Problem Sheet 5.

1. If we change the # of particles in a gas keeping other things constant

$$\Rightarrow dU = \mu \, dN$$

dN: change in # of particles

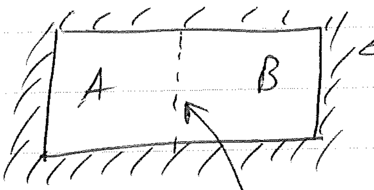
μ: chemical potential

dU: change in internal energy

$$\Rightarrow \mu = \left.\frac{\partial U}{\partial N}\right|_{S,V}$$

[We could also derive $\mu = -\frac{1}{T}\frac{\partial S}{\partial N}$ or $\mu = \frac{\partial F}{\partial N}$ or $\mu = \frac{\partial H}{\partial N}$ etc. here]

For a closed system with fixed # particles we can derive the condition for equilibrium



isolated

fixed partition permeable to particles only

$$N = N_A + N_B$$

$$\Rightarrow dS = dS_A + dS_B$$

$$= -(\mu_A - \mu_B)\frac{dN_A}{T}$$

$\therefore$ $\mu_A = \mu_B$ in equilibrium & particles flow to side with lowest μ otherwise.

Examples of use –

- phase equilibria (look up Clausius-clapeyron equ. if interested!)
- chemical reactions

e.g. $2H_2 + O_2 \rightleftharpoons H_2O$

$$\Rightarrow 2\mu_{H_2O} + \mu_{O_2} = \mu_{H_2O}$$

in equilibrium.

- Chemical potential of ideal gas

$$\mu = -k_B T \ln\left(n_Q(T) \cdot \frac{V}{N}\right) + \text{const.}$$

(See lecture notes for derivation).

- Isothermal atmosphere model

Atmosphere in equilibrium

$$\Rightarrow \mu = \text{const}$$

$$\mu = \underbrace{-k_B T \ln\left(n_Q(T) \frac{V}{N}\right)}_{\text{ideal gas}} + \underbrace{mgh}_{\text{gravitational potential}}$$

$= \text{const.}$

$$\Rightarrow \frac{N}{V} = n(h) = n(0) e^{-mgh/k_BT}$$

- Semiconductors
- Grand canonical ensemble
- dependence of μ on T etc..

2. $$\Xi = \sum_{\text{states}} e^{-(E_i - \mu N_i)/k_B T}$$

$$= \sum_{N=0}^{M} \frac{M!}{N!(M-N)!} e^{-(N\epsilon - \mu N)/k_B T}$$

gibbs factor.

degeneracy when N of M sites filled

Sum over cases from N=0 (no sites filled) up to N=M (all filled)

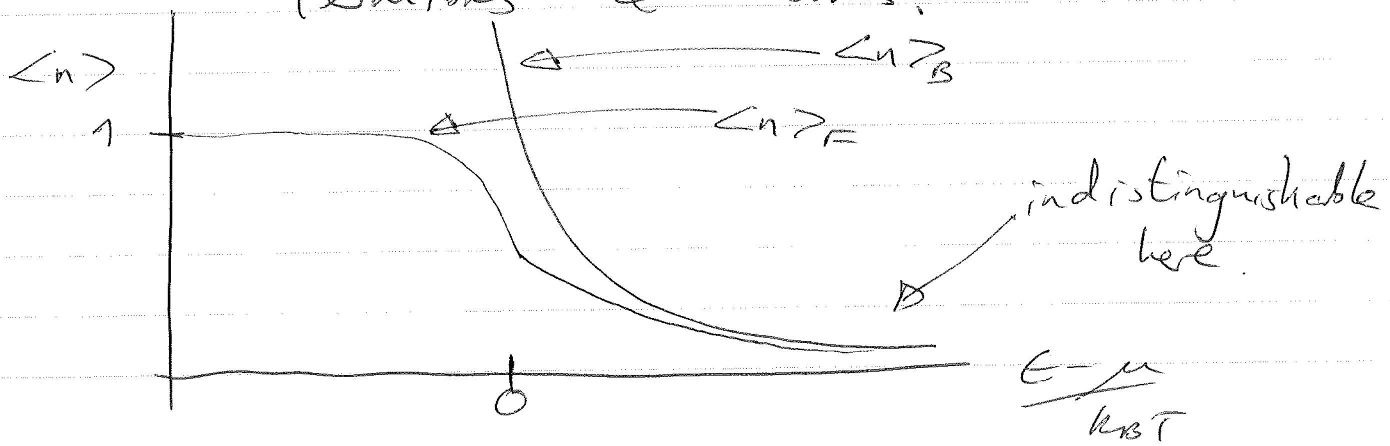
$$= \left(1 + e^{-(\epsilon-\mu)/k_B T}\right)^M.$$

3. $$\langle n \rangle_B = \frac{1}{e^{(\epsilon-\mu)/k_B T} - 1} \qquad \langle n \rangle_F = \frac{1}{e^{\frac{\epsilon-\mu}{k_B T}} + 1}.$$

$$\frac{\langle n \rangle_B}{\langle n \rangle_F} = \frac{e^{\frac{(\epsilon-\mu)}{k_B T}} + 1}{e^{(\epsilon-\mu)/k_B T} - 1}$$

$$\lim_{\frac{\epsilon-\mu}{k_B T} \to \infty} \frac{\langle n \rangle_B}{\langle n \rangle_F} = 1 + O\left(e^{-\frac{(\epsilon-\mu)}{k_B T}}\right).$$

$\therefore$ at high energy compared with $k_B T$ there is no need to distinguish fermions & bosons.



4. $\langle n \rangle_p = \dfrac{1}{e^{\epsilon/k_B T} - 1}$.

$\lambda = 50\mu m \Rightarrow \epsilon = \dfrac{hc}{\lambda} = 3.97 \times 10^{-21}$ J.

At $T = 300K$

$\dfrac{\epsilon}{k_B T} = 0.9592$.

$\therefore \langle n \rangle_p \cong 0.62$

5. a) $\Xi_B = \dfrac{1}{1 - e^{-(\epsilon-\mu)/k_B T}}$.

$\langle n \rangle_B = \dfrac{1}{e^{(\epsilon-\mu)/k_B T} - 1}$.

for $\epsilon - \mu = 10^{-22}$ J & $T = 300K$

$\dfrac{\epsilon - \mu}{k_B T} \simeq 0.0241$

$\therefore \Xi_B = 40.995 \simeq 41$.

& $\langle n \rangle_B \cong 41$

b) $\Xi_F = 1 + e^{-\frac{\epsilon-\mu}{k_B T}} \simeq 1.9761$

$\langle n_F \rangle \cong 0.494$

$\left(= \dfrac{1}{e^{\epsilon-\mu/k_B T} + 1} \right)$

6.

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mk_BT}} \qquad \left(E = \frac{p^2}{2m} \right).$$

For a density $n = \frac{N}{V}$ the ~~Spacing~~ volume per particle is $\frac{V}{N} = \frac{1}{n}$ hence the Spacing is

$$\left(\frac{1}{n}\right)^{\frac{1}{3}} \approx \lambda.$$

$$\therefore \quad \frac{h}{\sqrt{2mk_BT}} \approx \left(\frac{1}{n}\right)^{\frac{1}{3}}$$

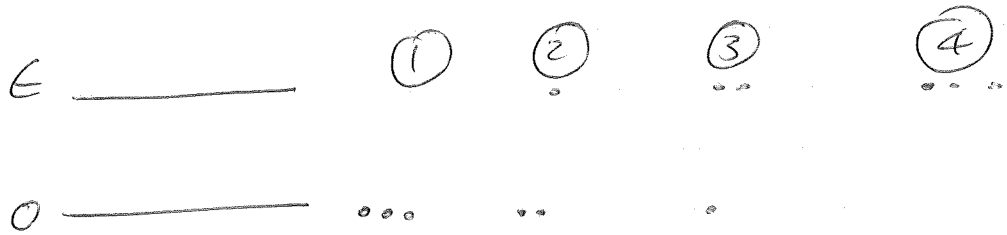
$$\Rightarrow \quad T \approx \frac{h^2 n^{2/3}}{2mk_B}$$

If $n = 10^{27}\,m^{-3}$ then

$$T \approx 2.38\,K.$$

(NB He Liquifies at 4.2K at 1atm).

7. i)

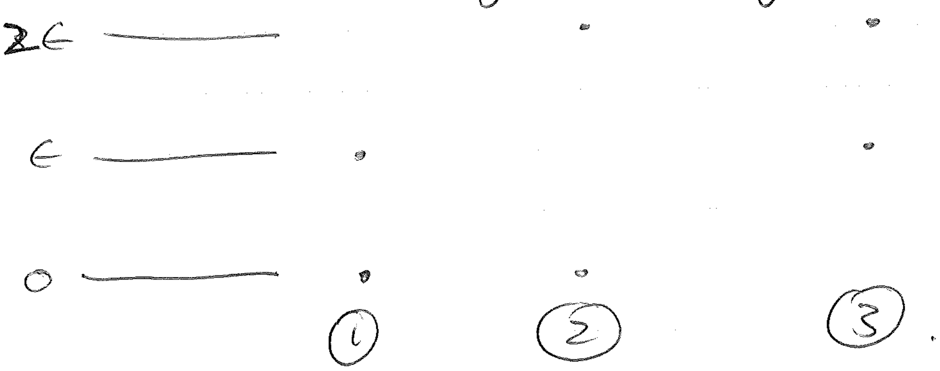


① Energy	0,	Boltzmann factor 1.
②	ϵ	$e^{-\epsilon/k_BT}$
③	2ϵ	$e^{-2\epsilon/k_BT}$
④	3ϵ	$e^{-3\epsilon/k_BT}$

$$\therefore \langle E \rangle = \frac{\epsilon e^{-\epsilon/k_BT} + 2\epsilon e^{-2\epsilon/k_BT} + 3\epsilon e^{-3\epsilon/k_BT}}{1 + e^{-\epsilon/k_BT} + e^{-2\epsilon/k_BT} + e^{-3\epsilon/k_BT}}$$

(Note - this is just the first few terms from the ~~Bose Einstein~~ i.e. SHO average energy).

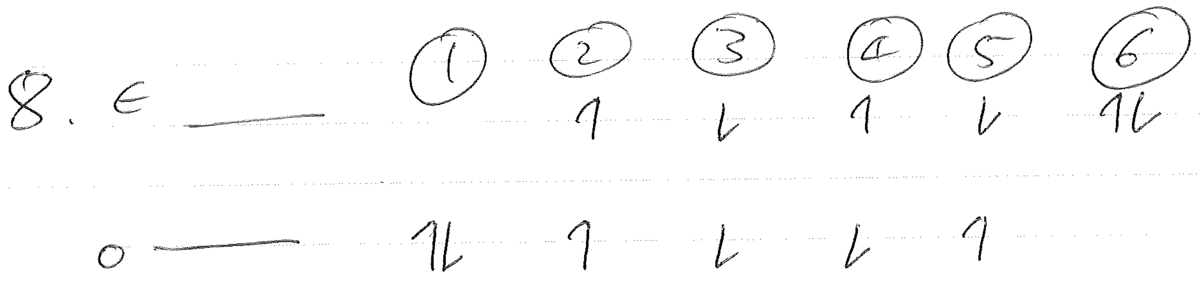
ii)



	①	②	③
Energy	ϵ	2ϵ	3ϵ
BF.	$e^{-\epsilon/k_BT}$	$e^{-2\epsilon/k_BT}$	$e^{-3\epsilon/k_BT}$

$$\therefore \langle E \rangle = \frac{\epsilon e^{-\epsilon/k_BT} + 2\epsilon e^{-2\epsilon/k_BT} + 3\epsilon e^{-3\epsilon/k_BT}}{e^{-\epsilon/k_BT} + e^{-2\epsilon/k_BT} + e^{-3\epsilon/k_BT}}.$$

8.



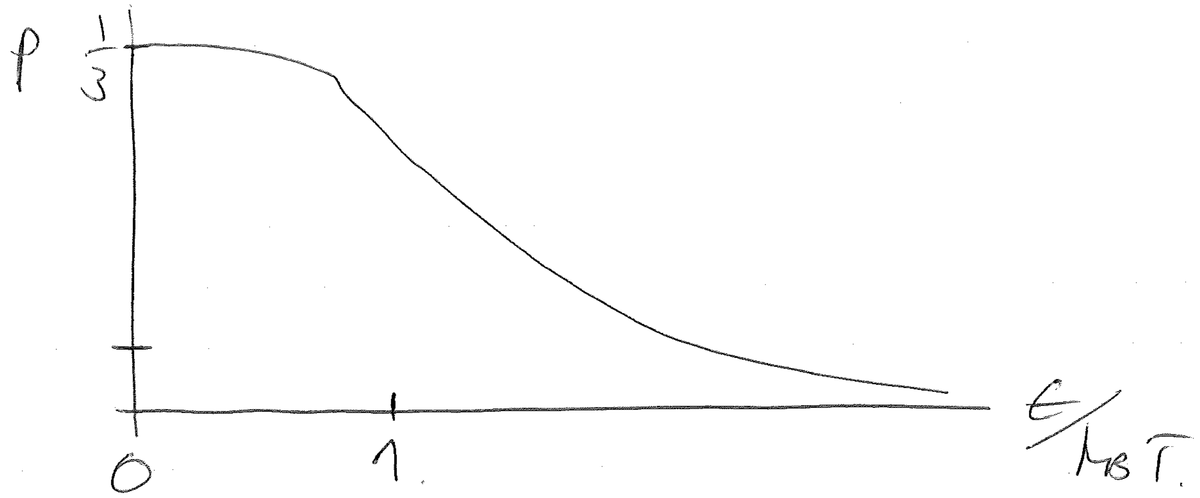
State	Energy	Boltzmann factor	Spin
1	0	1	0
2	ϵ	$e^{-\epsilon/k_BT}$	1
3	ϵ	$e^{-\epsilon/k_BT}$	-1
4	ϵ	$e^{-\epsilon/k_BT}$	0
5	ϵ	$e^{-\epsilon/k_BT}$.	0
6	2ϵ	$e^{-2\epsilon/k_BT}$	0

$$\therefore \quad Z = 1 + 4e^{-\epsilon/k_BT} + e^{-2\epsilon/k_BT}.$$

Average Spin in States 2 & 3 non-zero.

Prob. of being in state 2 or 3 is:

$$P = \frac{2e^{-\epsilon/k_BT}}{1 + 4e^{-\epsilon/k_BT} + e^{-2\epsilon/k_BT}}.$$



P simplifies to

$$P = \frac{1}{\frac{1}{2}\left(e^{\epsilon/k_B T} + e^{-\epsilon/k_B T}\right) + 2}$$

$$= \frac{1}{\cosh \epsilon/k_B T + 2}.$$