{1}{2}\beta\hbar\omega_j \right]$$

$$- k_B \cancel{T} \sum_{j=1}^{N} \left[\frac{-e^{-\beta\hbar\omega_j} \times \frac{\hbar\omega_j}{k_B T^{\cancel{2}}}}{1-e^{-\beta\hbar\omega_j}} \mp \frac{1}{2} \frac{\hbar\omega_j}{k_B T^{\cancel{2}}} \right]$$

$T \to 0$
$\beta \to \infty$

$$S = -k_B \sum_j \left(-e^{-\beta\hbar\omega_j} + \cancel{\frac{1}{2}\beta\hbar\omega_j} \right.$$

$$\left. - \frac{\hbar\omega}{k_B T} e^{-\beta\hbar\omega_j} \mp \cancel{\frac{1}{2}\beta\hbar\omega_j} \right)$$

$$= k_B \left(\sum_j \left(1 + \frac{\hbar\omega_j}{kT}\right) e^{-\frac{\hbar\omega_j}{kT}} \right) \to 0$$

$$U = -\frac{\partial}{\partial\beta} \ln Z = +\frac{\partial}{\partial\beta} \sum_{j=1}^{N} \left\{ \ln\left(1-e^{-\beta\hbar\omega_j}\right) + \beta\frac{\hbar\omega_j}{2} \right\}$$

$$= \sum_{j=1}^{N} \left\{ \frac{e^{-\beta\hbar\omega_j}(\hbar\omega_j)}{1-e^{-\beta\hbar\omega_j}} + \frac{\hbar\omega_j}{2} \right\}$$

$$f_j = \frac{1}{e^{\beta\hbar\omega_j}-1}$$

$$= \sum_j \hbar\omega_j \left(f_j + \frac{1}{2}\right)$$

$$= \sum_{j=1}^{N} \left\{ \frac{\hbar\omega_j}{e^{\beta\hbar\omega_j}-1} + \frac{\hbar\omega_j}{2} \right\}$$

$\hbar \to 0$

$$= \sum_{j=1}^{N} \left\{ \frac{1}{\beta} + \frac{\hbar\omega_j}{2} \right\} = N k_B T$$

$$C = \frac{dU}{dT} = \sum_{j=1}^{N} \frac{\hbar\omega_j \, (-1)}{(e^{\beta\hbar\omega_j}-1)^2} e^{\beta\hbar\omega_j}\left(-\frac{\hbar\omega_j}{k_B T^2}\right) \qquad \beta\hbar\omega_j = x_j$$

$$= k_B \sum_{j=1}^{N} \frac{e^{x_j} x_j^2}{(e^{x_j}-1)^2}$$

$$\frac{\hbar\omega_M}{k_B T_D} = O(1)$$

Debye Temperature

Date

Lebesgue

Debye temperature

Euler-Maclaurin integr form

More precise formula

$$\ln n! = n\ln n - n + \frac{1}{2}\ln n + \ln\sqrt{2\pi} + \frac{1}{12n} - \frac{1}{360n^3} + \cdots$$

Arfken, Mathematical methods for physicists

Yvon's theorem

$$\int d\Gamma\, (A,B)C = \int d\Gamma\, A(B,C)$$

let $A = \frac{e^{-\beta H}}{Z}$ $B = B(t)$, $C = A$

note that $(\rho, B(t)) = \frac{\partial \rho}{\partial H}(H, B(t)) = -\frac{1}{k_B T}(H, B(t))$

$\frac{\partial \rho}{\partial q} = \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial q}$ similar for $\frac{\partial}{\partial p}$

prove $\int d\Gamma\, (A,B)C = \int d\Gamma\, A(B,C)$

consider $\int d\Gamma\, C \frac{\partial A}{\partial q_j}\frac{\partial B}{\partial p_j} = \int d\Gamma \left[\frac{\partial}{\partial q_j}\left(CA\frac{\partial B}{\partial p_j}\right) - A\frac{\partial C}{\partial q_j}\frac{\partial B}{\partial p_j} - AC\frac{\partial^2 B}{\partial q_j \partial p_j}\right]$

exercise

$q \leftrightarrow p$ sum over j, we get the result

$\frac{\partial^2}{\partial q \partial p} = \frac{\partial^2}{\partial p \partial q}$

$\oint CA\frac{\partial B}{\partial p}$ surface term is assumed zero.

① Stirling formula $n! = 1\cdot 2\cdot 3\cdots(n-1)\cdot n$

$$\ln n! = \sum_{i=1}^{n} \ln i \approx \int_1^n \ln x\, dx$$

$$= x\cdot \ln x\Big|_1^n - \int_1^n x\, d\ln x \qquad \int_1^n 1\,dx = n-1$$

$$= n\ln n - n \cancel{+1}$$

②
$$\int_{-\infty}^{\infty} e^{-\frac{x^2}{2}}\,dx = I$$

$$I^2 = \int_{-\infty}^{\infty} e^{-\frac{x^2}{2}}\,dx \int_{-\infty}^{\infty} e^{-\frac{y^2}{2}}\,dy = \int e^{-\frac{x^2+y^2}{2}}\,dx\,dy$$

$$= \int e^{-\frac{r^2}{2}}\, r\,dr\,d\theta = 2\pi \int_0^\infty e^{-\frac{r^2}{2}}\, d\frac{r^2}{2} = 2\pi$$

$$I = \sqrt{2\pi}$$

③
$$\Omega_n = \int_{\sum x_i^2 < R^2} dx_1 dx_2 \cdots dx_n = C_n R^n \qquad S_n = \frac{d\Omega_n}{dR} = nC_n R^{n-1}$$

$$\pi^{\frac{n}{2}} = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n\, e^{-x_1^2+x_2^2+\cdots x_n^2} = \int_0^\infty dR\, S_n(R)\, e^{-R^2}$$

gaussian

$$= nC_n \int_0^\infty dR\, R^{n-1} e^{-R^2} \qquad \Gamma(x+1) = x\Gamma(x)$$

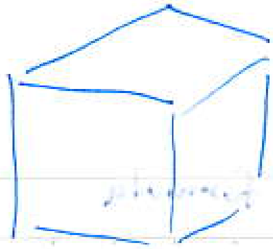
$R^2 = t$

$$= \frac{1}{2} n C_n \int_0^\infty dt\, t^{\frac{n}{2}-1} e^{-t} = \frac{1}{2} n C_n \Gamma\left(\frac{n}{2}\right)$$

n $\cancel{\Gamma(x)}$

$$\pi^{\frac{n}{2}} = \frac{1}{2} n \Gamma\left(\frac{n}{2}\right) C_n$$

$$= \Gamma\left(\frac{n}{2}+1\right) C_n \qquad R^2 = t$$



single particle states

$$-\frac{\hbar^2}{2m}\nabla^2\varphi_r = E_r\varphi_r$$

periodic B.C. $\varphi_r(x,y,z) = \frac{1}{\sqrt{V}} e^{\frac{i}{\hbar}(p_x x + p_y y + p_z z)}$

$$-\frac{\hbar^2}{2m}\left[\left(\frac{i}{\hbar}p_x\right)^2 + \left(\frac{i}{\hbar}p_y\right)^2 + \left(\frac{i}{\hbar}p_z\right)^2\right] = E_r$$

$$\rightarrow \quad E_r = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

$$e^{\frac{i}{\hbar}p_x x} = e^{\frac{i}{\hbar}p_x(x+L)} \quad \text{periodic B.C.}$$

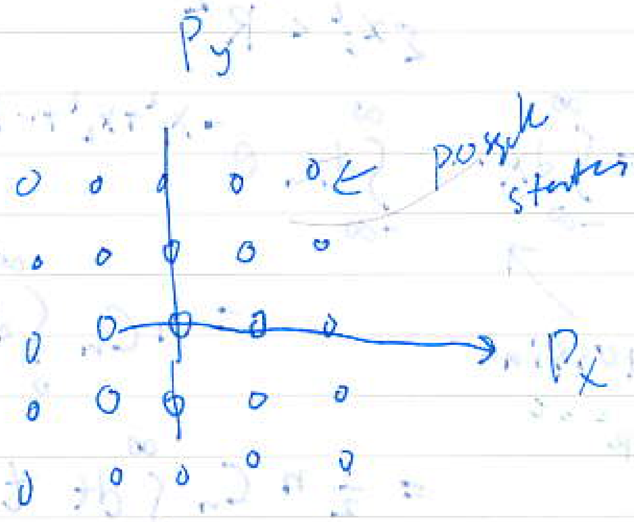
$$e^{\frac{i}{\hbar}p_x L} = 1$$

$$\frac{p_x L}{\hbar} = 2\pi m_x \qquad m_y = 0, \pm 1, \pm 2, \cdots$$

$$\therefore p_x = \frac{2\pi m_x \hbar}{L} = \frac{m_x h}{L}$$

$$p_y = \frac{m_y h}{L}$$

$$p_z = \frac{m_z h}{L}$$



quantum number

$$r = (m_x, m_y, m_z)$$

Many-particle system $\quad N$ identical partils Date

Talk about this general principle first.

$$\mathcal{H} = \sum_{j=1}^{N} \mathcal{H}^{(j)} + \underset{\substack{\| \\ 0}}{\text{interaction}}$$

E.g. electrons in a periodic lattice potential

$$\mathcal{H}^{(j)} = -\frac{\hbar^2}{2m}\vec{\nabla}_j^2 + V(\vec{x}_j) \qquad \text{e.g.}$$

Let $\quad H^{(j)}\varphi_r(j) = \varepsilon_r \varphi_r(j) \qquad r = 0, 1, 2, 3, \cdots$

set of eigen energy and eigen function of a single particle.

full wave function

quantum system is described by a ray in Hilbert space

$\psi \to e^{i\theta}\psi$ represent the same physical reality.

$\vec{x} = (\vec{r}, \sigma)$ in case there is spin

$$\Psi(1, 2, \cdots N) \equiv \Psi(\vec{x}_1, \vec{x}_2, \cdots \vec{x}_N)$$

$\psi \to \lambda\psi$ is the sure $\quad \|\psi\| = 1$ fix λ up to a phase factor

$$\Psi(1, 2, i, \cdots, j, \cdots N) = \underset{\substack{\uparrow \\ \text{phase (indpt of } i, j)}}{\alpha}\, \Psi(1, 2, \cdots j, \cdots i, \cdots N)$$

$$= \alpha^2 \Psi(1, 2, \cdot\, i, \cdots j, \cdot\cdot N) \qquad \Rightarrow \quad \alpha^2 = 1$$

$$\alpha = e^{i\phi} \qquad \phi = 0, \pi$$

$\alpha = \pm 1$

$\alpha = +1$ bosons

$ -1$ fermions

$$\Psi_B(1, 2, \cdots N) = \underset{\substack{P \\ \nwarrow \text{full permutation}}}{\sum} P \prod_j \varphi_{r_j}(j)$$

$\leftarrow$ each state r can be occupied by any number of particle $n_r = 0, 1, 2, \cdots$

Pauli exclusion principle $n_r = 0, 1$ only apply

$$\Psi_F(1, 2, \cdots N) = \sum_P (-1)^P P \prod \varphi_{r_j}(j) \propto \text{Slater determinante}$$

grand-partition function for non interacting Boson / Fermion system of identical particle

Date

$$\Xi = \mathrm{Tr}\, e^{-\beta(\mathcal{H} - \mu N)}$$

occupation number representation

$$|\Psi\rangle = |n_0\, n_1\, n_2 \cdots n_r \cdots\rangle \propto (a_0^\dagger)^{n_0} (a_1^\dagger)^{n_1} \cdots |0\rangle$$

$$= \sum_{\Psi} \langle \Psi | e^{-\beta(H - \mu N)} | \Psi \rangle$$

$$= \sum_{n_0 n_1 n_2 \cdots n_r \cdots} e^{-\beta\left(\sum_{r=0}^{\infty} \varepsilon_r n_r - \mu \sum_{r=0}^{\infty} n_r\right)}$$

r specifies the "states" not energy

$$= \sum_{n_0 n_1 n_2 \cdots n_r \cdots} \prod_{r=0}^{\infty} e^{-\beta(\varepsilon_r - \mu) n_r} = \prod_{r=0}^{\infty} \sum_{n_r} e^{-\beta(\varepsilon_r - \mu) n_r}$$

$$\sum_{i,j,k\cdots} a_i \cdot b_j \cdot c_k \cdots = \left(\sum_i a_i\right)\left(\sum_j b_j\right)\left(\sum_k c_k\right)\cdots$$

$$= \prod_{r=0}^{\infty} \begin{cases} \left[1 + e^{-\beta(\varepsilon_r - \mu)}\right] & \text{Fermions} \\ \dfrac{1}{1 - e^{-\beta(\varepsilon_r - \mu)}} & \text{Bosons} \end{cases}$$

$$= \prod_{r=0}^{\infty} \left[1 + \eta\, e^{-\beta(\varepsilon_r - \mu)}\right]^{\eta}$$

$\eta = +1$ Fermi, -1 Boson

· grand potential

$$\Psi = U - TS - \mu N = -pV = -k_B T \ln \Xi$$

$$= -k_B T \sum_{r=0}^{\infty} \eta \ln\left(1 + \eta\, e^{-\beta(\varepsilon_r - \mu)}\right)$$

$$d\Psi = -S\,dT - p\,dV - \langle N \rangle d\mu$$

$$S = -\frac{\partial \Psi}{\partial T} = \frac{\partial}{\partial T}\left[k_B T \sum \eta \ln\left(1 + \eta\, e^{-\beta(\varepsilon_r - \mu)}\right)\right]$$

② $$S = k_B \sum_r \eta \ln\left(1+\eta e^{-\beta(\varepsilon_r-\mu)}\right) + k_B T \sum_r \eta \cdot \frac{\eta e^{-\beta(\varepsilon_r-\mu)}}{1+\eta e^{-\beta(\varepsilon_r-\mu)}} \frac{(\varepsilon_r-\mu)}{k_B T^2}$$

Date

$$= k_B \sum \eta \ln\left(1+\eta e^{-\beta(\varepsilon_r-\mu)}\right) + k_B \sum_r \frac{\frac{\varepsilon_r-\mu}{k_B T} e^{-\beta(\varepsilon_r-\mu)}}{1+\eta e^{-\beta(\varepsilon_r-\mu)}}$$

① $$\langle N\rangle = -\frac{\partial\Psi}{\partial\mu} = k_B T \sum_{r=0}^{\infty} \eta \frac{\cdot\,\eta e^{-\beta(\varepsilon-\mu)}}{1+\eta e^{-\beta(\varepsilon_r-\mu)}}\beta$$

$$= \sum_{r=0}^{\infty} \frac{1}{e^{\beta(\varepsilon_r-\mu)}+\eta} = \sum_r \langle n\rangle_r$$

$$\langle n_r\rangle = \frac{1}{e^{\beta(\varepsilon_r-\mu)} \pm 1}$$

+ Fermi

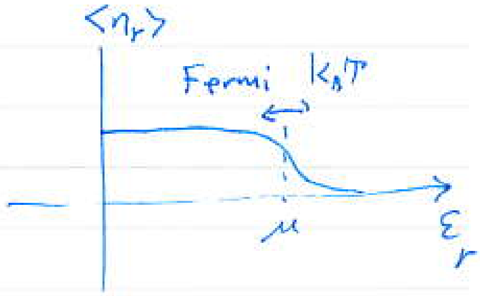
− Boson

③ $$U = \Psi + TS + \mu\langle N\rangle$$

$$= -k_B T \sum_{r=0}^{\infty} \eta \cancel{\ln\left(1+\eta e^{-\beta(\varepsilon_r-\mu)}\right)}$$

$$+ k_B T \sum \eta \cancel{\ln\left(1+\eta e^{-\beta(\varepsilon_r-\mu)}\right)}$$

$$+ \cancel{k_B T} \sum \frac{(\varepsilon_r-\mu)\cancel{k_B} e^{-\beta(\varepsilon_r-\mu)}}{1+\eta e^{-\beta(\varepsilon_r-\mu)}} + \mu \sum \frac{1}{e^{\beta(\varepsilon_r-\mu)}+\eta}$$



$$= \sum_r \frac{\varepsilon_r}{e^{\beta(\varepsilon_r-\mu)}+\eta} = \sum_{r=0}^{\infty} \varepsilon_r \langle n_r\rangle$$

ave occupation number

$$\langle n_r\rangle = \frac{1}{e^{\beta(\varepsilon_r-\mu)}+\eta}$$

$\eta = +1$ fermi

-1 boson

Eq. of state

$$PV = k_B T \sum_{r=0}^{\infty} \eta \ln\left(1+\eta e^{-\beta(\varepsilon_r-\mu)}\right)$$

$$S = k_B \sum_r \left\{ \eta \left[-\beta(\varepsilon_r - \mu) - \ln\langle n_r\rangle \right] + k_\beta \beta(\varepsilon_r - \mu)\langle n_r\rangle \right\}$$

$$\ln(1 \mp \eta\langle n_r\rangle) = \ln\left(\frac{e^{\beta(\varepsilon_r-\mu)}}{e^{\beta(\varepsilon_r-\mu)}+\eta}\right)$$

$$= \ln\left(1 \mp \frac{\eta}{e^{\beta(\varepsilon_r-\mu)}+\eta}\right) = \ln\left(\frac{e^{\beta(\varepsilon_r-\mu)}+\eta \mp \eta}{e^{\beta(\varepsilon_r-\mu)}+\eta}\right)$$

$$= \beta(\varepsilon_r - \mu) + \ln\langle n_r\rangle$$

$$= k_B \sum_r \left\{ \eta\left[-\ln(1-\eta\langle n_r\rangle) + \cancel{\ln\langle n_r\rangle} - \cancel{\ln\langle n_r\rangle} \right] + \left[\ln(1-\eta\langle n_r\rangle) - \ln\langle n_r\rangle\right]\langle n_r\rangle \right\}$$

$$S = k_B \sum \eta \ln\left[e^{-\beta(\varepsilon_r-\mu)}\left(e^{\beta(\varepsilon-\mu)}+\eta\right)\right] +$$

$$k_B \beta(\varepsilon_r - \mu) \frac{1}{e^{\beta(\varepsilon-\mu)}+\eta}$$

$$= k_B \sum_r \left\{ -\eta \ln(1-\eta\langle n_r\rangle) + \underset{\langle n_r\rangle}{\ln(1-\eta\langle n_r\rangle)} - \underset{\langle n_r\rangle}{\ln\langle n_r\rangle} \right\}$$

$$= k_B \sum_r \left\{ (\langle n_r\rangle - \eta)\ln(1-\eta\langle n_r\rangle) - \langle n_r\rangle \ln\langle n_r\rangle \right\}$$

$\eta = +1$ fer

-1 bos

Date

He^4 was thought to be a realization of Bose-Einstein condensation system. but He^4 is not ideal quantum gas as He^4 has strong interaction.

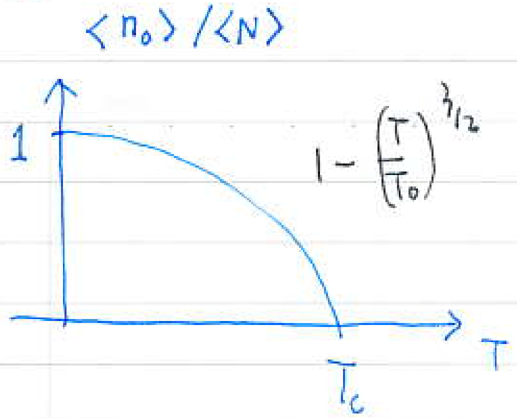
alkali atom

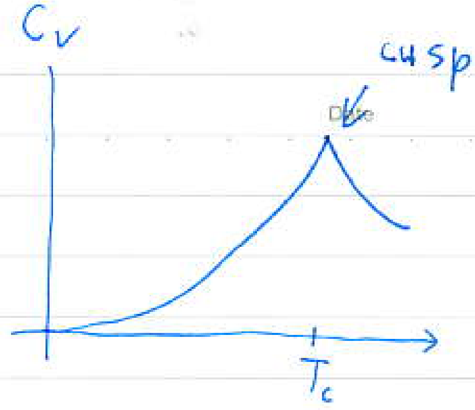
observed in dilute gas of Li .. in 1995.

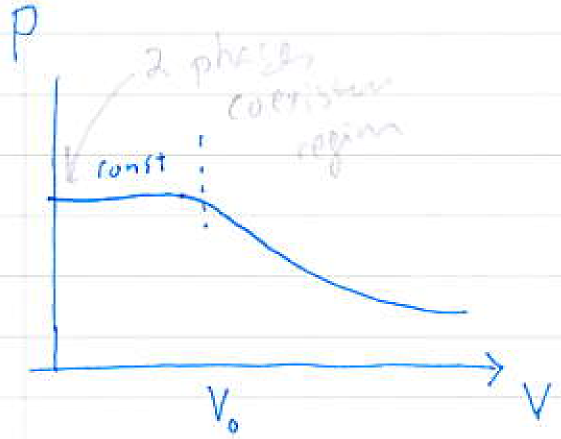
around microkelvin $\sim 10^{-6}$ K

or Sodium atoms

Bose-Einstein condensation

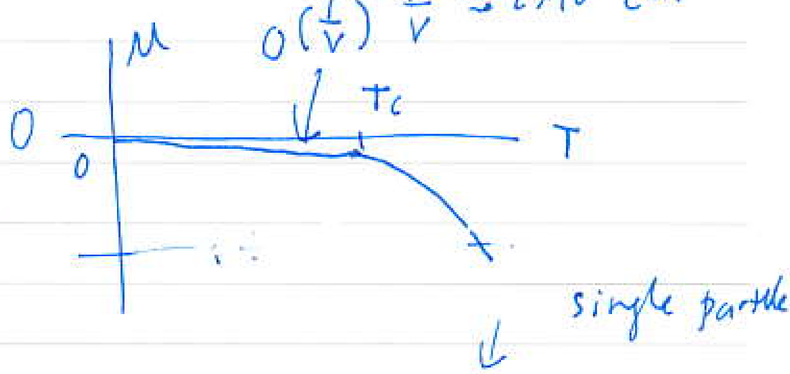






E.g. ^4He $T_0 \approx 2K$

$\frac{N}{V} \approx 2 \times 10^{22}\ cm^{-3}$



what is T_c ?

gap of energy levels $E_0 = 0$ $\quad E_1 = \frac{p^2}{2m} \approx \frac{1}{m}\frac{h^2}{L^2}$

thermal energy $k_B T$ becomes compare to ΔE

$$k_B T_c \simeq \underbrace{\frac{h^2}{m a^2}}_{a:\ \text{avg spacing between particles}} \simeq \frac{h^2}{m\left(\frac{V}{N}\right)^{2/3}}$$

$$\frac{N}{V} = 2.612 \frac{(2\pi m k_B T_c)^{3/2}}{h^3} \qquad \left(\frac{N}{V}\right)^{2/3} = (2.612)^{2/3} \frac{2\pi m k_B T_c}{h^2}$$

$$k_B T_c \simeq \frac{(2.612)^{2/3}}{2\pi m} \frac{h^2}{\left(\frac{V}{N}\right)^{2/3}} \approx 0.3 \frac{h^2}{m\left(\frac{V}{N}\right)^{2/3}}$$

13 Feb 07

ch. 2. A. L. Fetter & J. D. Walecka "Quantum Theory of many-particle systems"

Date

convert discrete sum by integration

$$\sum_r f_r = \sum_{\Delta p} f_{\varepsilon(p)} \overset{3 \leftarrow \text{momentum}}{(\Delta p)} \left(\frac{L}{h}\right)^3 = \sum_p f_{\varepsilon(p)} \cdot 1$$

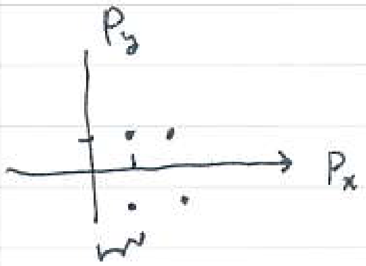
lim $L \to +\infty$

$r = (m_x, m_y, m_z)$ $\quad m_{x\,y\,z} = 0, \pm 1, \pm 2,$

$d^3p = dp_x dp_y dp_z$

$$= \frac{V}{h^3}\int f(\varepsilon(p))\, d^3p$$

$$= \frac{V}{h^3}\int f \cdot 4\pi p^2 dp$$



in terms of energy

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

$$\frac{h}{L} = \Delta p_x \qquad \frac{p\,dp}{m} = d\varepsilon \qquad dp = \frac{m\,d\varepsilon}{p} = \frac{m\,d\varepsilon}{\sqrt{2m\varepsilon}}$$

$\left(\frac{L}{h}\right)^3$: density of state per unit momentum volume

$$\sum_r f_r = \frac{V}{h^3}\int f(\varepsilon) \cdot 4\pi \cdot 2m\varepsilon \cdot \frac{m\,d\varepsilon}{\sqrt{2m\varepsilon}}$$

$$= \int \frac{V}{h^3} \cdot 4\pi \sqrt{2\varepsilon}\, m^{\frac{3}{2}}\, f(\varepsilon)\, d\varepsilon$$

$$= \int_0^\infty D(\varepsilon) f(\varepsilon)\, d\varepsilon \qquad = \cancel{\frac{V 2\pi (2m\varepsilon)^{\frac{1}{2}}}{h^3}}$$

$$D(\varepsilon) = \frac{V}{h^3} 4\pi m^{\frac{3}{2}} \sqrt{2\varepsilon}$$ ← density of states in energy

$$\Psi(T, V, \mu) = -k_B T \int_0^\infty d\varepsilon \cdot D(\varepsilon) \ln\left(1 + \eta\, e^{-\beta(\varepsilon - \mu)}\right) = -pV$$

$\eta = +1$ ferm
$\quad\;\; -1$ boson

$$\langle N \rangle = \int_0^\infty d\varepsilon \, \frac{D(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+\eta}$$

$D(\varepsilon) \propto \sqrt{\varepsilon}$

Let $D(\varepsilon) = a\sqrt{\varepsilon}$

Date

$$U = \int_0^\infty d\varepsilon \, \frac{\varepsilon \, D(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+\eta}$$

$$PV = k_B T \int_0^\infty d\varepsilon \, D(\varepsilon) \cdot \eta \, \ln(1+\eta e^{-\beta(\varepsilon-\mu)})$$

$$= \frac{1}{\beta}\eta \cdot \int_0^\infty \ln(1+\eta e^{-\beta(\varepsilon-\mu)}) \, d(a\,\varepsilon^{\frac{3}{2}}) \, \frac{2}{3}$$

$$= \frac{2\eta}{3\beta}\left[a\varepsilon^{\frac{3}{2}}\ln(1+\eta e^{-\beta(\varepsilon-\mu)})\Big|_0^\infty - \int_0^\infty \frac{a\,\varepsilon^{3/2} \cdot \eta e^{-\beta(\varepsilon-\mu)}(-\beta)}{1+\eta e^{-\beta(\varepsilon-\mu)}} d\varepsilon\right.$$

$$= \frac{2}{3}\int_0^\infty \frac{\varepsilon \, D(\varepsilon)}{e^{-\beta(\varepsilon-\mu)}+\eta} d\varepsilon = \frac{2}{3}U$$

(ideal gas $U = \frac{3}{2}NkT$)

$$\varepsilon^{3/2}\ln(1+\cancel{\phi} e^{-\beta\varepsilon}) \begin{cases} \varepsilon \to 0 & 0 \cdot \ln 1 = 0 \\ \varepsilon \to \infty & \varepsilon^{3/2} e^{-\beta\varepsilon} \to 0 \end{cases}$$

$\varepsilon^{\frac{3}{2}}\ln(1-e^{-\beta\varepsilon})|_{\varepsilon\to 0}$

$\varepsilon^{\frac{3}{2}}\ln(\beta\varepsilon) \to 0$ $\quad \ln(1+x) \approx x \quad x$ small

Bose-Einstein condensatis

The replacent $\sum_r f_r = \int f(\varepsilon) D(\varepsilon) \, d\varepsilon$ was wrong for $T < T_c$

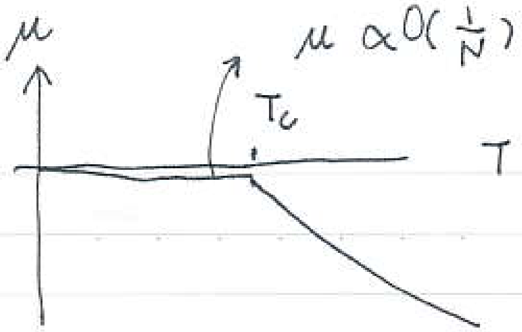
$$\sum_r f_r = \sum_{r=0} f_0 + \sum_{r\neq 0} f_r$$

$$= f_0 + \int f(\varepsilon) D(\varepsilon) \, d\varepsilon$$

E.g. $\langle N \rangle = n_0 + \int_0^\infty d\varepsilon \, \frac{D(\varepsilon)}{e^{\beta(\varepsilon-\mu)} \cancel{+\eta} -1}$ for $T < T_c$

$\mu \to 0$

how to deter T_c ?



T_c is determined by $\mu = 0$

$$\langle N \rangle = \int_0^\infty d\varepsilon \frac{D(\varepsilon)}{e^{\frac{\varepsilon}{k_B T_c}} - 1}$$

for $T < T_c$

$\beta \varepsilon = x$

$\varepsilon = \frac{x}{\beta} = k_B T x$

$$\langle N \rangle = n_0 + \int_0^\infty d\varepsilon \frac{a \varepsilon^{1/2}}{e^{\beta\varepsilon} - 1}$$

$$= n_0 + \int_0^\infty \frac{(k_B T)^{3/2} a x^{\frac{1}{2}} dx}{e^x - 1} = n_0 + b T^{3/2}$$

$$n_0 = \langle N \rangle - b T^{3/2} = \langle N \rangle (1 - (T/T_c)^{3/2})$$

$$\langle N \rangle = \int_0^\infty d\varepsilon \frac{D(\varepsilon)}{e^{\beta(\varepsilon - \mu)} - 1}$$

$\varepsilon \geq 0$

$\langle N \rangle > 0$

if $\mu > 0$

$e^{\beta \underbrace{(\varepsilon - \mu)}_{<0}} < 1$

then $\langle N \rangle < 0$

which is impossible

when $T = 0$

$$\mu = \frac{E(N+1) - E(N)}{(N+1) - N} = 0$$

$\varepsilon_0 = 0$

$$\langle n_0 \rangle = \frac{1}{e^{\beta(\varepsilon_0 - \mu)} - 1} = \frac{1}{e^{-\beta\mu} - 1}$$

$\langle n_0 \rangle > 0$

so $\mu \cancel{\leq} 0$

assuming μ small

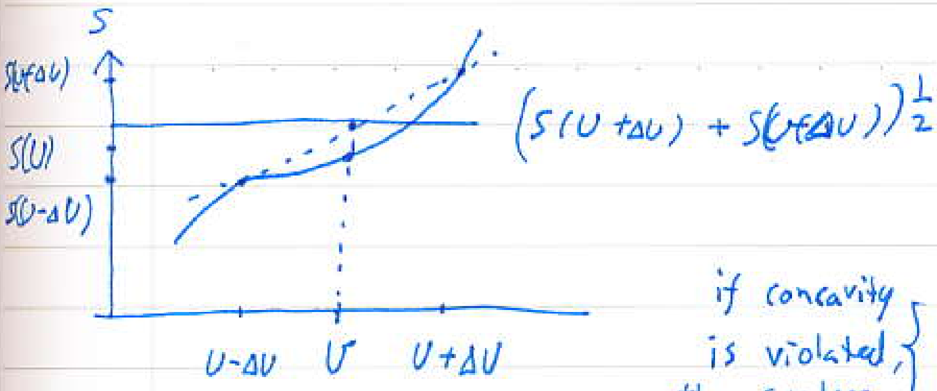
$$= \frac{1}{1 - \beta\mu + \cdots - 1} = \frac{1}{\beta(-\mu)} \propto N$$

so $\mu \propto \frac{1}{N}$

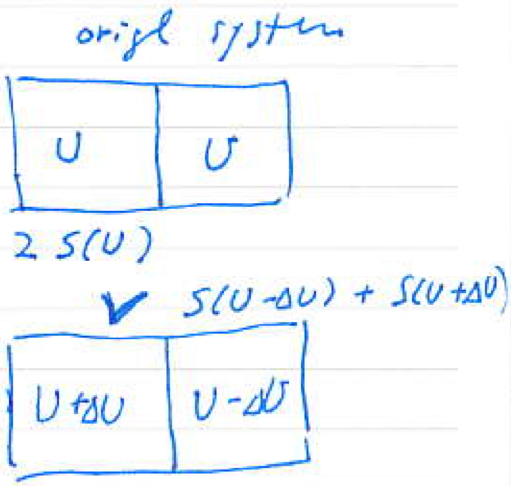
$$= \frac{k_B T}{(-\mu)}$$

$\mu \propto - \frac{k_B T}{N}$

concavity/convexity of thermodynamical fundamental relations



if concavity is violated, the system develops inhomogeneity



concavity condition

$$2S(U) \geq S(U-\Delta U) + S(U+\Delta U) \leftarrow \text{global condition}$$

↑ i.e. entropy is maximum not minimum again constraints of partition the energy

or

$$S(U+\Delta U) - 2S(U) + S(U-\Delta U) \leq 0$$

$$S(U+\Delta U) - S(U) - (S(U) - S(U-\Delta U)) \leq 0$$

$$S'(U)\Delta U - S'(U-\Delta U)\Delta U \leq 0$$

$$S'(U) - S'(U-\Delta U)\Delta U \leq 0$$

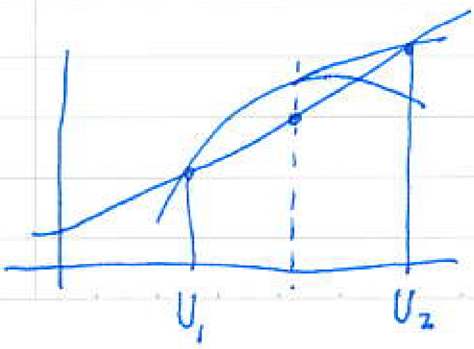
$$S''(U)(\Delta U)^2 \leq 0$$

$$\rightarrow S''(U) \leq 0 \rightarrow \frac{\partial^2 S}{\partial U^2} \leq 0$$

local condition less restrictive

$\rightarrow$ similarly $\dfrac{\partial^2 S}{\partial V^2} \leq 0$

$$S(U+\Delta U, V+\Delta V, N) + S(U-\Delta U, V-\Delta V, N) \leq 2S(U, V, N)$$

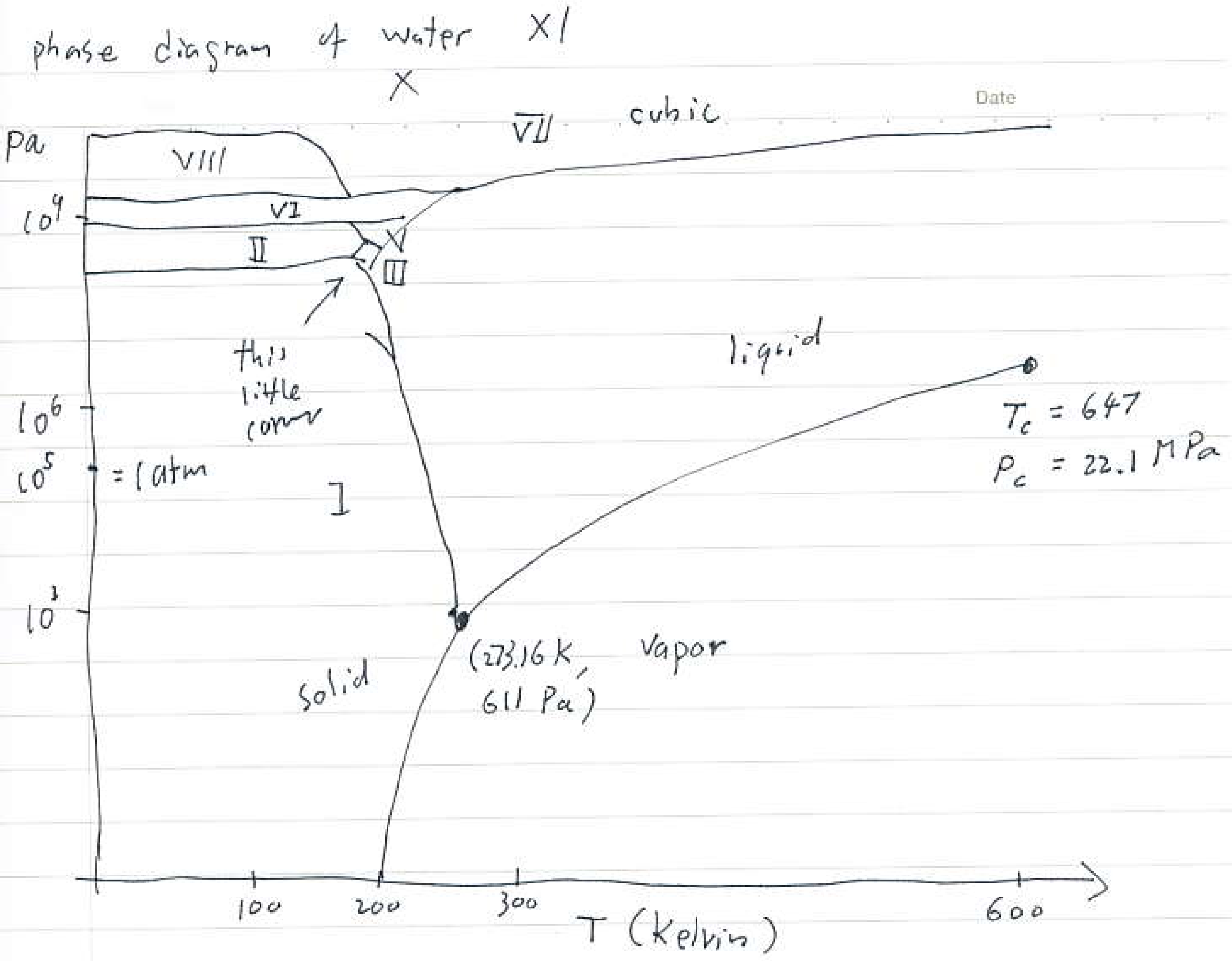


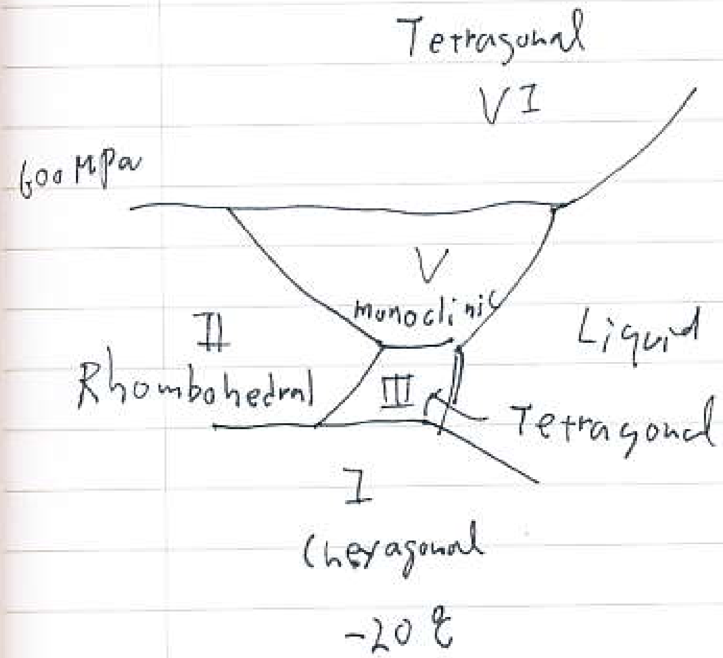
$$\lambda S(U_1) + (1-\lambda) S(U_2) < S(\lambda U_1 + (1-\lambda) U_2)$$

$$0 \leq \lambda \leq 1$$

phase diagram of water

Date



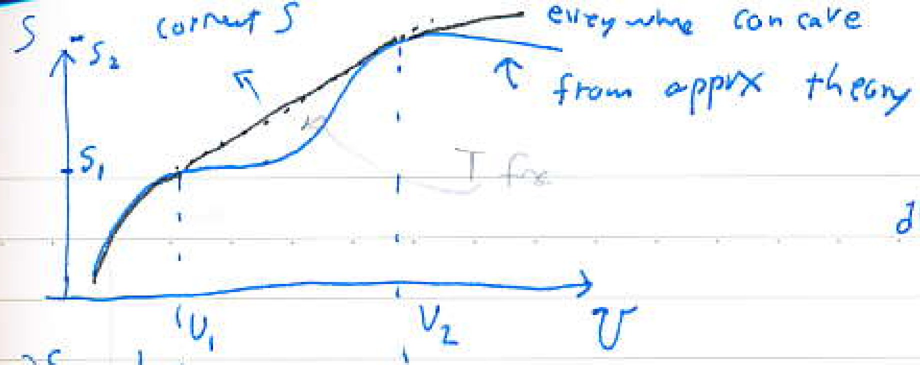


1 atm = 101325 Pa
$\approx 10^5$ Pa

1 Pa = 1 kg/(m·s²)
= 1 N/(m²)

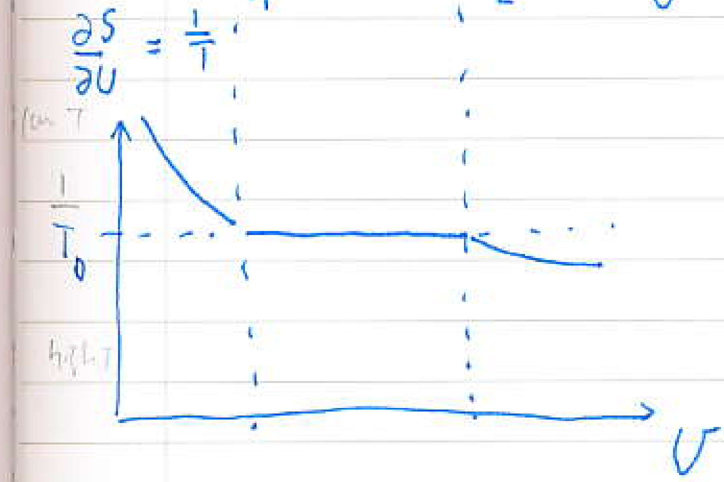
snow?

pascal



$dU = TdS - pdV + \mu dN$

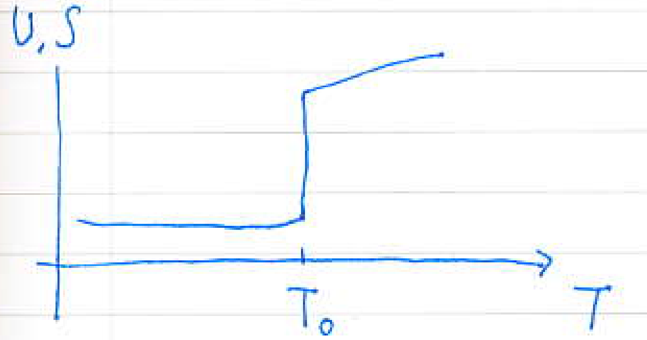
$= \delta Q \quad dV = 0 \quad dN = 0$



$\Delta Q = T_0(S_2 - S_1)$

↑
latent heat

going from states $T < T_0$ to state $T > T_0$ energy & entropy jump discontinuously



1st order phase transition

consequence of the stability condition

$$\frac{\partial^2 S}{\partial U^2} \leq 0 \rightarrow \frac{\partial}{\partial U}\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{\partial}{\partial U}\left(\frac{1}{T}\right)_{V,N} = -\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_{V,N}$$

$$= -\frac{1}{T^2}\frac{1}{C_V} < 0 \rightarrow C_V \geq 0$$

$$\frac{\partial^2 S}{\partial V^2} \leq 0 \rightarrow \frac{\partial}{\partial V}\left(\frac{\partial S}{\partial V}\right) = \frac{\partial}{\partial V}\left(\frac{P}{T}\right)_{U,N} ?$$

stability in other fundamental relation

S : concave in U, V $\quad \frac{\partial^2 S}{\partial U^2} \le 0 \quad \frac{\partial^2 S}{\partial V^2} \le 0$

$U(S,V,N)$ convex in S, con~~cave~~vex in V

$$\frac{\partial^2 U}{\partial S^2} \geq 0 \qquad \frac{\partial^2 U}{\partial V^2} \geq 0$$

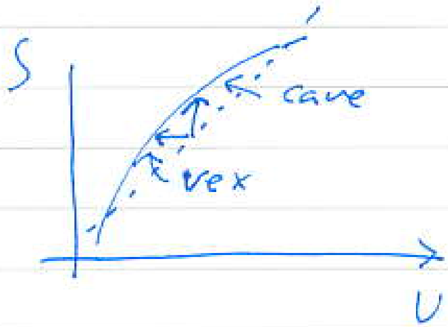
$F(T,V,N)$ concave in T

$$\frac{\partial^2 F}{\partial T^2} \leq 0 \qquad \frac{\partial^2 F}{\partial V^2} \geq 0$$

$G(T,P,N) = F - \mu N$ concave in T & P

$$\frac{\partial^2 G}{\partial T^2} \leq 0 \qquad \frac{\partial^2 F}{\partial P^2} \leq 0$$

proof: from $\frac{\partial^2 S}{\partial U^2} \le 0 \quad \frac{\partial^2 S}{\partial V^2} \le 0$ to condition for U



$F = U - TS$

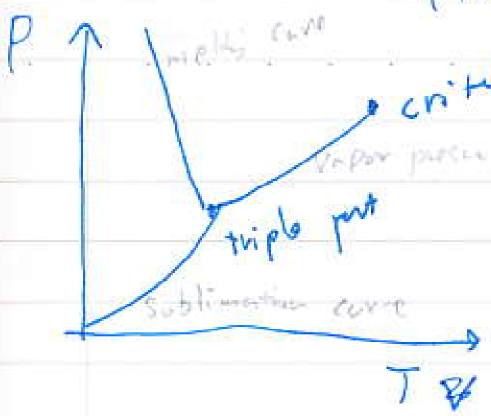
$$T = \frac{\partial U}{\partial S}\bigg|_{V,N} \qquad S = -\frac{\partial F}{\partial T}\bigg|_{V,N}$$

$$\frac{\partial S}{\partial T}\bigg|_{V,N} = -\frac{\partial^2 F}{\partial T^2}\bigg|_{V,N}$$

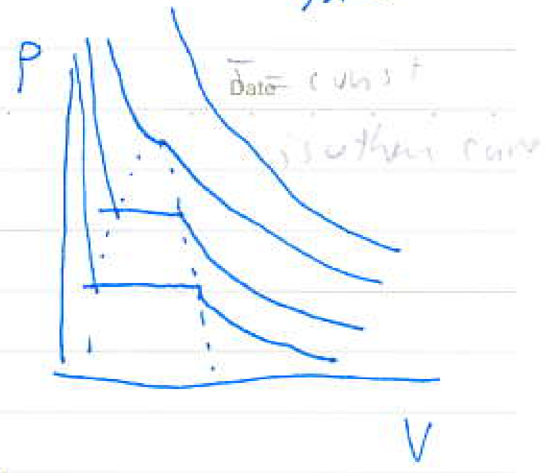
$$= \left(\frac{\partial T}{\partial S}\right)^{-1}_{V,N} = \frac{\partial^2 U}{\partial S^2}\bigg|_{V,N}$$

qualitative features of phase diagram in simple one-component system

(Thomas Andrews 1860s)



Ar (Argon)



Clapeyron eqn.

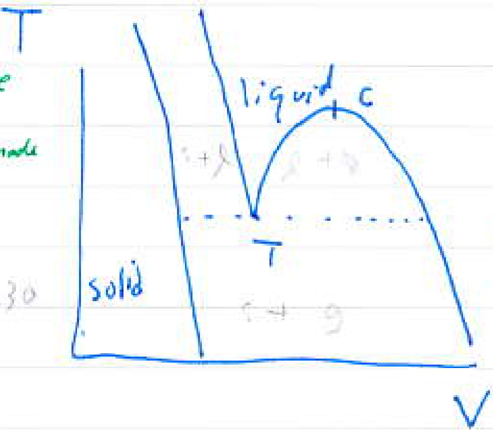
$$\frac{dP}{dT} = \frac{\ell}{T \Delta v}$$

latent heat per mole

← volume change per mole

$\ell = T \Delta s$

See Callen page 229-230



condition for phase equilibrium

$T_1 = T_2$

$P_1 = P_2$

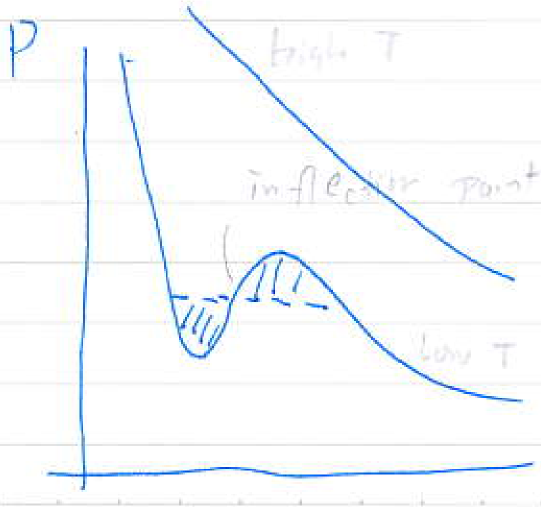
$\mu_1 = \mu_2$

Van der Waals invented the law of corresponding states

van der Waals theory of phase transition (plus theory)

Year (1873) nobel prize in 1910

$$\left[P + a\left(\frac{N}{V}\right)^2\right](V - Nb) = Nk_BT$$



Maxwell construction by requiring $\mu_1 = \mu_2$

16 Feb 07

derivation of van der Waals equation

van der Waals theory of phase transition 1873.

Ideal gas $\quad Z = \int dp_1 \cdots dp_{3N} \int dq_1 \cdots dq_{3N}\, e^{-\frac{\sum \frac{1}{2m} p_j^2}{k_B T}} \frac{1}{N!}\frac{1}{h^{3N}}$

$F = -k_B T \ln Z$

$$= V^N \cdot T^{\frac{3N}{2}} \cdot \text{const}$$

$$F = -k_B T N \ln V + f(T) = U(T) - TS$$

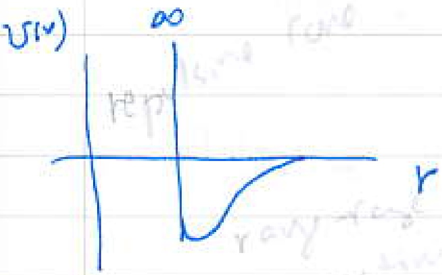
$$p = -\frac{\partial F}{\partial V} = \frac{k_B T N}{V} \qquad S = -\frac{\partial F}{\partial T} = k_B N \ln V + \text{terms indept of } V$$

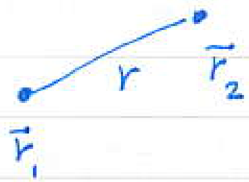
$v(r)$

Lennard-Jones potential

$$v(r) = \epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right)$$

r = distance between two particles





when $v \to \infty$

$$e^{-\infty} = 0$$

$$Z = \int dq_1 \cdots dq_{3N}\, e^{-\beta \sum_{ij} v(\cdots)} \cdot T^{\frac{3N}{2}}$$

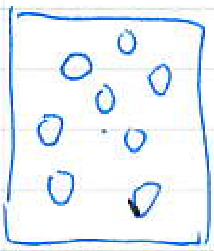
$\vec{r}_1 = (q_1\, q_2\, q_3)$

$\vec{r}_2 = (q_4\, q_5\, q_6)$

$\cdots$

$$\int d\vec{r}\, e^{-\beta \cdots} < V$$

mean-field approx.



other particles are fixed at their equlm position

look at one fixed particle say $\vec{r}_1$

$$\int d\vec{r}\, e^{-\beta \sum v(\cdots)} = V - bN$$

excluded volume effect

$\to \quad S = k_B N \ln(V - bN) + \text{terms indept of } V$

volume dependent contribution to internal energy U

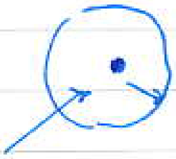
$$U = -a\left(\frac{N}{V}\right)\cdot N + V \text{ indept part.}$$

attractive

every particle contributes

Date

$\frac{N}{V} = \rho$ is density



range of attract

if there is a particle there will be contribution

$\sum_{i<j} v(\vec{r}_{ij})$ $\vec{r}_i$: random

$U = \sum_{i<j} \langle \Sigma v \rangle = N(N-1)\langle v \rangle$

$\langle v \rangle = \frac{\sigma^3}{V}\varepsilon_0 + 0$

$\rho \cdot \sigma^3$ is total contribution to each particle

$$F = U - TS$$

$$= -a\left(\frac{N^2}{V}\right) - Nk_BT\ln(V - Nb) + \text{terms indept of volume.}$$

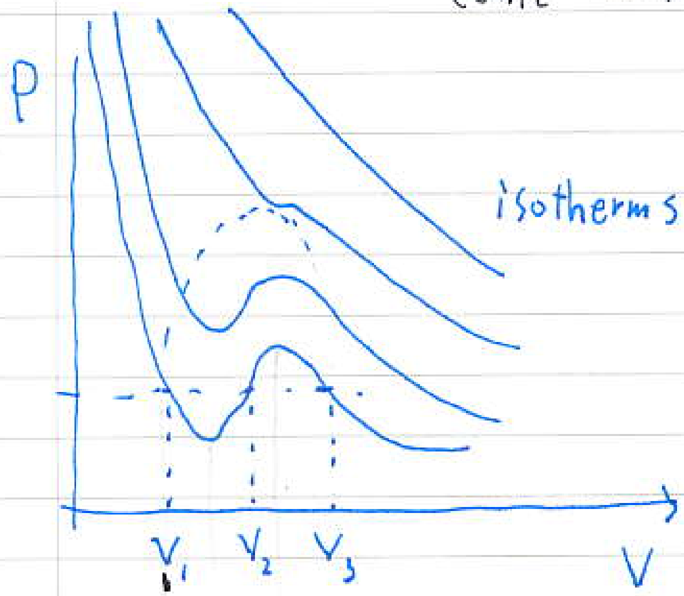
terms indept of volume has no contribution to equation of state

$$p = -\frac{\partial F}{\partial V} = -a\frac{N^2}{V^2} + \frac{Nk_BT}{V - Nb}$$

$U \propto \frac{N^2}{V}$

$$\left[p + a\left(\frac{N}{V}\right)^2\right](V - bN) = Nk_BT$$

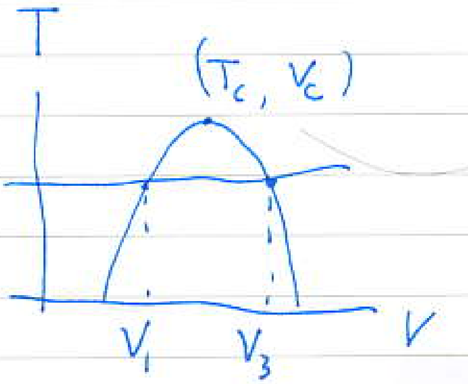
cubic in V



critical point

$\left.\frac{\partial p}{\partial V}\right|_T = 0$ two extrema

$\frac{\partial^2 p}{\partial V^2} = 0$ point in inflection



$$\frac{\partial P}{\partial V} = \frac{2aN^2}{V^3} + \frac{(-Nk_BT)}{(V-Nb)^2} = 0 \qquad (1)$$

$$\frac{\partial^2 P}{\partial V^2} = -6\frac{aN^2}{V^4} + 2\frac{Nk_BT}{(V-Nb)^3} = 0 \qquad (2)$$

$$\frac{(1)}{(2)} \qquad \frac{2}{3}V = V - Nb, \quad bN = \frac{1}{3}V$$

$$V_c = 3bN, \qquad \frac{2aN^2}{(3bN)^3} = \frac{Nk_BT_c}{\left[\frac{2}{3}(3bN)\right]^2}$$

$$k_BT_c = \frac{8}{27}\frac{a}{b} \qquad \text{substitute into (1)} \qquad \frac{2a}{3\cdot b}\left(\frac{2}{3}\right)^2 = k_BT_c$$

$$P_c = -a\left(\frac{N}{V_c}\right)^2 + \frac{Nk_BT_c}{V_c-Nb} = -a\frac{1}{(3b)^2} + \frac{8}{27}\frac{a}{b}\frac{1}{2b}$$

$$= \frac{a}{27b^2}$$

Maxwell construction

Gibbs-Duhem relation: $U(\lambda S, \lambda V, \lambda N) = \lambda U(S,V,N)$

$\rightarrow \frac{\partial}{\partial \lambda}$ on both side, let $\lambda = 1$

$$U = TS - PV + \mu N$$

$$dU = TdS - pdV + \mu dN \Rightarrow SdT - Vdp + Nd\mu = 0$$

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP \qquad \text{on isotherm curve } dT = 0,\ T = \text{const}$$

$$d\mu = \frac{V}{N}dp$$

$$\int_1^3 d\mu = \frac{1}{N}\int_1^3 V\,dp = \mu(3) - \mu(1) = 0$$

Date

① $N = N_g + N_\ell$ "$\rho V = N$"

$N_g = \frac{N}{V_g} V_g^{\,x}$

$N_\ell = \frac{N}{V_\ell} V_\ell^{\,x}$

② $v_g N_g + v_\ell N_\ell = V^x = V$

volume per molecule in the phase

$N_g + N_\ell = N$

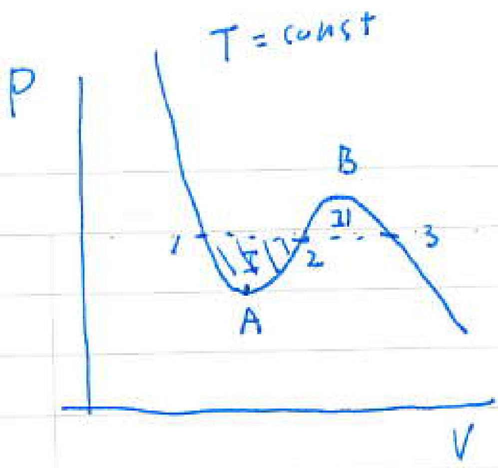
$v_g N_g + v_\ell (N - N_g) = V$

$(v_g - v_\ell) N_g = V - V_\ell$

$N_g = \frac{V - V_\ell}{v_g - v_\ell}$ $\quad x_g = \frac{N_g}{N} = \frac{V - V_\ell}{V_g - V_\ell}$

$N_\ell = \frac{V_g - V}{v_g - v_\ell}$ $\quad x_\ell = \frac{N_\ell}{N} = \frac{V_g - V}{V_g - V_\ell}$

$v_g N = V_g$



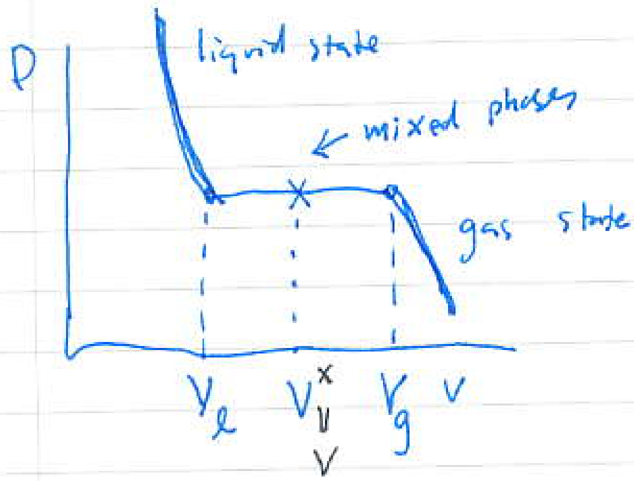
$$\int_1^3 v\,dP = \int_1^A + \int_A^2 + \int_2^B + \int_B^3 = 0$$

Date

$$= \int_A^2 - \int_A^1 + \int_2^B - \int_3^B$$

$$\cancel{= \text{Area}} = \text{Area}_{I} - \text{Area}_{II} = 0$$

areas are equal.



same P
same T
same μ

$$V_g^x + V_\ell^x = V^x$$

see Callen ch. 9.

The fraction of the system that exists in each of the two phases is governed by the "lever rule".

Let $v_\ell = \frac{V_\ell}{N}$ (volume per mole) $\quad x_\ell = \frac{N_\ell}{N} \quad x_g = \frac{N_g}{N}$

$v_g = \frac{V_g}{N}$

$$\cancel{V^x = V_g^x + V_\ell^x = \frac{V_g^x}{N^g} N^g + \frac{V_\ell^x}{N^\ell} N^\ell = v_g N^g + v_\ell N^\ell}$$

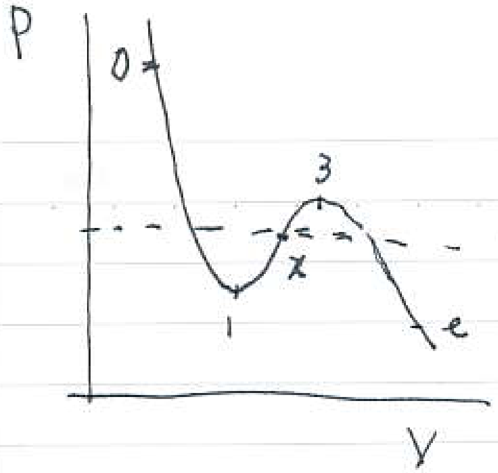
① $N = N_g + N_\ell$

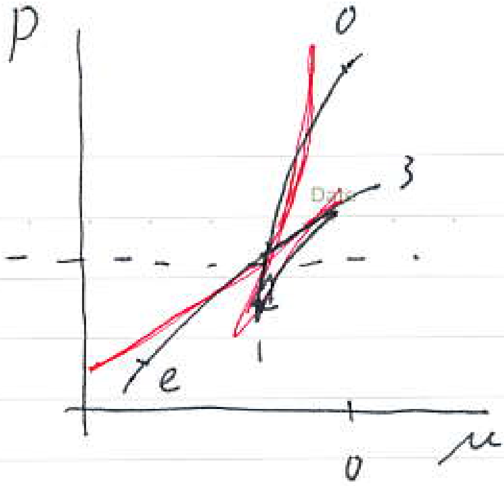
② $V_g^x + V_\ell^x = V^x$

③ $V_g^x = \frac{V_g}{N} N_g = v_g N_g$

④ $V_\ell^x = \frac{V_\ell}{N} N_\ell = v_\ell N_\ell$

$$\cancel{V_g^x + V_\ell^x = V^x}$$





$$\mu = \mu_0 + \int_0^x \frac{V}{N} dP = \mu_0 + \int_0^x v\, dP = \frac{G}{N}$$

minimization principle in G or μ at fixed T, P, N
the system takes one that has smallest μ.

there are $T, P, \mu_1, \mu_2 \cdots \mu_r$
$2+r$ intensive parameters
M phases in each phase there are
1 Gibbs-Duhem relation so
total free intensive
params is $r+2-M$

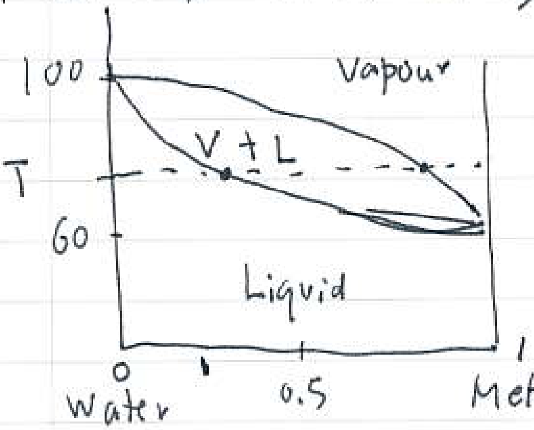
phase digrams of binary systems

constant P

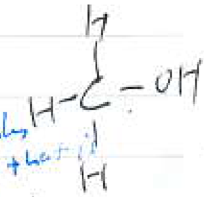
Gibbs phase rule

$f = r - M + 2$

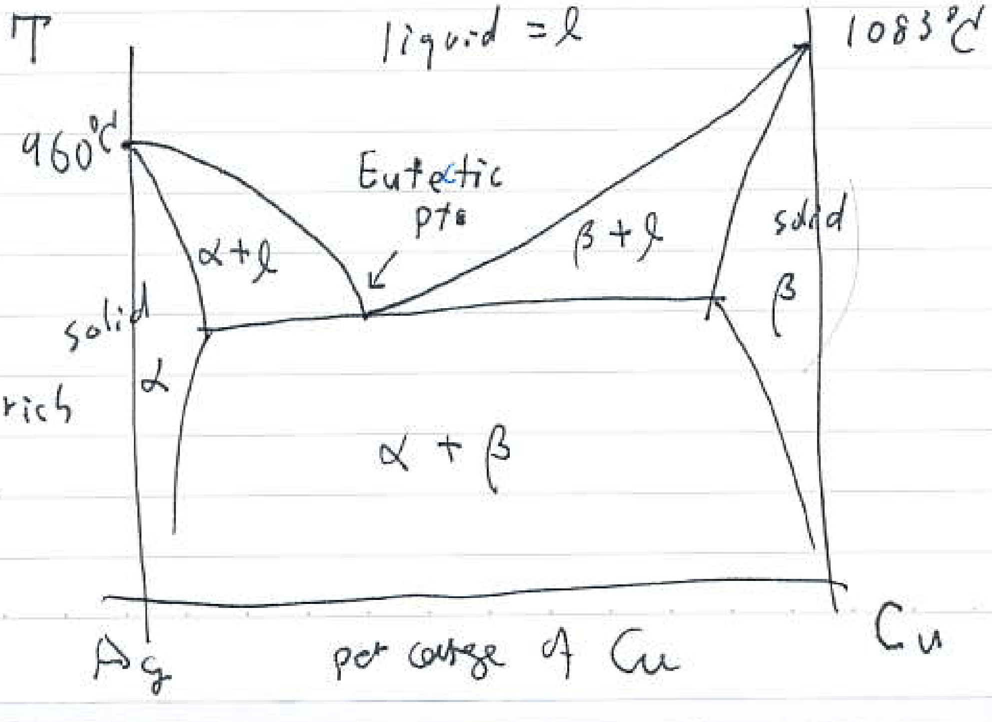
r: # of components
M: # of phases (intensive)
f: number of variables (how many variables that can vary
still ~~var~~ can vary. that can still in that phase)
constant P



Mole fraction of methanol 甲醇



CH_3OH



α: Ag rich
FCC

β Cu-rich
FCC

$$q(t) = A\cos\omega t + B\sin\omega t$$

$$B = \frac{p}{m\omega}$$

Date

$$q(0) = A$$

$$\dot{q}(0) = A(-\omega)\sin\omega t + B\cos\omega t\cdot\omega = \frac{p}{m}$$

$$q(t) = q\cos\omega t + \frac{p}{m\omega}\sin\omega t$$

3.

$$Z = \frac{1}{N!\,h^{3N}}\int dp_1\cdots dp_{3N}\, e^{-\beta\sum_j \frac{p_j^2}{2m}} \int q_1 \cdots \int q_{3N}$$

$$= \frac{1}{N!\,h^{3N}} V^N \left[\int_{-\infty}^{\infty} dp\, e^{-\frac{\beta p^2}{2m}}\right]^{3N}$$

$$= \frac{1}{N!\,h^{3N}} V^N \left(m 2\pi k_B T\right)^{\frac{3N}{2}} = \frac{1}{N!}\left[\frac{V(2\pi m k_B T)^{\frac{3}{2}}}{h^3}\right]^N$$

$$= \frac{N^N}{N!\,\lambda^{3N}}$$

$$F = -k_B T \ln Z$$

$$= -k_B T\left\{N \ln\left[\frac{V(2\pi m k_B T)^{\frac{3}{2}}}{h^3}\right] - N\ln N + N\right\}$$

$$= -N k_B T\left\{\ln\left(\frac{V}{N}\frac{(2\pi m k_B T)^{\frac{3}{2}}}{h^3}\right) + 1\right\}$$

$$S = -\frac{\partial F}{\partial T} = N k_B\left\{\ln\left(\frac{V}{N\lambda^3}\right) + 1\right\} + N k_B T\,\frac{3}{2}\,\frac{1}{T} \qquad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$= N k_B\left\{\frac{5}{2} + \ln\left(\frac{V}{N\lambda^3}\right)\right\}$$

$$P = -\frac{\partial F}{\partial V} = \frac{N k_B T}{V}$$

$$\mu = \frac{\partial F}{\partial N} = -k_B T\left\{\ln\frac{V}{N\lambda^3} + 1\right\} + k_B T = -k_B T \ln\frac{V}{N\lambda^3}$$

$$U = F + TS = -NK_BT\left\{\ln\frac{V}{N\lambda^3} + 1\right\}$$

$$+ NK_BT\left\{\frac{5}{2} + \ln\frac{V}{N\lambda^3}\right\} = \frac{3}{2}Nk_BT$$

grand canonical

$$\Xi = \sum_{N=0}^{\infty} Z_N e^{\beta\mu N} = \sum_{N=0}^{\infty}\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N e^{\beta\mu N}$$

$$= \sum_{n=0}^{\infty}\frac{1}{N!}\left(\frac{V}{\lambda^3}e^{\beta\mu}\right)^N = e^{\frac{V}{\lambda^3}e^{\beta\mu}}$$

$\lambda \propto T^{-\frac{1}{2}}$

$$\Psi(T, V, \mu) = -k_BT\ln\Xi = -k_BT\frac{V}{\lambda^3}e^{\beta\mu}$$

$$\left[\frac{(2\pi m k_BT)^{3/2}}{h^3}\right]'$$

$$pV = k_BT\left(\frac{V}{\lambda^3}e^{\beta\mu}\right) = k_BTN = -k_BTN$$

$$= \frac{3}{2}\frac{(2\pi m k_B)^{3/2}T^{1/2}}{h^3}$$

$$S = -\frac{\partial\Psi}{\partial T} = \left[-k_B\frac{V}{\lambda^3}e^{\beta\mu} + \cancel{k_BT}\frac{V}{\lambda^3}e^{\beta\mu}\frac{\mu}{\cancel{k_B}T^2} - k_B\cancel{T}\frac{Ve^{\beta\mu}}{\lambda^3}\frac{3}{2}\cdot\frac{1}{\cancel{T}}\right]$$

$$= +\frac{5}{2}k_B\frac{V}{\lambda^3}e^{\beta\mu} - \left(\frac{\mu}{T}\right)\frac{V}{\lambda^3}e^{\beta\mu}$$

$$N = -\frac{\partial\Psi}{\partial\mu} = k_BT\frac{V}{\lambda^3}e^{\beta\mu}\cdot\beta = \frac{V}{\lambda^3}e^{\beta\mu}$$

$$+\frac{5}{2}k_BN - \frac{\mu}{T}N$$

$$\Psi = U - TS - \mu N$$

$$p = -\frac{\partial\Psi}{\partial V} = k_BT\frac{e^{\beta\mu}}{\lambda^3} = \frac{k_BTN}{V}$$

$$U = \Psi + TS + \mu N = -k_BTN + \frac{5}{2}k_BTN - \mu N + \mu N = \frac{3}{2}k_BTN$$

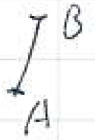
Tutal 3.

partition function for 1 molecule

$$Z = \frac{z^N}{N!}$$

$$z_{trans} = \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} e^{-\frac{\beta p^2}{2m}} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}$$

$$z = z_{trans}\, z_{rot} \cdot z_{vib}$$



$$z_{rot} = \sum_{j=0,1,2,\ldots} e^{-\frac{\beta \hbar^2 (j+1)j}{2I}} \cdot (2j+1)$$

due to degeneracy

$$\frac{2\pi m k_B T}{h}$$

$$z_{vib} = \sum_{n=0,1,2,\ldots} e^{-\beta \hbar\omega n} = \frac{1}{1-e^{-\beta\hbar\omega}}$$

$$F = -k_B T N\left(\ln z_{tran} + \ln z_{rot} + \ln z_{vib}\right) \qquad -\frac{\partial}{\partial\beta}$$

$$\frac{U}{N} = -\frac{\partial}{\partial\beta}\left(\ln z_{trans} + \ln z_{rot} + \ln z_{vib}\right) \qquad = -\frac{\partial T}{\partial\beta}\frac{\partial}{\partial T} \qquad = -\frac{\partial \frac{1}{\beta}}{\partial\beta} = \frac{1}{\beta^2}$$

$$= -\frac{\partial}{\partial\beta}\left[\left(-\frac{3}{2}\right)\ln\beta\right) + \ln\sum_j (2j+1) e^{-\beta\frac{\hbar^2(j+1)j}{2I}} \oplus \ln\left(1-e^{-\beta\hbar\omega}\right)\Big]$$

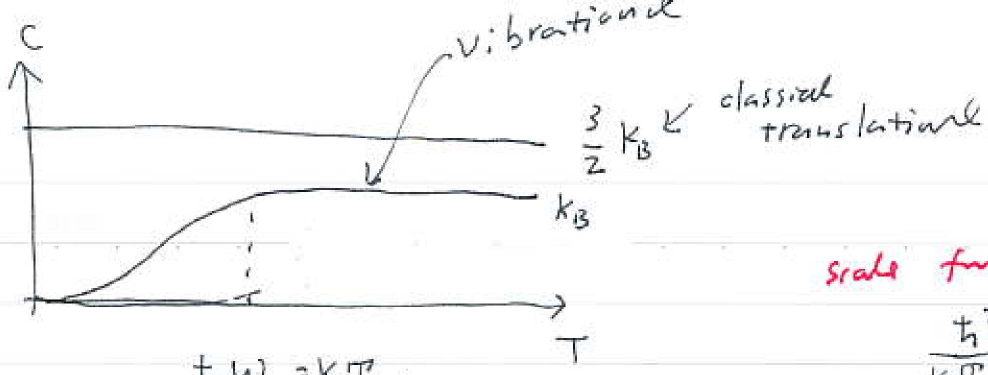
$$= \frac{3}{2}\frac{1}{\beta} + \frac{1}{z_{rot}}\sum_j (2j+1)\left(\frac{\hbar^2(j+1)j}{2I}\right) e^{-\beta\frac{\hbar^2 j(j+1)}{2I}} + \frac{e^{-\beta\hbar\omega}\,\hbar\omega}{1-e^{-\beta\hbar\omega}}$$

$$= \frac{3}{2}k_B T + \frac{1}{z_{rot}}\sum_j \frac{\hbar^2(j+1)j}{2I}\cdot(2j+1)\, e^{-\beta\frac{\hbar^2 j(j+1)}{2I}} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$$\frac{C_v}{N} = \frac{d}{dT}\left(\frac{U}{N}\right) = \frac{3}{2}k_B + \frac{\hbar\omega\, e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^2}\,\frac{\hbar\omega}{k_B T^2} +$$

$$+ \frac{1}{z_{rot}}\sum_j \left(\frac{\hbar^2(j+1)j}{2I}\right)^2 (2j+1)\, e^{-\beta\frac{\hbar^2 j(j+1)}{2I}}\,\frac{1}{k_B T^2}$$

$$- \left(\frac{1}{z_{rot}}\left[\sum_j \frac{\hbar^2(j+1)j}{2I}(2j+1)\, e^{-\beta\frac{\hbar^2 j(j+1)}{2I}}\right]\right)^2 \frac{1}{k_B T^2}$$



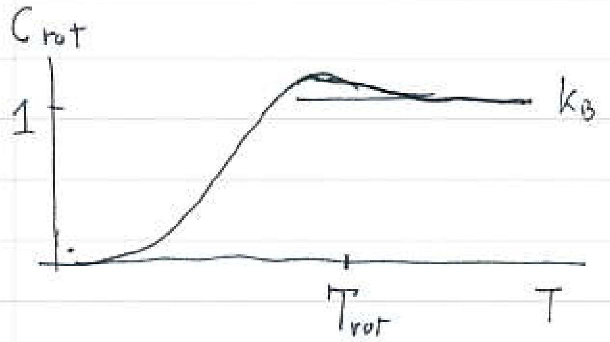
$\hbar\omega_D = k_B T_{vib}$

$\omega = \omega_D$

Date

scale for rotational part

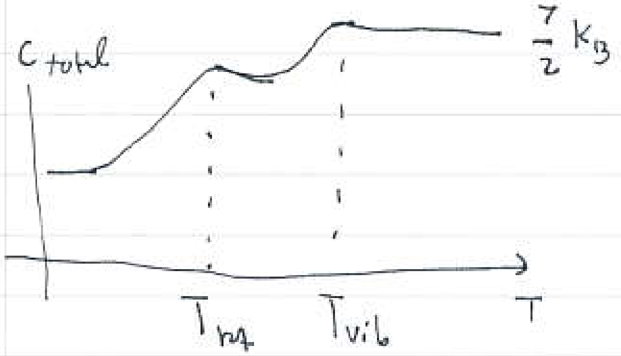
$$\frac{\hbar^2}{k_B T I} = O(1)$$



~~high T limit~~ $\quad Z_{rot} \approx \int_0^\infty dj\, e^{-\left(\frac{\beta\hbar^2 j(j+1)}{2I}\right)}(2j+1) = \frac{2I}{\beta\hbar^2}$

$$U = -\frac{\partial \ln Z_{rot}}{\partial\beta} = -\frac{\partial}{\partial\beta}(-\ln\beta) = \frac{1}{\beta} = k_B T$$

$C = k_B \quad (\text{as } T\to\infty)$



van der Waals Eq. behavior near the critical point

Date

$$\left[p + a\left(\frac{N}{V}\right)^2\right](V - bN) = Nk_BT \qquad \text{consider} \quad p = P_c + \Delta p$$

$$T = T_c + \Delta T$$

$$P_c = \frac{a}{27b^2}, \quad k_BT_c = \frac{8}{27}\frac{a}{b}, \quad V_c = 3bN \qquad V = V_c + \Delta V$$

$$\cancel{\left[P_c + \Delta p + a\frac{N^2}{V}\right.}$$

$$\left[\frac{a}{27b^2} + \Delta p + a\frac{N^2}{(3bN + \Delta V)^2}\right]\left[3bN + \Delta V - bN\right] = Nk_B\Delta T + N\frac{8}{27}\frac{a}{b}$$

$$\left[\left(\frac{a}{27b^2} + \Delta p\right)(3bN + \Delta V)^2 + aN^2\right]\left[2bN + \Delta V\right]$$

$$+ \left(Nk_B\Delta T + N\frac{8}{27}\frac{a}{b}\right)(3bN + \Delta V)^2$$

when $\Delta T = 0$

$$\left[\left(\frac{a}{27b^2} + \Delta p\right)(9b^2N^2 + 6bN\cdot\Delta V + \Delta V^2) + aN^2\right]\left[2bN + \Delta V\right]$$

$$= \frac{8}{27}N\frac{a}{b}(9b^2N^2 + 6bN\cdot\Delta V + \Delta V^2)$$

$$\left[\delta p + aN^2\left(-2\frac{\delta V}{V_c^3}\right)\right](V_c - bN) + \left[\left(P_c + a\left(\frac{N}{V_c}\right)^2\right]\delta V = Nk_B\delta T$$

$$\left[\delta p - \frac{2aN^2\delta V}{(3bN)^3}\right](2bN) + \left[\frac{a}{27b^2} + \frac{a}{9b^2}\right]\delta V = Nk_B\delta T$$

isothermal compressibility

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

Date

$$\left.\frac{\partial P}{\partial V}\right|_T = \frac{2aN^2}{V^3} - \frac{Nk_BT}{(V-Nb)^2}$$

$$\text{at } V=V_c \Big\} = \frac{2aN^2}{27b^3N^3} - \frac{Nk_BT}{4N^2b^2}$$

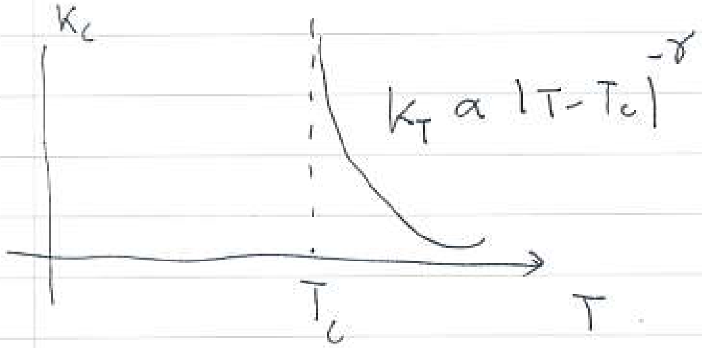
$$= \frac{2a}{27b^3N} - \frac{k_BT}{4Nb^2}$$

$$= \frac{1}{4}\left(\frac{8a}{27b}\right)\frac{1}{b^2N} - \cdots$$

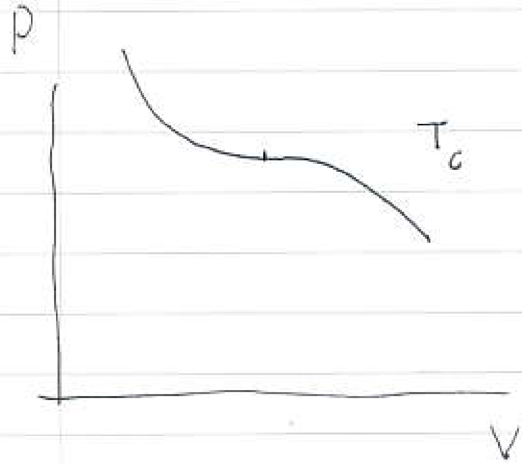
$$= \frac{k_B(T_c - T)}{4Nb^2}$$

$$\kappa_T = -\frac{1}{3bN}\cancel{\frac{k_B(T_c-T_c)}{4N}}\frac{4Nb^2}{k_B(T_c-T)}$$

$$= \frac{4}{3}b\frac{1}{k_B(T-T_c)}$$



$\gamma = 1$



critical isotherm curve

extreme

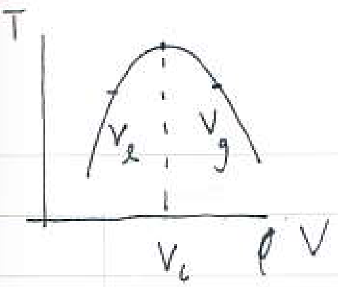
$$P(V,T_c) = P_c + \left.\frac{\partial P}{\partial V}\right|_{V_cT_c}(V-V_c)$$

inflection pt.

$$+\frac{1}{2}\left.\frac{\partial^2 P}{\partial V^2}\right|_{V_cT_c}(V-V_c)^2 + \frac{1}{6}\left.\frac{\partial^3 P}{\partial V^3}\right|_{V_cT_c}(V-V_c)^3 + \cdots$$

$$\Delta P \propto (\Delta V)^3 = (\Delta V)^\delta$$

$\delta = 3.$



$V_g - V_l \propto (T_c - T)^{\frac{1}{2}}$ $\beta = \frac{1}{2}$

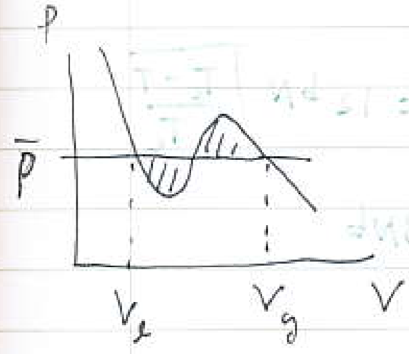
asymptotic result near the critical point.

why.

Date

$$\bar{P} = -\frac{aN^2}{V_l^2} + \frac{Nk_BT}{V_l - Nb}$$

Maxwell construction



$$P = -a\frac{N^2}{V^2} + \frac{Nk_BT}{V-Nb}$$

$$\int_{V_l}^{V_g} (P - \bar{P})\,dV = 0$$

$$\int_{V_l}^{V_g} \left(-\frac{aN^2}{V^2} + \frac{Nk_BT}{V-Nb} - \bar{P}\right)dV = \frac{aN^2}{V} + Nk_BT\ln(V-Nb) - \bar{P}V \Big|_{V_l}^{V_g}$$

$$\Rightarrow \frac{aN^2}{V_g} + Nk_BT\ln(V_g - Nb) + \frac{aN^2}{V_g} - \frac{Nk_BT}{V_g - Nb}\cdot V_g =$$

same exp with V_g replaced by V_l

$$\ln(V-Nb) + \frac{2aN}{k_BTV} - \frac{V}{V-Nb} = f(V)$$

$f(V_g) = f(V_l)$ $V_g = V_c + x$ $V_g - V_l = 2x$

$V_l = V_c - x$

$$f(V_g) = f(V_c) + f'(V_c)x + \frac{1}{2}f''(V_c)x^2 + \frac{1}{6}f'''(V_c)x^3 + \dots$$

$$f(V_l) = f(V_c) + f'(V_c)(-x) + \frac{1}{2}f''(V_c)x^2 + \frac{1}{6}f'''(V_c)(-x)^3 + \dots$$

$f(V_g) = f(V_l) \rightarrow$ $2f'x + \frac{1}{3}f'''x^3 = 0$

$$2f' + \frac{1}{3}f'''x^2 = 0$$

Date

entropy change near T_c

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \qquad \Delta V = 2x = 12\,bN\sqrt{\frac{T_c - T}{T_c}}$$

$$\frac{dP}{dT} = \frac{N k_B}{V - Nb} \approx \frac{N k_B}{2bN} = \frac{k_B}{2b} \qquad V_c = 3Nb$$

$$\text{so} \quad \Delta S = \frac{N k_B}{2bN} \cdot 12\,bN\sqrt{\frac{T_c - T}{T_c}}$$

$$= 6 k_B N\sqrt{\frac{T_c - T}{T_c}}$$

$$f' = \cancel{\frac{1}{V_c - Nb}} \quad 0 - \frac{2aN}{k_B T V_c^2} \quad \cancel{-\frac{1}{V_c - Nb}} + \frac{V_c}{(V_c - Nb)^2}$$

Date

$$= \frac{-2aN}{k_B T (9b^2N^2)} + \frac{3bN}{(2bN)^2}$$

$$k_B T_c = \frac{8}{27}\frac{a}{b}$$

$$= -\frac{2}{9}\frac{a}{k_B T b^2 N} + \frac{3}{4}\frac{1}{bN}$$

$$= -\frac{2}{9 k_B T}\left(\frac{27}{8} k_B T_c\right)\frac{1}{bN} + \frac{3}{4}\frac{1}{bN}$$

T close to T_c

$$= -\frac{3}{4}\frac{T_c}{T}\frac{1}{bN} + \frac{3}{4}\frac{1}{bN} = \frac{3}{4bN}\left(1 - \frac{T_c}{T}\right) \approx \frac{3}{4bN}\frac{(T-T_c)}{T_c}$$

$$\lambda(T - T_c) + f''' X^2 = 0$$

$$X \propto \sqrt{T_c - T}$$ as expected

$$f''' = \frac{5}{8b^3N^3} - \frac{4a}{27b^4 T N^3} \approx \frac{1}{8(bN)^3}$$

$$2 \cdot \frac{3}{4bN}\left(\frac{T - T_c}{T_c}\right) + \frac{1}{3}\frac{1}{8(bN)^3} X^2 = 0$$

$$2^2 \cdot 3^2 (bN)^2 \left(\frac{T - T_c}{T_c}\right) + X^2 = 0$$

$$X = 6(bN)\cdot\sqrt{\frac{T_c - T}{T_c}}$$

$$= 2V_c\sqrt{\frac{T_c - T}{T_c}}$$

Date

magnetic moment

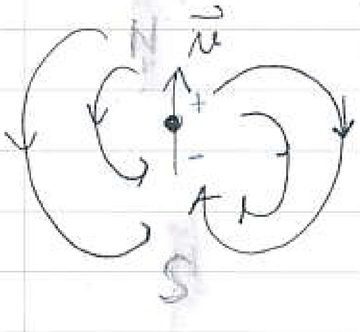
$$\vec{\mu} = \frac{1}{2c} \int \vec{r} \times \vec{j}(\vec{r})\, dV = \frac{I}{c} \times (\text{Area})$$

NO: c

$$\vec{A} = \frac{\mu_0}{4\pi} \frac{\vec{\mu} \times \vec{r}}{r^3}$$

$$\vec{B} = \frac{\mu_0}{4\pi} \frac{3\hat{r}(\hat{r}\cdot\mu) - \vec{\mu}}{r^3}$$

energy $U = -\vec{\mu}\cdot\vec{B}$



$\vec{B}$: magnetic induction

$\vec{H} = \frac{1}{\mu_0}\vec{B} - \vec{M}$ magnetic field

μ_0 ↑ magnetic permeability in the vacuum

$\vec{J} = \vec{L} + \vec{S}$

27 Feb 07

atoms/ions has magnetic moments (unpaired electron has spin $\vec{S}$, electrons has orbital angle momentum $\vec{L}$)

$$\vec{\mu} = -g \mu_B \vec{J}/\hbar \qquad g(JLS)$$

↑ Landé factor

$$\mu_B = \frac{e\hbar}{2m_e}$$

nucleus μ is 10^3 smaller

$$[\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_z \quad \text{etc.} \qquad \hat{J} \times \hat{J} = i\hbar \hat{J}$$

Energy of magnetic moment in a field

$$E = -\vec{\mu} \cdot \vec{B} = \underline{g \mu_B m B}$$

$\uparrow \hat{z}$ $\hat{H}$

Zeeman interactions

$\mu_0 H = B$

electron spin $\vec{S} = \frac{\hbar}{2} \hat{\vec{\sigma}}$ ← Pauli matrix

$g = 1$ for $\vec{L}$

$g = 2$ for spin

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$\vec{\mu} = -g\mu_0 \vec{J}/\hbar$ classical

$\vec{J} = \vec{L} + \vec{S}$

$$\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$\vec{\mu}_1 \uparrow \qquad \uparrow \vec{\mu}_2$

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

magnet dipole moment interactions

$$U = \frac{1}{r^3}[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{r})(\vec{\mu}_2 \cdot \hat{r})]$$

$U \simeq 10^{-4}\,\text{eV}$ too small for ferromagnetism

Heisenberg model ← exchange interactions

originate from Pauli

Pauli exclusion principle

$$E = -J \sum_{\langle ij \rangle} \hat{\vec{\sigma}}_i \cdot \hat{\vec{\sigma}}_j + g\mu_B B \sum \hat{\vec{\sigma}}_i$$

Take only z-component

Ising model $\qquad E = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i \qquad \sigma_i = \pm 1$

X-Y model

Date

$$S = Nk_B\left[\ln 2 - \tfrac{1}{2}(1+m)\ln(1+m) - \tfrac{1}{2}(1-m)\ln(1-m)\right]$$

canonl

① use results of S & M, eliminate h & β

② microcanl use $S = k_B \ln \Omega$ in ...

Paramagnetism

Date

$\mathcal{H} = -h\sum_i \sigma_i$ no interactions between spins (free spins)

$$Z = \sum_{\sigma_i} e^{-\beta\mathcal{H}} = \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N} e^{\beta h \sum_{i=1}^{N}\sigma_i} = \left[\sum_\sigma e^{\beta h\sigma}\right]^N$$

$$= (e^{\beta h} + e^{-\beta h})^N$$

$$F = -\frac{1}{\beta}\ln Z = -\frac{N}{\beta}\ln(e^{\beta h} + e^{-\beta h}) = -k_B T N \ln\left(2\cdot\cosh\frac{h}{k_B T}\right)$$

$$S = -\frac{\partial F}{\partial T} = k_B N \ln\left(2\cdot\cosh\frac{h}{k_B T}\right) + k_B T N \frac{2\cdot\sinh\frac{h}{k_B T}}{2\cosh\frac{h}{k_B T}}\cdot\left(-\frac{h}{k_B T^2}\right)$$

$$= k_B N \ln\left(2\cosh\frac{h}{k_B T}\right) - k_B N\left(\frac{h}{k_B T}\right)\tanh\frac{h}{k_B T}$$

$$U = F + TS = -hN\tanh\frac{h}{k_B T} = -\frac{\partial \ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\ln\left[2\cosh\beta h\right]^N$$

total magnetization $= -\tanh(\beta h)\times hN$

$$M \overset{\text{def}}{=} -\frac{\partial F}{\partial h} = -\frac{\partial}{\partial h}\left(-\frac{1}{\beta}\ln Z\right) = \frac{1}{\beta}\frac{1}{Z}\frac{\partial}{\partial h}\left[e^{\beta h\sum_{i=1}^{N}\sigma_i}\right]$$

$$= \frac{1}{\beta}\frac{1}{Z}\sum_{\{\sigma\}}\left(\beta\sum_{i=1}^{N}\sigma_i\right)e^{\beta h\sum\sigma_i} = \left\langle\sum_{i=1}^{N}\sigma_i\right\rangle = +\frac{N}{\beta}\frac{\partial}{\partial h}\ln(e^{\beta h} + e^{-\beta h})$$

$$= \frac{N}{\beta}\frac{e^{\beta h} - e^{-\beta h}}{e^{\beta h} + e^{-\beta h}}\cdot\beta = N\tanh(\beta h)$$

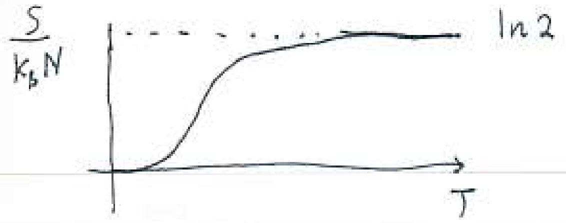
$F(T, h)$

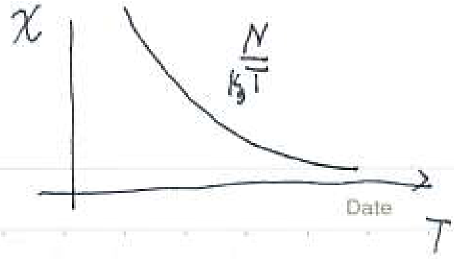
$$dF = \frac{\partial F}{\partial T}dT + \frac{\partial F}{\partial h}dh = -S\,dT - M\,dh$$

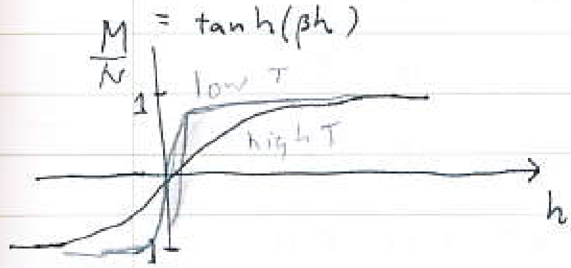
compare fluid (gas) $(-S\,dT - p\,dV)$

magnetic susceptibility

$$\chi \overset{\text{def}}{=} \left.\frac{\partial M}{\partial h}\right|_{h=0} = N\left.\frac{1}{\cosh^2(\beta h)}\cdot\beta\right|_{h=0} = \frac{N}{k_B T}$$ for Curie (-Weiss) law







Read chap. 14 & 15 of K. Huang

Mean-field theory of paramagnet $\rightleftarrows$ ferromagnetic

$$H = -J\sum_{\langle ij \rangle} \sigma_i \sigma_j - h\sum_i \sigma_i$$

look at one fixed spin, say $i = 0$

$$H_0 = -J \sum_{\langle 0j \rangle} \sigma_0 \sigma_j - h\sigma_0$$

← replace actual value by average

$$= -\Big(J\sum_j \langle \sigma_j \rangle + h\Big)\sigma_0 = -(Jqm + h)\sigma_0$$

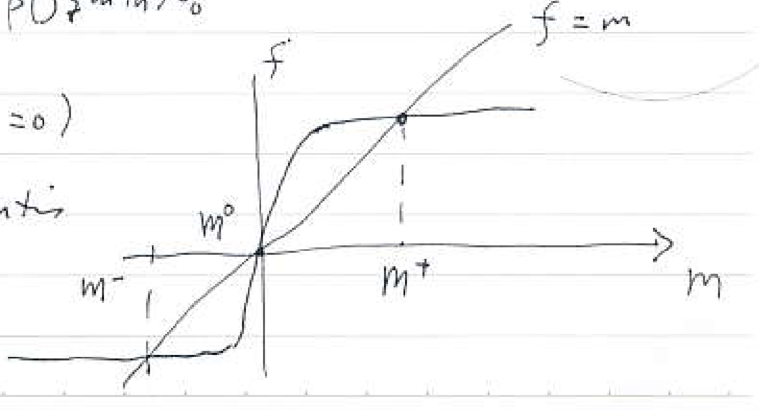
$$\langle \sigma_j \rangle = \langle \sigma_0 \rangle = m = \frac{M}{N}$$

$$m = \langle \sigma_0 \rangle = \frac{\sum_{\sigma_0 = \pm 1} \sigma_0 e^{\beta(Jqm+h)\sigma_0}}{\sum_{\sigma_0} e^{\beta(Jqm+h)\sigma_0}} = \tanh(\beta(Jqm+h))$$

solution for m (when $h=0$)

$m^0 = 0$ is always a solution

$m^\pm \neq 0$ if T is small



Date

comparism of k_BT_c/J on hypercubic lattice

d	1	2	3	4	5
MF	2	4	6	8	10
exact	0	2.27	4.5	6.68	8.78

$$\frac{k_BT_c}{J} = \left(d - \frac{1}{2} - \frac{1}{3d} + \cdots\right) 2$$

$$= \left(q - \frac{1}{2} - \frac{1}{}\right.$$

critical T $\quad \tanh(\beta J q m) \simeq \beta J q m$

we get intersect if slope of tanh is > 1

i.e. $\beta_c J q = 1$, or $\frac{Jq}{k_B} = T_c$

value of spontaneous magnetization $\qquad \tanh x = x - \frac{x^3}{3} + \frac{2x^5}{15} + \cdots$

$h = 0$

$$m = \tanh(\beta(qJm + h))$$

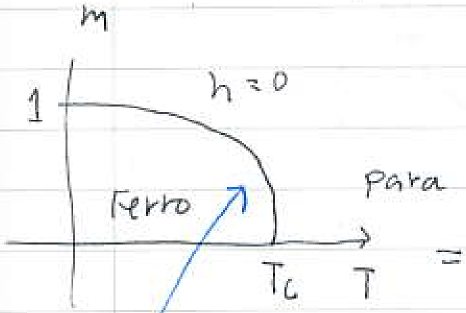
$$= \beta q J m - \frac{1}{3}(\beta q J)^3 m^3 + \cdots \qquad m \text{ small}$$

$$1 = \beta q J - \frac{1}{3}(\beta q J)^3 m^2 \qquad (\tanh x)' = \frac{1}{\cosh^2 x}$$

$$\beta q J - 1 = \frac{1}{3}(\beta q J)^3 m^2$$

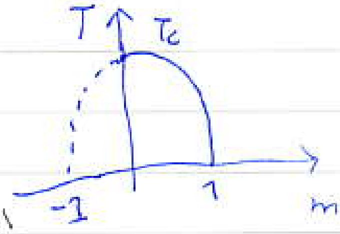
$$m^2 = \cancel{3\left(\frac{1}{(\beta q J)^2}\right)} = \frac{3}{(\beta q J)^3}(\beta q J - 1)$$

$$\frac{qJ}{k_B} = T_c$$



$$= \frac{3}{(\beta q J)^3}\left(\frac{qJ}{k_B T} - 1\right)$$

$$= \frac{3}{(\beta q J)^3}\left(\frac{T_c - T}{T}\right)$$



$$m \propto (T_c - T)^{\frac{1}{2}} \qquad (T \to T_c) \qquad \beta = \frac{1}{2}$$

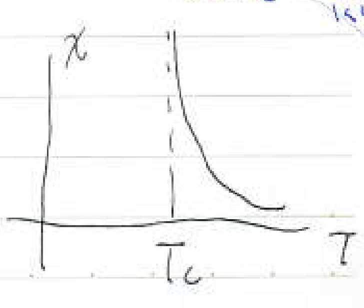
exact curve is given by
$\beta = \frac{1}{k_B T} = \frac{1}{2qJm} \ln \frac{1+m}{1-m}$

susceptibility

$$\chi = \frac{\partial m}{\partial h} = \frac{1}{\cosh^2(\beta(qJm + h))} \cdot \left[\beta q J \frac{\partial m}{\partial h} + \beta\right] \qquad \Big| \; T > T_c \quad m = 0$$

$h = 0$ $\quad$ Curie-Weiss law

$$\chi = \beta q J \chi + \beta$$



what is χ for $T < T_c$

$$\chi = \frac{\beta}{1 - \beta q J} = \frac{1}{1 - \frac{T_c}{T}} = \frac{T}{T - T_c}$$

$$= \cancel{6}\, |T - T_c|^{-\gamma} \qquad \gamma = 1$$

solution to $m = \tanh(\beta(qJm + h))$

$$h = -mqJ + \frac{1}{\beta}\operatorname{arctanh}(m)$$

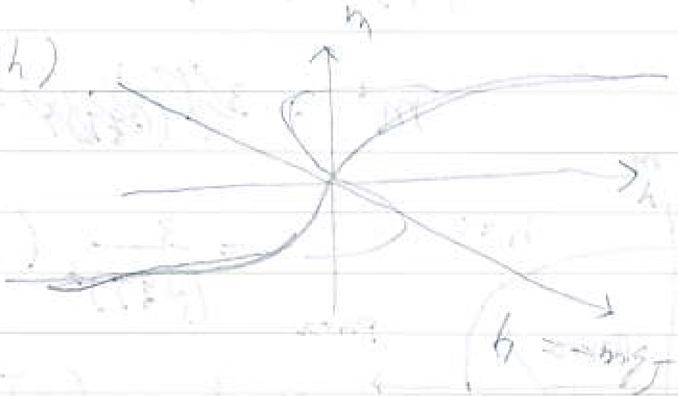
$h \to 0$ $\quad k_B T = \dfrac{mqJ}{\operatorname{arctanh}(m)}$

$$y = \operatorname{arctanh}(x) = \tanh^{-1}(x) = \frac{1}{2}\ln\frac{x+1}{-x+1} \quad |x| < 1.$$

$$\tanh(y) = x$$

$h = k_B T \tanh^{-1}(m)$

$\to m = \tanh(\beta h)$



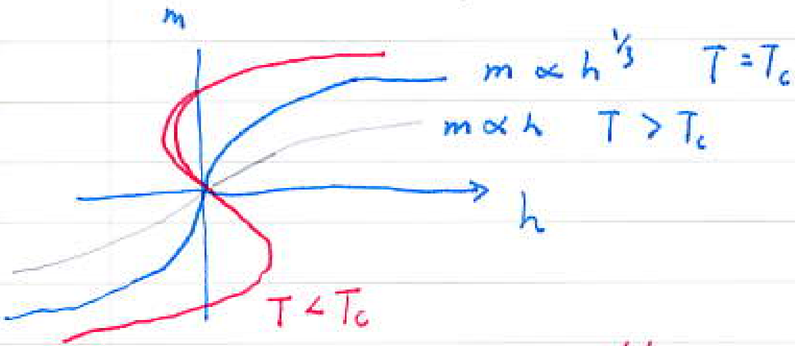
$h = -mqJ$

critical isotherm $\quad T = T_c$

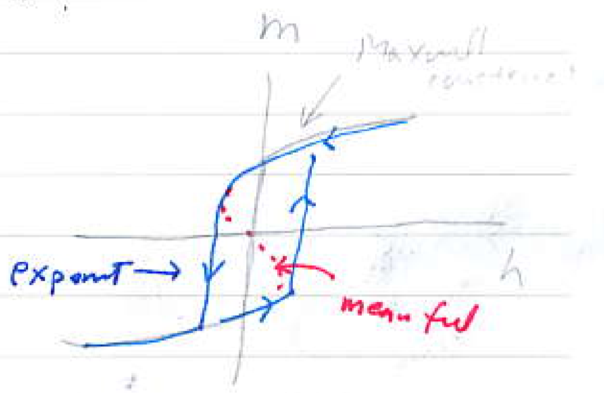
Date

$$m = \tanh(\beta_c(qJm + h))$$
$$= \tanh(m + \beta_c h) \qquad m \text{ small}$$
$$= m + \beta_c h - \frac{1}{3}(m + \beta_c h)^3 \qquad h \text{ small},\ T = T_c$$

$$\beta_c h = \frac{1}{3}(m + \beta_c h)^3 \qquad h \sim m^3$$
$$\approx \frac{1}{3} m^3 \qquad \delta = 3$$



Maxwell construction is needed



hysteresis

$F = U - TS$

$dU = dF + TdS + SdT$
$= -SdT - Mdh + SdT + TdS = TdS - Mdh$

Landau theory $\qquad$ magnetic system

"Helmholtz" free energy $\quad F_{(T,h)} = -\frac{1}{\beta} \ln Z \qquad Z = \sum_{\{\sigma_i\}} e^{-\beta \mathcal{H}}$

$$dF = -SdT - Mdh \qquad F = F(T, h)$$

"Gibbs" free energy $\qquad M = Nm$

$$G = F + Mh = G(T, M) \quad \text{order parameter}$$

$$dG = -SdT - Mdh + Mdh + hdM = -SdT + hdM$$

$\square$ G is even in M. $\quad$ (1) sign of M is same as h $(m \to -m,\ h \to -h)$

assumption 1 $\qquad$ so $Mh(M)$ is even in M

$F = -\frac{1}{\beta} \ln 2\cosh(\beta(Jqm + h))$ ← even functs in m

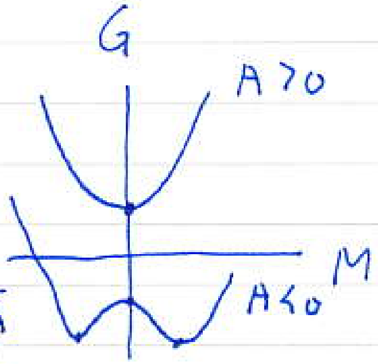
(at least in MF G is even in M. but should be generally true.

□ assumptis 2

$$G(T,M) = G(T,0) + A(T)M^2 + B(T)M^4 + \cdots$$

M small near critical pt

G is analytic in M (order parameter)



$$h = \frac{\partial G}{\partial M} = 2AM + 4BM^3$$

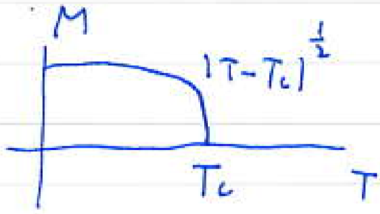
At $h = 0$ $\quad (2A + 4BM^2)M = 0$

$M = 0$ or $M = \pm\sqrt{\frac{-A}{2B}}$

□ assumptis 3

Let $A = a(T - T_c)$. $\quad a > 0$

$\rightarrow \quad M \propto (T_c - T)^{\frac{1}{2}} \quad T < T_c$



$\beta = \frac{1}{2}$

at T_c, $A = 0$

so $\quad h = 4BM^3 \qquad \delta = 3.$

susceptibility

$$\chi_T = \frac{\partial M}{\partial h}\Big|_{T,\,h=0} = \frac{\partial h}{\partial M}\Big|_T^{-1} = \frac{\partial^2 G}{\partial M^2}\Big|_T^{-1}$$

$T < T_c \quad h = 0$

$BM^2 = -\frac{1}{2}A$

$\chi_T^{-1} = 2A + (12)(-\frac{1}{2})A$

$= -4A$

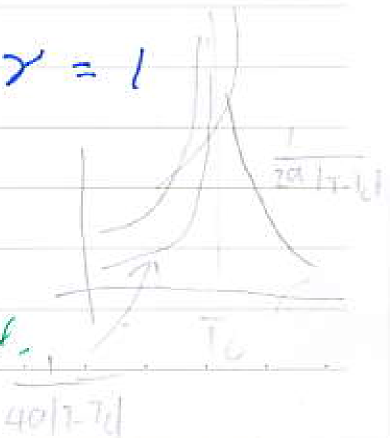
$= 4a(T_c - T)$

$$\chi_T^{-1} = 2A + 12BM^2\Big|_{T > T_c} = 2A$$

$M = 0$ for $T > T_c$

both below and above T_c make sense

$$\chi_T = \frac{1}{2a(T - T_c)} \propto |T - T_c|^{-\gamma} \qquad \gamma = 1$$



when does mean-field is valid ?

connection between Van der Waals theory, mean-field, & Landau theory.