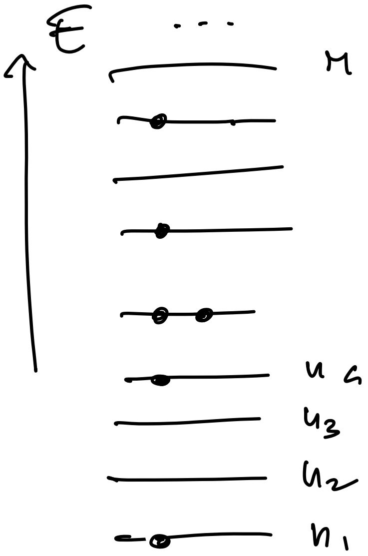
Second quantization



$|n_1, n_2, \ldots, n_M, \ldots\rangle \to$ Fock state

$(M \to \infty)$

vacuum $|0, 0, 0, \ldots, 0, \ldots\rangle = |0\rangle$

$a_\alpha, \; a_\alpha^+$

$\downarrow$

$\boxed{|\phi_\alpha\rangle \text{ orthonormal basis of } \mathcal{H}^{(1)}}$

$$|n_1, n_2, \ldots, n_M, \ldots\rangle = \frac{(\hat{a}_1^+)^{n_1}}{\sqrt{n_1!}} \frac{(\hat{a}_2^+)^{n_2}}{\sqrt{n_2!}} \cdots \frac{(\hat{a}_M^+)^{n_M}}{\sqrt{n_M!}} \cdots |0\rangle$$

statistics $\to$ commutation relations

bosonic $(\eta = 1)$

fermionic $(\eta = -1)$

$$[\hat{a}_\alpha, \hat{a}_\beta^+]_\eta = \delta_{\alpha\beta}$$

$$[\hat{a}_\alpha, \hat{a}_\beta]_\eta = [\hat{a}_\alpha^+, \hat{a}_\beta^+]_\eta = 0$$

Fermions : $(\hat{a}_\alpha^+)^2 = 0 \qquad (\hat{a}_\alpha)^2 = 0$

Observables $\to$ hermitian operators

single-particle / one-body operators

e.g. kinetic energy $\dfrac{\hat{\vec{p}}^2}{2m}$

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \frac{\hat{\vec{p}}_i^2}{2m} \to \text{first-quantization expression}$$

$$\hat{O}^{(1)}_{\text{symm}} = \sum_{i=1}^{N} \hat{O}_i^{(1)}$$

$$\hat{O}^{(1)}|\lambda_\alpha\rangle = \lambda_\alpha|\lambda_\alpha\rangle$$

Fock state for $\{|\lambda_\alpha\rangle\}$ $\quad |n_1, n_2, \dots, n_M, \dots\rangle$

$$\hat{O}^{(1)}_{symm}|n_1, n_2, \dots, n_M, \dots\rangle = \Big(\sum_\alpha n_\alpha \lambda_\alpha\Big)|n_1, n_2, \dots n_M \dots\rangle$$

$$\hat{a}^+_\alpha \hat{a}_\alpha = \hat{n}_\alpha$$

$$\hat{O}^{(1)}_{symm} = \sum_\alpha \lambda_\alpha \hat{a}^+_\alpha \hat{a}_\alpha$$

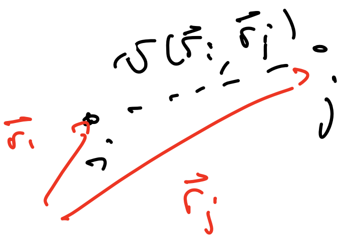
$$= \sum_\alpha \langle\lambda_\alpha|\hat{O}^{(1)}|\lambda_\alpha\rangle \hat{a}^+_\alpha \hat{a}_\alpha$$

$$\{|\lambda_\alpha\rangle\} \to \{|\psi_\nu\rangle\}$$

$$= \sum_{\mu\nu} \langle\psi_\nu|\hat{O}^{(1)}|\psi_\mu\rangle \hat{a}^+_\nu \hat{a}_\mu$$

Two-body operators $\to$ interactions

$$\hat{O}^{(2)}_{ij} = v(\hat{\vec{r}}_i, \hat{\vec{r}}_j) = f(\hat{\vec{r}}_i, \hat{\vec{r}}_j)$$



more generally

$$\hat{O}^{(2)}_{ij} = f(\hat{O}^{(1)}_i, \hat{O}^{(1)}_j)$$

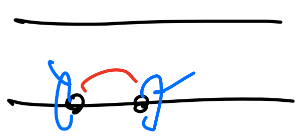
$$\hat{O}^{(2)}_{symm} = \frac{1}{2}\Big[\sum_{ij} \hat{O}^{(2)}_{ij} - \sum_i \hat{O}^{(2)}_{ii}\Big]$$

Fock state for $\{|\lambda_\alpha\rangle\}$

$$\hat{O}^{(2)}_{symm}|n_1, n_2, \dots, n_M, \dots\rangle =$$

$$= \frac{1}{2}\Big[\sum_{\alpha\beta} \hat{n}_\alpha \hat{n}_\beta f(\lambda_\alpha, \lambda_\beta) - \sum_\alpha f(\lambda_\alpha, \lambda_\alpha)\hat{n}_\alpha\Big]$$

$|n_1, n_2, \ldots, n_M\rangle$



$|\lambda_\alpha\rangle$

$$[a_\alpha, a_\beta^\dagger]_\eta = \delta_{\alpha\beta}$$

$$\hat O^{(2)}_{\text{symm}} = \frac{1}{2}\sum_{\alpha\beta} f(\lambda_\alpha, \lambda_\beta)\; a_\alpha^\dagger \underbrace{a_\alpha\, a_\beta^\dagger}_{\eta\, a_\beta^\dagger a_\alpha + \delta_{\alpha\beta}} a_\beta \;-\; \frac{1}{2}\sum_\alpha f(\lambda_\alpha, \lambda_\alpha)\, a_\alpha^\dagger a_\alpha$$

$$= \frac{1}{2}\sum_{\alpha\beta} f(\lambda_\alpha, \lambda_\beta)\, \cancel{\eta}\, a_\alpha^\dagger a_\beta^\dagger \underbrace{a_\alpha a_\beta}_{\cancel{\eta}\, a_\beta a_\alpha}$$

$$+ \frac{1}{2}\sum_\alpha \cancel{f(\lambda_\alpha, \lambda_\alpha)\, a_\alpha^\dagger a_\alpha - (\quad)}$$

$$\hat O^{(2)}_{\text{symm}} = \frac{1}{2}\sum_{\alpha\beta} f(\lambda_\alpha, \lambda_\beta)\; \underbrace{a_\alpha^\dagger a_\beta^\dagger a_\beta a_\alpha}_{\text{excludes self interactions}}$$

$$\langle \lambda_\alpha, \lambda_\beta | \hat O^{(2)}_{ij} | \lambda_\alpha, \lambda_\beta \rangle$$

bosons: $\alpha = \beta$

$$\frac{1}{2} a_\alpha^\dagger \underbrace{a_\alpha^\dagger a_\alpha}_{a_\alpha a_\alpha^\dagger - 1} a_\alpha$$

$$= \frac{1}{2} a_\alpha^\dagger a_\alpha a_\alpha^\dagger a_\alpha - a_\alpha^\dagger a_\alpha$$

$$= \frac{1}{2} n_\alpha (n_\alpha - 1)$$

$$\{|\lambda_\alpha\rangle\} \to \{|\psi_\mu\rangle\}$$

Exercise

$$\hat{O}^{(2)}_{\text{syum}} = \frac{1}{2} \sum_{\mu\nu\gamma\delta} \langle \psi_\mu \psi_\nu | \hat{O}^{(2)}_{ij} | \psi_\gamma \psi_\delta \rangle \, a^\dagger_\mu a^\dagger_\nu a_\delta a_\gamma$$

Example : interaction energy

$$\hat{U} = \frac{1}{2} \sum_{i \neq j} v(\vec{r}_i, \vec{r}_j) \qquad \text{first quantization}$$

$$\rightarrow \frac{1}{2} \int d^d r \int d^d r' \, v(\vec{r}, \vec{r}') \, \psi^\dagger(\vec{r}) \psi^\dagger(\vec{r}') \psi(\vec{r}') \psi(\vec{r})$$

$|\lambda_\alpha\rangle = |\vec{r}\rangle$

$$\left([a_\alpha, a^\dagger_\beta]_\eta = \underline{\underline{\delta_{\alpha\beta}}} \rightarrow [\psi(\vec{r}), \psi^\dagger(\vec{r}')] = \delta(\vec{r} - \vec{r}') \right)$$

$$\hat{K} = \sum_{i=1}^{N} \left(\frac{\hat{\vec{p}}_i^2}{2m} + \hat{V}_{ext}(\vec{r}_i) \right)$$

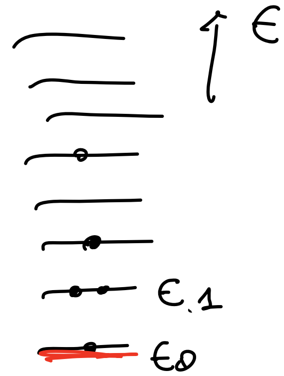
$$\rightarrow \int d^d r \, \hat{\psi}^\dagger(\vec{r}) \left(-\frac{\hbar^2}{2m} \vec{\nabla}^2 + V_{ext}(\vec{r}) \right) \hat{\psi}(\vec{r})$$

Ideal Bose gas : Bose-Einstein condensation

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \hat{\mathcal{H}}_i^{(1)}$$

$$\hat{\mathcal{H}}^{(1)} = \frac{\hat{\vec{p}}^2}{2m} + \hat{V}_{ext}(\bar{r})$$

$$\hat{\mathcal{H}}^{(1)} |\phi_\alpha\rangle = \epsilon_\alpha |\phi_\alpha\rangle$$



$$\hat{\mathcal{H}} = \sum_\alpha \epsilon_\alpha \hat{a}_\alpha^+ \hat{a}_\alpha$$

Fock state $|n_1, n_2, \dots, n_n, \dots\rangle$

Thermodynamics : grand-canonical ensemble

$\hat{\mathcal{H}} - \mu \hat{N}$ grand Hamiltonian

$$Z_G = \mathrm{Tr}\left[e^{-\beta(\hat{\mathcal{H}} - \mu\hat{N})}\right]$$

$$\left(= \sum_c e^{-\beta(E_c - \mu N_c)} \right)$$

$$\beta = \frac{1}{k_B T}$$

basis $|\{n_\alpha\}\rangle$

$$= \sum_{n_1, n_2 \dots} \langle n_1, n_2, \dots, | e^{-\beta(\hat{\mathcal{H}} - \mu\hat{N})} | n_1, n_2, \dots\rangle$$

$$\underset{\sum_{|\{n_\alpha\}\rangle}}{\overset{\shortparallel}{}}$$

$$= \sum_{n_1, n_2 \ldots} e^{-\beta\left(\sum_\alpha n_\alpha \epsilon_\alpha - \mu \sum_\alpha n_\alpha\right)}$$

$$= \sum_{n_1, n_2, \ldots} \prod_\alpha e^{-\beta(\epsilon_\alpha - \mu) n_\alpha}$$

$$= \prod_\alpha \underbrace{\left(\sum_{n_\alpha = 0}^{\infty} e^{-\beta(\epsilon_\alpha - \mu) n_\alpha} \right)}_{\frac{1}{1 - e^{-\beta(\epsilon_\alpha - \mu)}}}$$

$$\Omega_G = -k_B T \log Z_G$$

$$= k_B T \sum_\alpha \log\left(1 - e^{-\beta(\epsilon_\alpha - \mu)}\right)$$

$$\langle N \rangle = -\left.\frac{\partial \Omega_G}{\partial \mu}\right|_{T,V} = \ldots = \sum_\alpha \frac{e^{-\beta(\epsilon_\alpha - \mu)}}{1 - e^{-\beta(\epsilon_\alpha - \mu)}}$$

$$= \sum_\alpha \underbrace{\frac{1}{e^{\beta(\epsilon_\alpha - \mu)} - 1}}_{\langle \hat{n}_\alpha \rangle}$$

$$\langle \hat{n}_\alpha \rangle = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} - 1}$$

Bose-Einstein distribution

≥ 0

$$\underbrace{e^{\beta(\epsilon_\alpha - \mu)}}_{\geq 1} - 1 \geq 0$$

$$\epsilon_\alpha - \mu \geq 0$$

$$\mu \leq \epsilon_\alpha \qquad \forall \alpha$$

$$\rightarrow \boxed{\mu \leq \epsilon_0}$$

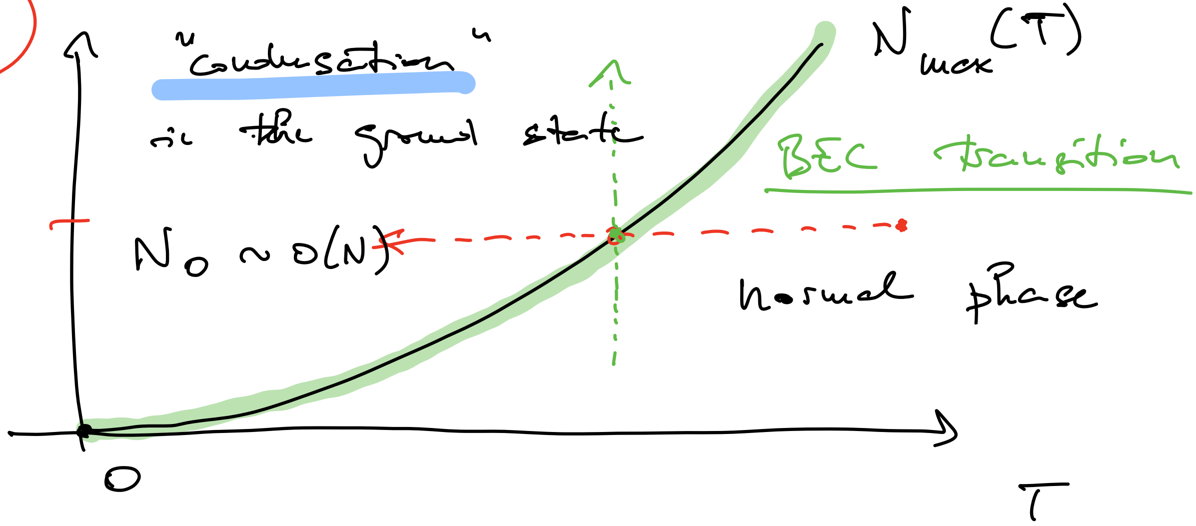
$$\bar{N}(T,\mu,V) = \sum_{\alpha>0} \langle \hat{n}_\alpha \rangle \qquad \text{\# of particles in the excited states}$$

$$= \sum_{\alpha>0} \frac{1}{\underbrace{e^{\beta(\epsilon_\alpha-\mu)}}_{e^{-\beta\mu}\, e^{\beta\epsilon_\alpha}} - 1}$$

$$\leq_{\mu=\epsilon_0} \bar{N}_{max}(T,V) = \sum_{\alpha>0} \frac{1}{e^{\beta(\epsilon_\alpha-\epsilon_0)} - 1}$$

$$< \infty$$

N



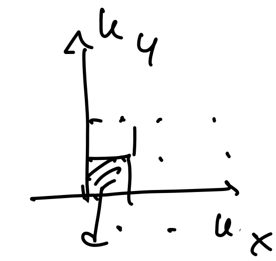
Ideal Bose gas in free space

$V_{ext} = 0$

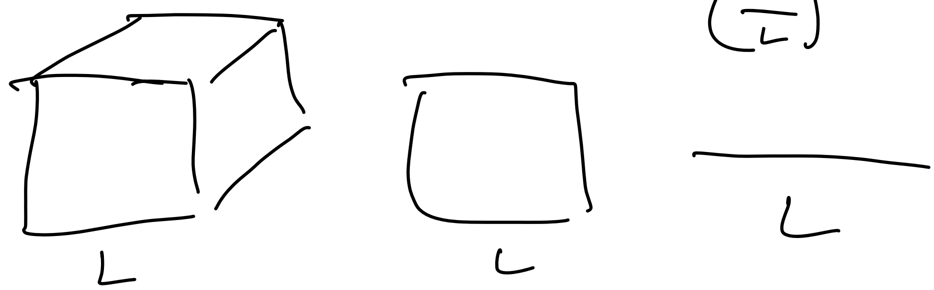
$$\hat{H}^{(1)} = \frac{\hat{p}^2}{2m} \longrightarrow \epsilon_\alpha = \frac{\hbar^2 \vec{k}^2}{2m} = \epsilon_{\vec{k}}$$

periodic boundary conditions $\quad \vec{k} = \frac{2\pi}{L}(n_x, n_y, \dots)$

$$n_x, n_y, \dots \in \mathbb{Z}$$



$$\left(\frac{2\pi}{L}\right)^2$$



G.S. $\quad \vec{k} = 0 \quad \epsilon_0 = 0$

$$\mu \leq 0$$

$$\bar{N}(T, \mu, V) = \sum_{\vec{k} \neq 0} \frac{1}{e^{\beta(\epsilon_{\vec{k}} - \mu)} - 1}$$

$$N = \sum_{\vec{k}} \frac{1}{e^{\beta(\epsilon_{\vec{k}} - \mu)} - 1} \qquad L \to \infty$$

$$= \left(\frac{L}{2\pi}\right)^d \sum_{\vec{k}} \left(\frac{2\pi}{L}\right)^d (\dots)$$

$f(\epsilon)$

$$\underset{L \to \infty}{\simeq} L^d \int_{\mathbb{R}^d} \frac{d^d k}{(2\pi)^d} \frac{1}{e^{\beta(\epsilon_{\vec{k}} - \mu)} - 1}$$

$$= \frac{L^d}{(2\pi)^d}\overbrace{\left(\int d\Omega_d\right)}^{d}\int dk\, k^{d-1}\,\frac{1}{e^{\beta(\epsilon_k-\mu)}-1}$$

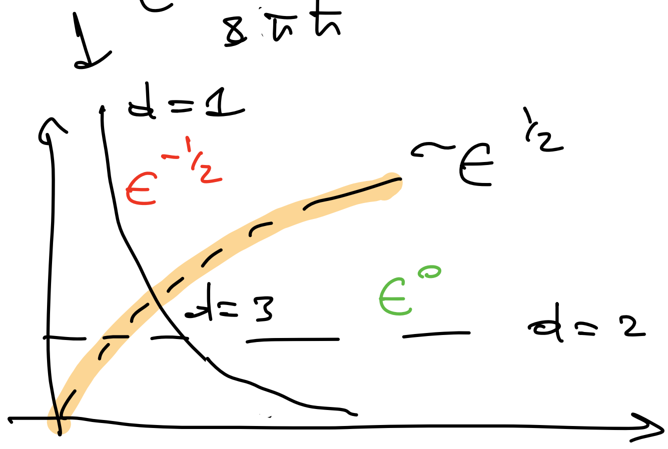
$$= \int_0^\infty d\epsilon\; \rho_d(\epsilon)\,\frac{1}{e^{\beta(\epsilon-\mu)}-1}$$

density of states

$$\frac{dN_\epsilon}{d\epsilon}$$

$$\rho_d(\epsilon) = C_d\, L^d\, \epsilon^{\frac{d-2}{2}}$$

$$C_d = \begin{cases} \dfrac{4\pi\sqrt{2}\, m^{3/2}}{(2\pi\hbar)^3} & d=3 \\[2ex] \dfrac{m}{2\pi\hbar^2} & d=2 \\[2ex] \dfrac{(2m)^{1/2}}{8\pi\hbar} & d=1 \end{cases}$$



$$\epsilon_k = \left(\frac{2\pi}{L}\right)^2 (\vec{n}^2)\,\frac{\hbar^2}{2m}$$

$$N \overset{L\to\infty}{=} \int_0^\infty d\epsilon\, \frac{\rho(\epsilon)}{e^{\beta(\epsilon-\mu)}-1} \overset{L\to\infty}{=} \bar{N}$$

$$\sum_{\vec{k}} \rightarrow \left(\frac{L}{2\pi}\right)^d \int d^d k$$

$\vec{k} = 0$ set of zero measure

$$N = L^d c_d \int_0^\infty d\epsilon \, (\beta)(\beta\epsilon)^{\frac{d}{2}-1} \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$

$\beta^{-1} \quad -\left(\frac{d}{2}-1\right)$

$z = e^{\beta\mu}$ "fugacity"

special function : Bose function

$$g_\alpha(z) = \frac{1}{\Gamma(\alpha)} \int_0^\infty dx \frac{x^{\alpha-1}}{e^x z^{-1} - 1}$$

$$\Gamma(\alpha) = \int_0^\infty dx' \frac{x^{\alpha-1}}{e^x}$$ Euler's gamma

$$= L^d c_d (k_B T)^{d/2} \underbrace{\int_0^\infty dx \frac{x^{\frac{d}{2}-1}}{e^x e^{-\beta\mu} - 1}}_{g_{d/2}(e^{\beta\mu})} \Gamma\left(\frac{d}{2}\right)$$

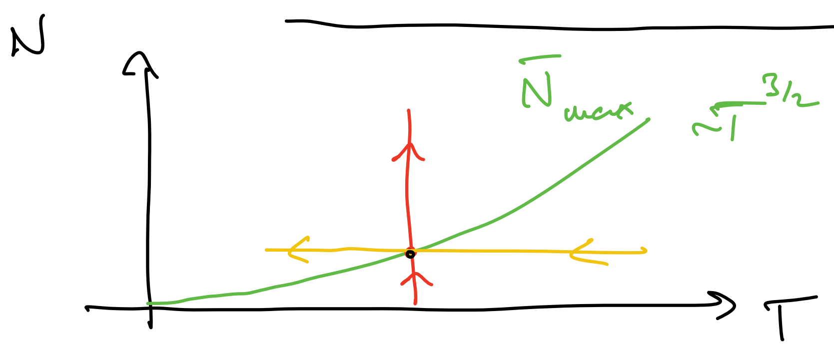
$$N = L^d c_d (k_B T)^{3/2} \Gamma\left(\frac{d}{2}\right) g_{d/2}(e^{\beta\mu}) = \bar{N}$$

$$\Gamma\left(\frac{d}{2}\right) \rightarrow \frac{\sqrt{\pi}}{2}$$

$\mu \to 0$ $\qquad$ $\underline{\underline{d=3}}$

$$g_{3/2}(1) = 2.612\ldots$$

$$\bar N \le \bar N_{max}(T,V) = \underbrace{L^3 C_3}_{V} (k_B T)^{3/2} \frac{\sqrt{\pi}}{2} (2.612)$$



N is increased

$\mu = \underline{\mu(N,T,V)}$

$$N = \begin{cases} (N \le \bar N_{max}(T)) & L^3 C_3 (k_B T)^{3/2} \frac{\sqrt{\pi}}{2}\, g_{3/2}(e^{\beta\mu}) \\ (N > \bar N_{max}(T)) & N_0 + \underbrace{L^3 C_3 (k_B T)^{3} \frac{\sqrt{\pi}}{2}\, g_{3/2}(1)}_{\bar N_{max}(T)} \end{cases}$$

$$\bar N_{max}(T,V) = \ldots = \frac{L^3}{\lambda_T^3}\, 2.612$$

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$$

thermal de Broglie wavelength

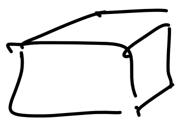
$$N \ge \bar N_{max}(T,V) = \frac{L^3}{\lambda_T^3}\, 2.612$$

$$\frac{N}{L^3} = \underset{\text{density}}{n} \geq \frac{2.612}{\lambda_T^3}$$

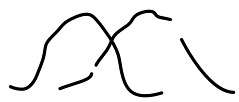
$$n\lambda_T^3 = \underset{\text{phase-space density}}{n_{ph}} \geq 2.612 \Rightarrow \text{condensation}$$

$$N_0 \sim \mathcal{O}(N)$$

→ quantum degeneracy



λ_T



λ_T

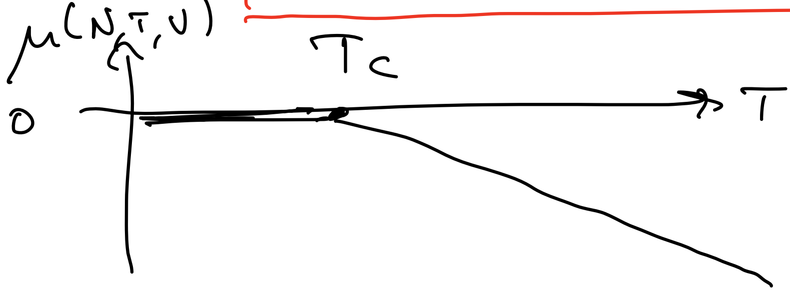
critical temperature @ fixed N

$T = T_c$: $\bar{N}_{max}(T_c) = N$

$$\frac{L^3}{\lambda_{T_c}^3} g_{3/2}(1) = N$$

$$\frac{(2\pi m k_B T_c)^{3/2}}{h^3} = \frac{n}{2.612}$$

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



$\boxed{T < T_c}$

@ $T = T_c$

$$N = \frac{L^3}{\lambda_{T_c}^3} g_{3/2}(1)$$

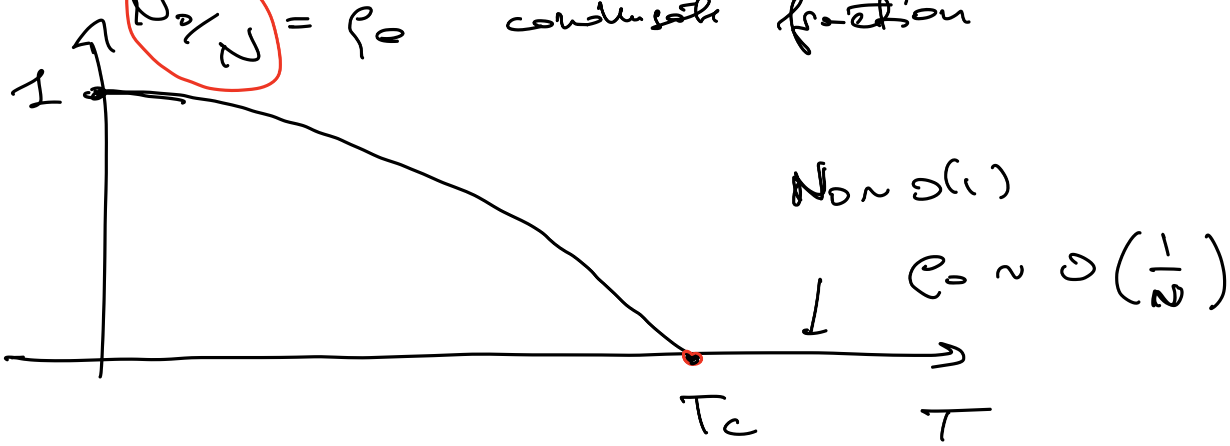
$$N = N_0 + \bar{N}_{max}(T)$$

$$= N_0 + \underbrace{\frac{L^3}{\lambda_T^3} g_{3/2}(1)}_{N \frac{\lambda_{T_c}^3}{\lambda_T^3} = N\left(\frac{T}{T_c}\right)^{3/2}}$$

$$= N_0^{(T)} + \underline{N\left(\frac{T}{T_c}\right)^{3/2}}$$

$$N_0(T) = N\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]$$

$N_0/N = \rho_0$ condensate fraction



Lower dimensions

$$g_{d/2}(1) = \infty \qquad d = 1, 2$$

$$\bar{N}_{max}(T, V) = \frac{L^d}{(2\pi)^d} \int d\Omega \int_0^\infty dk \, \frac{k^{d-1}}{\underbrace{e^{\beta \frac{\hbar^2 k^2}{2m}} - 1}}$$

$\leftarrow \mu = 0$

$k \to 0 \quad \simeq \rho \frac{\hbar^2 k^2}{2m}$

$$\sim \int_0^\infty dk \; k^{d-3} = \begin{cases} \text{finite} & d=3 \\ \infty & d=2 \\ \infty & d=2 \end{cases}$$

There is No BEC @ finite temperature in $d = 1, 2$

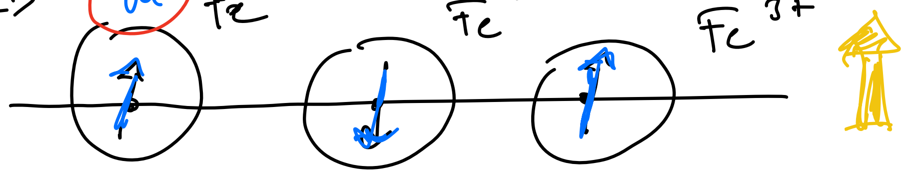
MAGNETISM

→ fundamental phenomenon in condensed matter

→ paradigm in statistical physics: spontaneous symmetry breaking

Magnetic materials : magnetic insulators

→ $\vec{m}$ Fe^{3+} Fe^{3+} Fe^{3+} $\vec{B}$



atomic / ionic magnetic moments

localized magnetic moments

characterize the equilibrium state of an ensemble of magnetic moments

$$\vec{M} = \sum_{i=1}^{N} \vec{m}_i \qquad \text{magnetization}$$

free energy

$$F = E - TS - \vec{B} \cdot \vec{M}$$

$$\vec{M} = - \vec{\nabla}_{\vec{B}} F = \vec{M}(\vec{B})$$

susceptibility

$$\chi^{\alpha\beta} = \frac{1}{N} \frac{\partial M^\alpha}{\partial B^\alpha} \to \beta \qquad \alpha, \beta = x, y, z$$

$$= - \frac{1}{N} \frac{\partial^2 F}{\partial (B^\alpha)^2}$$

$$\chi^{\alpha\alpha} = \begin{cases} > 0 & \text{paramagnetism (ferromagnetism)} \\ < 0 & \text{diamagnetism} \end{cases}$$

Physical origin of the atomic magnetic moment

N-electron atom

$g\mu_B\vec{S}$ $\quad g \simeq -2$

$-e^{-}$ $\quad e^{-}$ $\quad e^{-}$ $\quad e^{-}$ $\quad e^{-}$ $\quad e^{-}$

$$\boxed{\vec{m} \quad \vec{B} \qquad E = -\vec{m}\cdot\vec{B}}$$

$$\vec{B} = \vec{\nabla}\times\vec{A} \longrightarrow \vec{A} = \frac{1}{2}(\vec{B}\times\vec{r})$$

$$\boxed{\mu_B = \frac{e\hbar}{2m}}$$

N = # of electrons

$$H_{atom} = \sum_{i=1}^{N} \frac{(\vec{p}_i + e\vec{A}(\vec{r}_i))^2}{2m} + V_{pot} - g\mu_B \vec{B}\cdot\sum_{i=1}^{N}\vec{S}_i$$

$$= \sum_{i=1}^{N} \underbrace{\frac{e}{m}\,\vec{p}_i\cdot(\vec{B}\times\vec{r}_i)}_{\vec{B}\cdot\underbrace{(\vec{r}_i\times\vec{p}_i)}_{\vec{L}_i}} + \underbrace{\sum_{i=1}^{N}\frac{p_i^2}{2m} + V_{pot}}_{H_{at}} + o(A^2)$$

$$- g\mu_B \vec{B}\cdot\sum_{i=1}^{N}\vec{S}_i$$

$g \simeq -2$

$$= H_{at} + \sum_{i=1}^{N}\mu_B\frac{(\vec{L}_i + 2\vec{S}_i)}{\hbar}\cdot\vec{B} + o(B^2)$$

$$= H_{at} + \frac{\mu_B}{\hbar}\underbrace{(\vec{L}+2\vec{S})}\cdot\vec{B} + \ldots$$

$$\vec{L} = \sum_i \vec{L}_i \qquad \vec{S} = \sum_i \vec{S}_i$$

$$|\vec{L}|^2 = \hbar^2 L(L+1) \qquad |\vec{S}|^2 = \hbar^2 S(S+1)$$

values of L, S in the ground state

Hund's rules

$E = E(L, S, \dots)$

1) $S = S_{max}$

2) $L = L_{max}$

3) $\vec{J} = \vec{L} + \vec{S}$ $\quad |\vec{J}|^2 = \hbar^2 J(J+1)$

spin-orbit coupling

$$\Delta E_{so} = \frac{A_{LS}}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

$$A_{LS} = \begin{cases} > 0 & \text{if the last shell is half filled or less than half filled} \rightarrow J = J_{min} \\ < 0 & \text{otherwise} \rightarrow J = J_{max} \end{cases}$$

ground state of $\underline{\underline{H_{at}}}$: $|\gamma; L, S, J, M_J\rangle$

filled orbitals

J^z

$M_J = -J, \dots, J$

perturb with $\underbrace{\frac{\mu_B}{\hbar}(\vec{L} + 2\vec{S})}\cdot\vec{B}$

$\vec{B} = B\vec{e}_z$

Perturbation theory

$$\frac{\mu_B B}{\hbar}\langle \gamma_i\, LSJ M_j \,|\, (J^z + S^z) \,|\, \gamma_i\, LSJ M_j' \rangle$$

$$\mu_B B \underbrace{M_j}_{=} \delta_{M_j M_j'} + \frac{\mu_B B}{\hbar} \underbrace{\langle \gamma_i\, LSJM_j \,|\, S^z \,|\, \gamma_i\, LSJM_j' \rangle}$$

$$\frac{\langle \gamma_i\, LSJM_j \,|\, (\vec{J}\cdot\vec{S}) J^z \,|\, \gamma_i\, LSJM_j' \rangle}{\hbar^2 J(J+1)}$$

$$\vec{J}\cdot\vec{S} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 + \vec{S}^2\right)$$

$$= \mu_B B \left[1 + \frac{1}{2}\,\frac{J(J+1) + S(S+1) - L(L+1)}{J(J+1)}\right] M_j\, \delta_{M_j M_j'}$$

$$= g_{LSJ}\, \mu_B B\, \underset{=}{M_j}\, \delta_{M_j M_j'}$$

Landé factor

$$= \Delta E_B\, \delta_{M_j M_j'}$$

$$\Delta E_B = -\vec{m}_{LSJ}\cdot\vec{B}$$

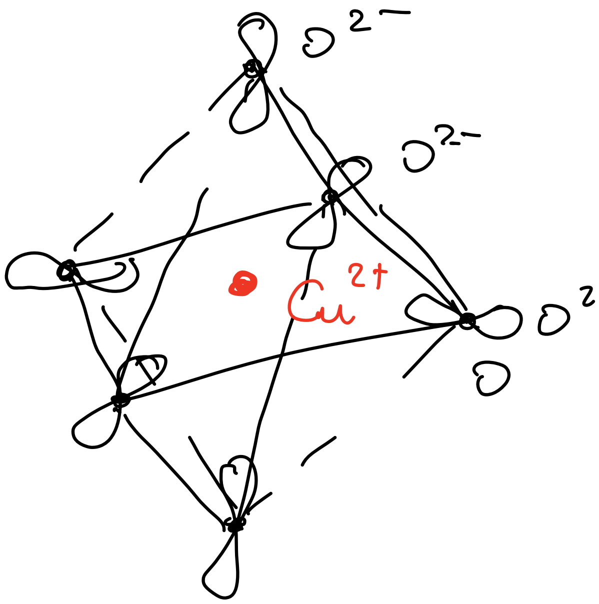
$$\vec{m}_{LSJ} = -g_{LSJ}\,\mu_B\, \vec{J}/\hbar$$

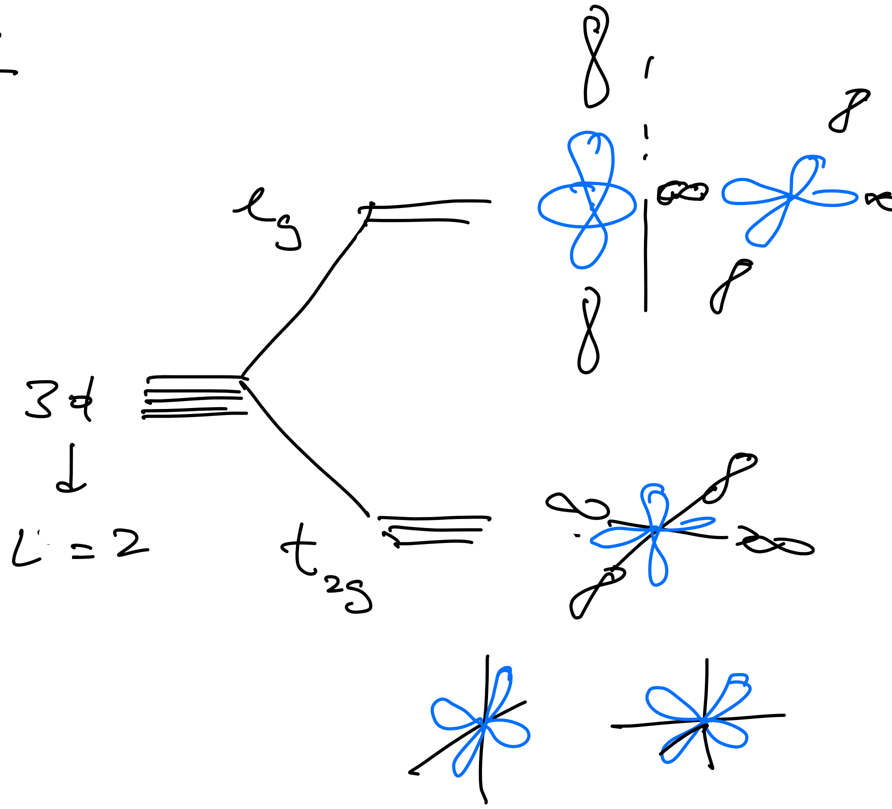
$$g = -g_{LSJ}$$

$$|\vec{m}|^2 = g^2 \mu_B^2\, J(J+1)$$

$$|\vec{m}| = g\mu_B \sqrt{J(J+1)}$$

Crystal-field effects





$\Rightarrow$ 3rd Hund's rule may no longer hold

transition metals partially filling the 3d shell

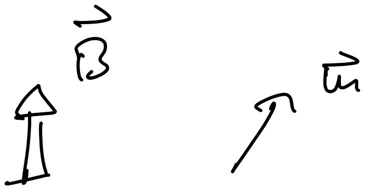
empirical rule: ORBITAL QUENCHING

eff. $\underline{L = 0}$ in the ground state

$$J = S$$

$$|\vec{m}| = g_{\underbrace{LSJ}_{\downarrow\ 0SS}}\, \mu_B \sqrt{S(S+1)}$$

Thermodynamics of paramagnetic moments



$$\hat{\vec{m}} = g\mu_B \hat{\vec{J}}$$

@ Temperature T :

partition function for a magnetic moment

$$\hat{\mathcal{H}} = -\hat{\vec{m}} \cdot \vec{B} \qquad \vec{B} = B\vec{e}_z$$

$$Z = \sum_{M=-J}^{J} \left(e^{+\beta g\mu B}\right)^M \qquad < 1$$

$$= e^{-\beta g\mu B J} \sum_{M=0}^{2J} \left(e^{\beta g\mu B}\right)^M$$

$$= e^{-\beta g\mu B J} \, \frac{1 - e^{\beta g\mu B(2J+1)}}{1 - e^{\beta g\mu B}}$$

$$= \frac{\sinh\left[\beta g\mu \frac{B}{2}(2J+1)\right]}{\sinh\left(\beta g\mu B/2\right)}$$