Thermodynamics 4230
Lecture Set 7

Nov. 21, 2011
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Grand Canonical Statistical Mechanics

- Boltzmann weight: system & reservoir @ μ, β
- Grand partition fnc + Grand free energy
- Examples:
  - lattice gas
  - Fermi gas & metals
  - Bose gas
  - Black-body radiation
  - Debye solid phonons

Boltzmann weight

- Recall isolated system:

μ-states : $i = 1, 2, 3, \ldots$

@ fixed E

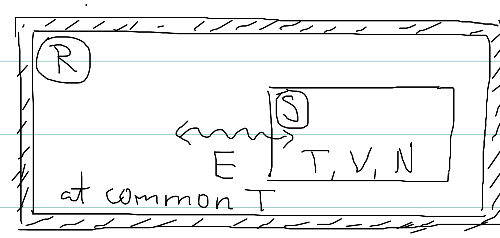
$$\boxed{\begin{array}{c} E, V, N \\ \Omega \rightarrow S = k_B \ln \Omega \end{array}}$$

probability of state i : $P(i) = \frac{1}{\Omega}$ for all i (same)

$$\sum_i P(i) = 1 = \sum_i \frac{1}{\Omega} = \Omega \cdot \frac{1}{\Omega} \quad \checkmark$$

- system in thermal contact w/ reservoir

$U_{tot} = U_R + E$ fixed $E \ll U_R$



$$P(i) = \frac{1}{Z} e^{-E_i/k_B T}$$

why? use μ-canonical description for R+S

$P(i) \propto$ # μstates in S+R, with S in state i

$$= \Omega_R(U_{tot} - E_i) \underbrace{\Omega(i)}_{1}$$

$$= e^{S_R(U_{tot} - E_i)/k_B}$$

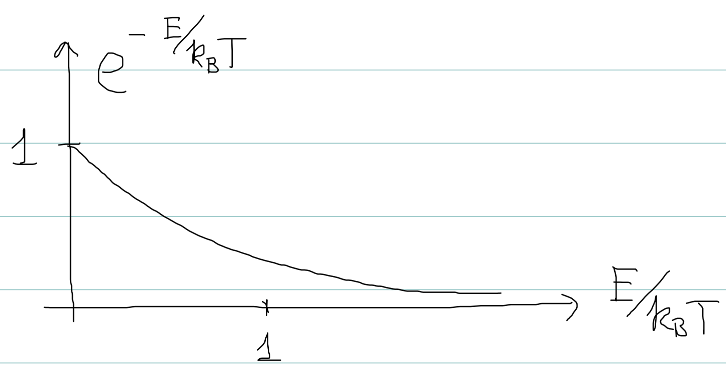
$$P(i) \propto e^{S_R(U_{tot}-E_i)/k_B} = e^{\underbrace{S_R(U_{tot})}_{const} - \underbrace{\left.\frac{\partial S}{\partial U}\right|}_{\frac{1}{T}} E_i} \quad ; \quad E_i \ll U_{tot}$$

$$\Rightarrow P(i) = \frac{1}{Z} e^{-\beta E_i} \quad , \quad \beta \equiv \frac{1}{k_B T}$$

Z ← normalization factor

$$Z = \sum_i e^{-\beta E_i} \rightarrow \underline{\text{the Partition fnc}}$$

$$\left(\text{check: } \sum_i P(i) = \frac{1}{Z}\sum_i e^{-\beta E_i} = 1 \quad \checkmark \right)$$



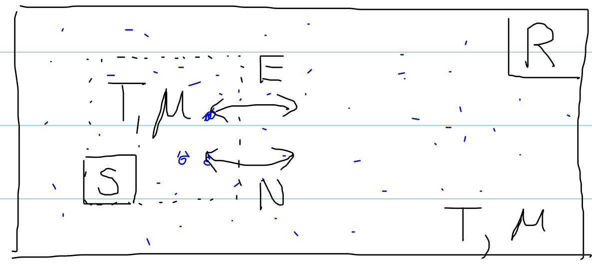
$$P(i) = \frac{1}{Z} e^{-\beta E_i} \simeq \begin{cases} 1, & \text{for } E_i \ll k_B T \\ 0, & \text{for } E_i \gg k_B T \end{cases}$$

Why?

bigger E_i reduces reservoir's energy $U_{tot} - E_i$

$\Rightarrow$ reduces $S_R \searrow$ with $E_i \nearrow$

System in contact w/ reservoir, exchanging E, N



particle & heat exchange

chemical (μ) & thermal (T) equilibrium

⇒ tune μ, T not N, E

high T $\xrightarrow[Q]{}$ low T

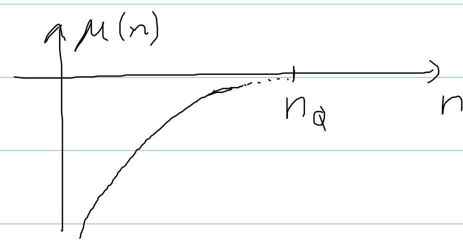
high μ $\xrightarrow[\text{particles}]{}$ low μ

$$dU = TdS - pdV + \mu dN$$

$$\Rightarrow \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \frac{G}{N}$$

For ideal Boltzmann gas:

$$\mu = +k_B T \ln \frac{n}{n_Q}$$



Grand-canonical distribution

via μ-canonical distrib. for $S+R$: $N_{tot} = N + N_R$

$E_{tot} = E_i + E_R$

$$P_\mu(N,i) \propto \Omega_R(E_{tot}-E_i, N_{tot}-N)\cdot \overbrace{\Omega_S(E_i,N)}^{1}$$

$$\propto e^{S_R(E_{tot}-E, N_{tot}-N)/k_B}$$

$$\propto e^{\frac{1}{k_B}\left[S_R(E_{tot},N_{tot}) - E_i \underbrace{\frac{\partial S_R}{\partial E}\Big|_{E_{tot},N_{tot}}}_{\frac{1}{T}} - N \underbrace{\frac{\partial S_R}{\partial N}\Big|_{E_{tot},N_{tot}}}_{-\frac{\mu}{T}}\right]}$$

$$\Rightarrow P_\mu(N,i) = \frac{1}{Z_\mu} e^{-(E_i-\mu N)/k_B T} \quad \leftarrow \text{Gibb's weight}$$

grand partition fnc: $Z_\mu = \sum_{N,i_N} e^{-\beta(E_i-\mu N)}$

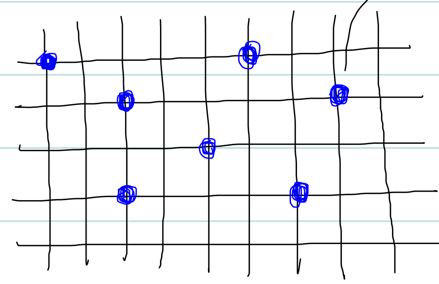
grand potential: $F_\mu = -k_B T \ln Z_\mu = U - TS - \mu N = -PV = F_\mu$

$$dF_\mu = -S\,dT - P\,dV - N\,d\mu$$

$$\Rightarrow \bar{N} = -\frac{\partial F_\mu}{\partial \mu}\Big|_{T,V} = k_B T \frac{\partial}{\partial \mu}\ln Z_\mu \,; \quad \langle E-\mu N\rangle = U-\mu N = -\frac{\partial}{\partial\beta}\ln Z_\mu$$

$\Rightarrow$ all of thermodynamics !

Example: <u>Lattice Gas</u>



ionization of site

site ionization energy: $E_1 = \varepsilon_0$

each occupied by $n_i = 1$

or ionized $n_i = 0$

note: $\sum_{i=1}^{L} n_i = N$ — $\underline{\underline{\text{not}}}$ fixed in grand canon. ensemble

ionizes into vapor

(e.g. H atom $\varepsilon_0 = -13.6\,\text{eV}$, Fe^{2+} hemoglobin O_2 site, ...)

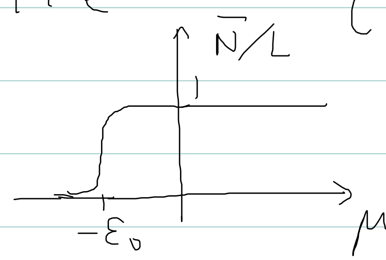
$$Z_\mu = \sum_{\{n_i = 0,1\}} e^{-\beta(E_{\{n_i\}} - \mu N)} = \sum_{\{n_i\}} e^{+\beta(\varepsilon_0 + \mu) n_i}$$

$$= \left(1 + e^{\beta(\varepsilon_0 + \mu)}\right)^{L}$$

L ← # lattice sites

$$\Rightarrow \bar{N} = k_B T \frac{\partial}{\partial \mu} \ln Z_\mu = \frac{L e^{\beta(\varepsilon_0 + \mu)}}{1 + e^{\beta(\varepsilon_0 + \mu)}} \simeq \begin{cases} L, & \beta\varepsilon_0 \gg 1 \\ \frac{L}{2}, & \beta\varepsilon_0 \gg 1 \end{cases}$$

$$\simeq \frac{L}{e^{\beta(-\varepsilon_0 - \mu)} + 1} \checkmark$$



tune $\mu \to \bar{N}$

compare to canonical:

$$Z_N = \sum_{\{n_i=0,1\}}{}' \; e^{-\beta \sum_i n_i(-\varepsilon_0)} \quad , \quad \sum_i n_i = N \text{ fixed}$$

$$= \frac{L!}{(L-N)!\,N!}\, e^{+\beta N \varepsilon_0}$$

(note: $\sum_{N=0}^{L} Z_N e^{+\beta \mu N} = \left(1 + e^{\beta(\varepsilon_0+\mu)}\right)^L = Z_\mu$ ✓)

To connect to grand-canonical open system

compute $\bar{\mu} = \left.\frac{\partial F}{\partial N}\right|_{T,V}$

and equate to μ of e.g. ideal gas $\mu = -k_B T \ln \frac{n_Q}{n}$

w/ which this lattice gas is in chemical equilibrium

using $n = \frac{P}{k_B T}$ in above $\Rightarrow N_{coverage}(P_{gas}/k_B T)$

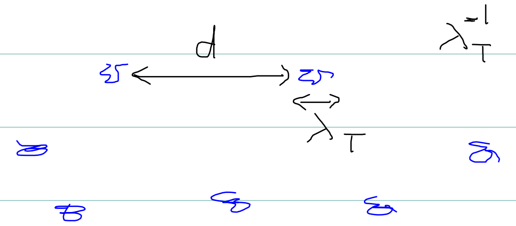
Quantum Statistical Mechanics

Recall Boltzmann gas of N particles:

$Z_N = \frac{1}{N!} Z_1^N$ OK for $Z_1 >> N$ dilute, i.e.

many thermally accessible states per particle

$d >> \lambda_T$ $\qquad \lambda_T^{-1} \simeq \sqrt{2 m k_B T / \hbar^2}$



$\Leftrightarrow n \lambda_T^3 << 1$

nondegenerate

quantum statistic does not matter at high T, low n.

But breakdown for $d \lesssim \lambda_T \leftrightarrow n \lambda_T^3 \gtrsim 1$, i.e.

for $T < T_d \simeq \frac{\hbar^2}{2m} n^{2/3} \simeq E_{Fermi}$ (recall $S<0$!)

degenerate

Quantum statistics (exchange of particles) matters:

$\Rightarrow$ dramatically different for:

$\boxed{\text{Bosons}}$ (integer spin)
e.g. He^4, photon, Rb^{87}, ...
even # of fermions

unlimited occupation

$n_i = 0, 1, 2, \ldots$

vs

$\boxed{\text{Fermions}}$ (half-int. sp)
e.g. He^3, e^-, p^-, n^-, q
odd # of fermions

obey Pauli Exclusion Princ.

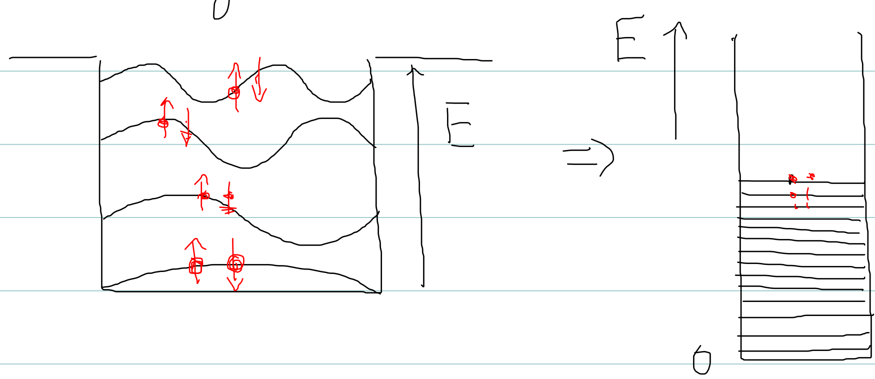
$\Rightarrow$ 1 fermion per state

$n_i = 0, 1$

Fermions

Degenerate Fermi Gas: noninteracting but still strongly affected by each other due to PEP.

Ex: conduction e's in a metal.
Strong Coulomb e-e & e-p interactions nearly cancel
almost all prop's of metals well captured by degener. electron gas (Sommerfeld '30s)

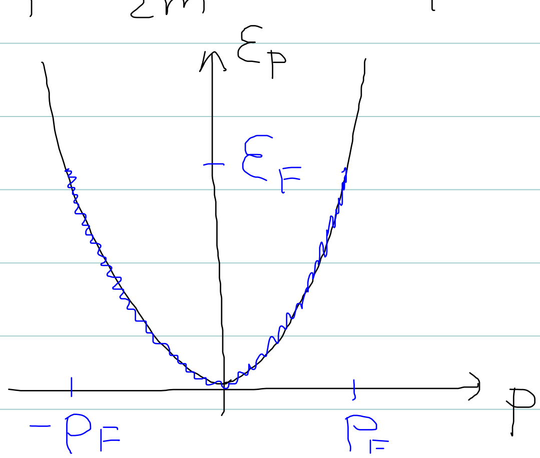


ε_F - Fermi level

2e's / orbital state $(\uparrow, \downarrow)$

$\varepsilon_F = \mu$ at $T = 0$

$\varepsilon_p = \frac{p^2}{2m} \longrightarrow \varepsilon_F = \frac{p_F^2}{2m}$ highest occupied energy at $T = 0$.

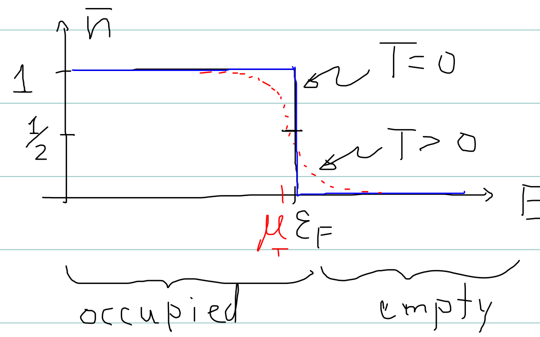


At $T=0$, only 1 N-fermion state $|k_0, k_1, k_2 \ldots k_{N/2}\rangle$

$\Rightarrow \Omega = 1 \Rightarrow S = 0$ $\qquad = \underset{\text{antisymmetrize}}{A} |k_0\rangle |k_1\rangle |k_2\rangle \ldots$

$$\mu = \frac{\Delta E}{\Delta N} = \frac{\varepsilon_F}{1} = \varepsilon_F \checkmark$$

$\bar{n}_E$ – ave # occupation of state w/ energy E:



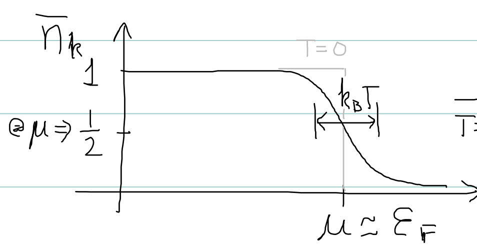
- $T_d^{\,metal} \sim 1\,eV \sim 10^4$ Kelvin
- $T_d^{\,He^4} \sim 10^4 K \times \frac{m_e}{m_{He^4}} \sim 1K$
- $T_d^{\,Rb^{87}} \sim 1K \times \frac{1}{20} \times \frac{1}{10^7} \sim 5\,nK$

$$Z_\mu = \sum_{N,k} e^{-\beta(\underbrace{E}_{\sum_k n_k \varepsilon_k} - \mu \underbrace{N}_{\sum_k n_k})} = \prod_k \sum_{n_k = 0,1} e^{-\beta(\varepsilon_k - \mu) n_k}$$

$$= \prod_k \left(1 + e^{-\beta(\varepsilon_k - \mu)}\right)$$

$$\Rightarrow \bar{n}_k = \sum_{n_k} \frac{n_k e^{-\beta n_k(\varepsilon_k - \mu)}}{Z_{\mu k}} = k_B T \frac{\partial}{\partial \mu} \ln Z_{\mu k}$$

$$\boxed{n_{FD}(\varepsilon_k) = \bar{n}_k = \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1}}$$



$\xrightarrow[T=0]{} \Theta(\mu - \varepsilon_k)$

$\times 2$ for spin $(\uparrow, \downarrow)$

Fermi-Dirac distribution

• "hot" e's at $T=0$ & $S=0$:

$$\varepsilon_F \simeq \frac{\hbar^2}{2md^2} \simeq 10\,\text{eV} \quad (\text{recall H-atom, Ry})$$

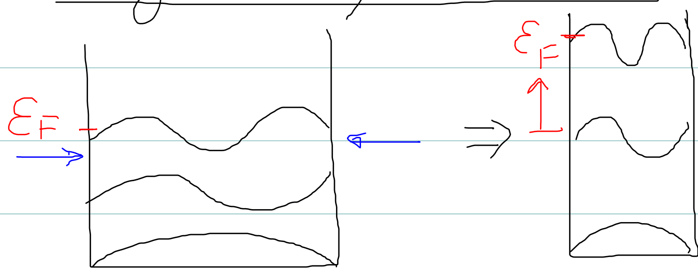
$$\sim 50{,}000\,\text{K} << k_B T_{room} \simeq \frac{1}{40}\,\text{eV}$$

$\Rightarrow$ e's in a metal are extremely degenerate

i.e. nearly at $T=0$, but $E_{Kinetic} \gtrsim 10^4$ Kelvin!

fastest e's moving $\frac{1}{100}c$ but $j=0$ since $\pm p_F$

• Degeneracy pressure at $T=0$:



squeeze $L\downarrow$, $E\nearrow$

$$E_n = \frac{\hbar^2 n^2}{2mL^2} \propto \frac{1}{L^2}$$

$$\boxed{P_d \simeq n\,\varepsilon_F}$$

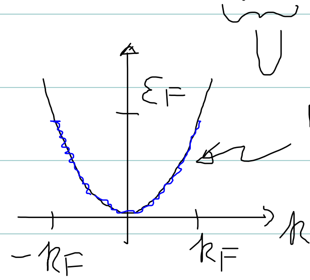
$(\text{cf } P \simeq n k_B T)$

$$dU = TdS - pdV \Rightarrow p = -\left.\frac{\partial U}{\partial V}\right|_S$$

$$U = \sum_k \varepsilon_k n_{FD}(\varepsilon_k) \underset{T=0}{=} \sum_k{}' \varepsilon_k = \frac{h^2}{8mL^2}\sum\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$\sim \frac{1}{L^2} \sim \frac{1}{V^{2/3}} \Rightarrow p = -\frac{\partial}{\partial V}\Big(\underbrace{\frac{c}{V^{2/3}}}_{U}\Big) = \frac{2}{3}\frac{U}{V}$$

$$U = \sum_k{}' \varepsilon_k \underset{T=0}{\propto} N\varepsilon_F$$



N states filled $0 < \varepsilon_k < \varepsilon_F$

Detailed computation

(in a box: $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$)

$$N = \overset{\text{spin} \uparrow,\downarrow}{2} \sum_k n_{FD}(\varepsilon_k) \underset{T=0}{=} 2\sum_k \Theta(\varepsilon_F - \varepsilon_k) = 2L^3 \int \frac{d^3k}{(2\pi)^3} \Theta(\varepsilon_F - \varepsilon_k)$$

$$= 2V \frac{4\pi}{8\pi^3} \int_0^{k_F} dk\, k^2\, \Theta(\varepsilon_F - \varepsilon_k) = \frac{V}{\pi^2}\frac{k_F^3}{3} \propto \varepsilon_F^{3/2}$$

$$E = 2\sum_k \varepsilon_k n_{FD}(\varepsilon_k) = 2L^3 \int \frac{d^3k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \Theta(\varepsilon_F - \varepsilon_k) = 2L^3 \int_0^{\varepsilon_F} d\varepsilon\, \underset{\text{density of states}}{\Omega(\varepsilon)}\, \varepsilon$$

$$\boxed{\frac{d^3k}{(2\pi)^3} = \frac{4\pi k^2 dk}{8\pi^3} = \underbrace{\frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}}_{\equiv \Omega(\varepsilon)} d\varepsilon}$$

$$E = \frac{L^3}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\varepsilon_F} d\varepsilon\, \varepsilon^{3/2} \propto \varepsilon_F^{5/2} \propto \varepsilon_F^{3/2}\varepsilon_F \propto \underline{N\varepsilon_F}$$

$$= \frac{\cancel{8\pi}}{\cancel{8\pi^3}2} L^3 \int_0^{k_F} dk\, k^4 \frac{\hbar^2}{2m} = \frac{L^3}{\pi^2}\frac{\hbar^2}{2m}\frac{k_F^5}{5} = \frac{\hbar^2 k_F^2}{2m} \underbrace{\frac{L^3}{\pi^2}\frac{k_F^3}{5}}_{\frac{3}{5}N} = \frac{3}{5} N\varepsilon_F$$

$$P = -\left.\frac{\partial E}{\partial V}\right|_{N,S} = -\frac{\partial}{\partial V}\left(\frac{3}{5} N c V^{-2/3}\right) = \frac{2}{5} n \varepsilon_F = \frac{2}{3}\frac{E}{V}$$ ($\sim 10^6$ Atm metal)

$$F = -k_B T \sum_k \ln\Big(\underbrace{1 + e^{-\beta(\varepsilon_k - \mu)}}_{= \begin{cases} 1, & \varepsilon_k > \mu \\ e^{\beta(\mu - \varepsilon_k)}, & \varepsilon_k < \mu \end{cases}}\Big) \underset{T\to 0}{=} -k_B T \sum_k^{k_F} \ln\left(e^{-\beta(\varepsilon_k - \mu)}\right) = \sum_k^{k_F} (\varepsilon_k - \mu)$$

$$= \frac{3}{5} N\varepsilon_F - \varepsilon_F N = -\frac{2}{5} N \varepsilon_F = -PV \Rightarrow P = \frac{2}{5} n\varepsilon_F \quad \checkmark$$

$$B = -V\frac{\partial P}{\partial V} = n\frac{\partial P}{\partial n} = V\frac{\partial^2 F}{\partial V^2} = n^2 \frac{\partial^2 f}{\partial n^2} = n\frac{\partial}{\partial n}\left.\left(\frac{2}{5} n^{5/3} c\right)\right|_N = \frac{2}{3} n \varepsilon_F$$

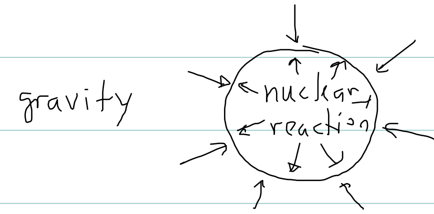
$$v = \sqrt{\frac{B}{nm}} = \sqrt{\frac{2}{3} n \frac{1}{2} m v_F^2 / nm} = \frac{v_F}{\sqrt{3}} \quad \checkmark$$

Stellar evolution

young star: fusion reaction $4H \rightarrow 2He + \gamma'$

exhausted H fuel (~10 Gyr Sun)

$\Rightarrow$ collapse due to gravity



- for $M_☆ \leq 1.4 M_S$

stopped by e's degeneracy pressure @ Earth size $\Rightarrow$ White dwarf

- for $M_☆ > 1.4 M_S$ (Chandrasekhar limit)

e's P_d not strong enough $\Rightarrow$ further collapse

@ high density: $e^- + p \rightarrow n + \nu$ $\Rightarrow$ supported by neutron degeneracy pressure

for $1.4 M_S < M_☆ < 5 M_S$

$\Rightarrow$ neutron star $\simeq 10\,km$ $\Rightarrow$ rapidly rotating (pulsar)

- for $M_☆ > 5 M_S$ $\Rightarrow$ collapse to singularity

Black Hole

Bosons

$$Z_\mu = \sum_{\{n_k\}} e^{-\beta n_k(\varepsilon_k - \mu)} = \prod_k \frac{1}{1 - e^{-\beta(\varepsilon_k - \mu)}}$$

μ: chemical potential
if conserved N
e.g. atoms, but not
photons, phonons...
$(\mu = 0)$

$$n_{BE}(\varepsilon_k) = \bar{n}_k = -\frac{\partial}{\partial \mu}\underbrace{\left(-k_B T \ln Z_{\mu k}\right)}_{F_{\mu k}} = \frac{1}{e^{\beta(\varepsilon_k - \mu)} - 1}$$

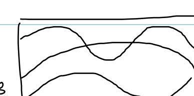
$$N = \sum_k \bar{n}_k = \sum_k \frac{1}{e^{\beta(\varepsilon_k - \mu)} - 1} \Rightarrow \mu(n) \quad \text{eqn. of state}$$

$$E = \sum_k \varepsilon_k \bar{n}_k = \sum_k \frac{\varepsilon_k}{e^{\beta(\varepsilon_k - \mu)} - 1}$$

Results depends on type of a boson:

- EM modes → photons: $\varepsilon_k = \hbar\omega_k = \hbar c k = cp$

$$\Rightarrow \mu = 0; \quad E = \sum_k \frac{\hbar c k}{e^{\beta\hbar c k} - 1} = \sigma_{SB} T^4 \quad (3d)$$

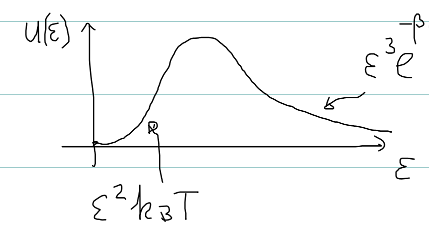


$$= k_B T\, N(T) = k_B T\, V k_T^3 \sim V k_B T \left(\frac{k_B T}{\hbar c}\right)^3$$

$N(T)$: # of classical modes

$$\equiv \int_0^\infty d\varepsilon\, U(\varepsilon)$$

$U(\varepsilon)$: energy density



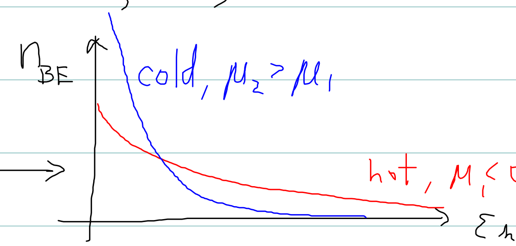
$$U(\varepsilon) = \frac{8\pi}{(hc)^3} \frac{\varepsilon^3}{e^{\beta\varepsilon} - 1}$$

$$\frac{P}{A} = I = \frac{1}{4} E c = \sigma T^4$$

- conserved bosons, e.g. atoms (Rb^{87}, ...)

μ adjusted to fix $\bar{N}$

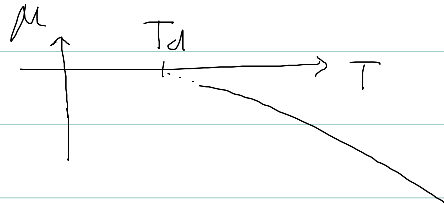
same area $= \bar{N}(\mu, T)$



$$\bar{N} = \sum_k n_{BE}(\varepsilon_k) = \sum_k \frac{1}{e^{\beta(\varepsilon_k - \mu)} - 1} = V \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} - 1}$$

→ For high $T \gg T_d \simeq \frac{\hbar^2}{2m} n^{2/3}$ → classical Boltzmann gas

$\Rightarrow \mu = -k_B T \ln\left(\frac{n_Q}{n}\right) \sim -T \ln T$



→ as $T \searrow$ toward T_d, increase μ

so that area $\Rightarrow \bar{N}$ (fixed)

→ for $T = T_d \equiv T_c \equiv T_{BEC} \Rightarrow \mu(T_c) = 0$

$$\frac{\bar{N}}{V} = \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta_c \varepsilon_k} - 1} = n_Q = \frac{1}{\lambda_{T_c}^3} \quad \underline{\text{finite}}!$$

What to do at lower $T < T_c$, or for $n > n_Q$?

$\Rightarrow$ put all additional bosons in the lowest state $k=0$

$$N = \underbrace{\underbrace{N_c(T)}_{N\left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right)}}_{\text{Bose-condensed}} + \underbrace{V n_Q(T)}_{N\left(\frac{T}{T_c}\right)^{3/2}} \Rightarrow \underline{\text{BEC}}$$

Nobel Prize '01 Cornell Wieman Ketterle