Chapter 13

The Nature of Thermodynamics

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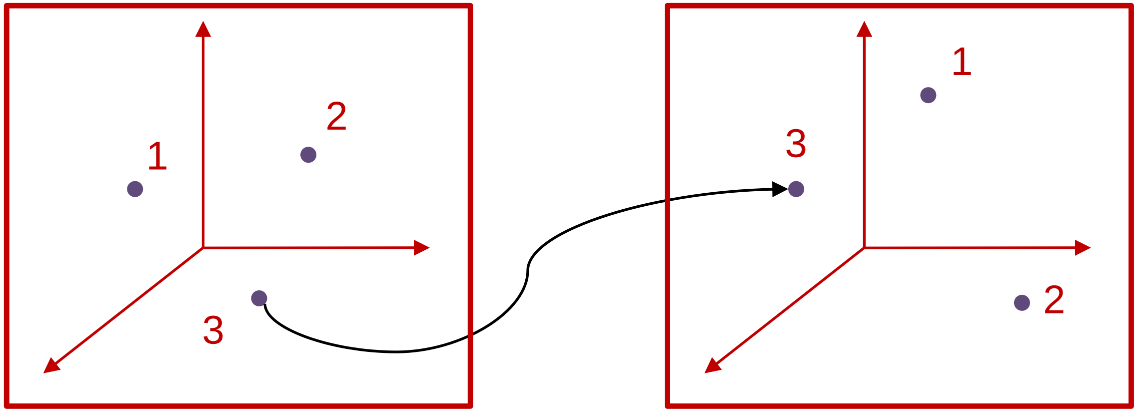
13.1 Boltzmann Statistics

- Distinguishability : Classical Statistics

  In classical mechanics, trajectories can be built up from the information of states of particles.

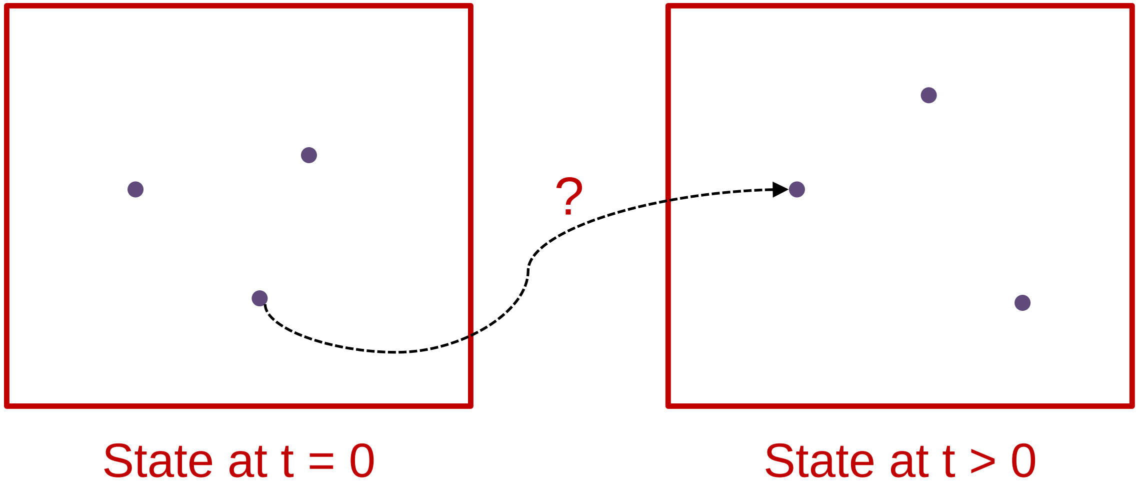
  The trajectories allow us to distinguish particle whether they are identical or not.



State at t = 0 State at t > 0

- Distinguishability : Quantum Statistics

  In quantum mechanics, Our knowledge of states is imperfect because the states are hobbled according to Heisenberg's uncertainty principle. It means that it is impossible to distinguish identical particles.



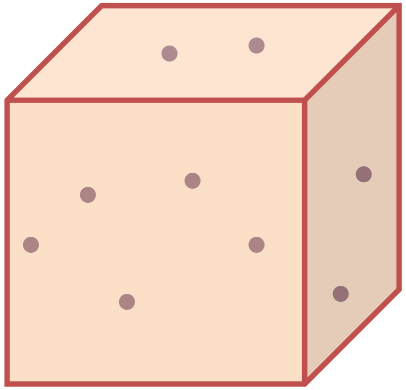
- Boltzmann statistics

  Boltzmann statistics is for distinguishable particles.

  Therefore, Boltzmann statistics is applied to particles of classical gas or on there positions in solid lattice.

  Consider N molecules with internal energy E in cubic volume V

  Each energy level, ϵ_i has N_i molecules with g_i degeneracies.

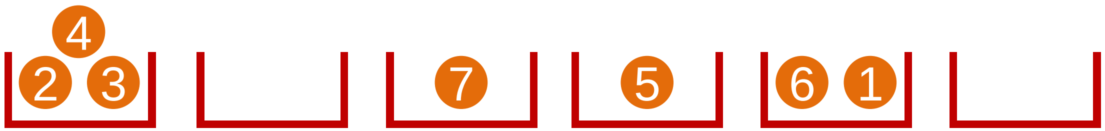


$$\left.\begin{aligned} \sum N_i &= N \\ \sum N_i \epsilon_i &= E \end{aligned}\right\} \text{two constraints of the system}$$

- Number of rearrangement

First, select N_1 distinguishable particles from a total of N to be placed in the first energy level with arrangement among g_1 choices.

Ex) seven particles for 1st energy level of $g_i = 6$



$$w_1 = {}_N C_{N_1} \cdot {g_1}^{N_1} = \frac{N! \cdot {g_1}^{N_1}}{(N - N_1)!\, N_1!}$$

13.1 Boltzmann Statistics

Next step is to do same work for 2nd energy level among $(N - N_1)$ particles

These works are done in sequence until last N_n particles are distributed.

Thus, the number of rearrangement becomes

$$w_B = \prod w_i = ({}_N C_{N_1} \cdot {g_1}^{N_1}) \times ({}_{N-N_1} C_{N_2} \cdot {g_2}^{N_2}) \times \cdots \times ({}_{N_n} C_{N_n} \cdot {g_n}^{N_n})$$

$$= \left(\frac{N!}{(N - N_1)!\, N_1!} {g_1}^{N_1} \right) \times \left(\frac{(N - N_1)!}{(N - N_1 - N_2)!\, N_2!} {g_2}^{N_2} \right) \times \cdots \times \left(\frac{N_n!}{0!\, N_n!} {g_n}^{N_n} \right)$$

$$\longrightarrow \quad w_B = N! \prod \frac{{g_i}^{N_i}}{N_i!}$$

- Boltzmann distributions

From Stirling's approximation, $\ln(N!) = N\ln(N) - N$

$$\ln(w_B) = \ln(N!) + \sum[N_i \ln(g_i) - \ln(N_i!)]$$
$$= \ln(N!) + \sum[N_i \ln(g_i) - N_i \ln(N_i) + N_i]$$

N_i for j^{th} energy level is undetermined yet

→ Method of Lagrange multiplier is used to obtain most probable macro state under two constraints, $\sum N_i = N$, $\sum N_i \epsilon_i = E$

$$\frac{\partial(\ln(w_B))}{\partial N_i} + \alpha \frac{\partial(\sum N_i - N)}{\partial N_i} + \beta \frac{\partial(\sum N_i \epsilon_i - E)}{\partial N_i} = 0$$

Applying method of Lagrange multipliers to Boltzmann distributions,

$$\frac{\partial(\sum N_i \ln(g_i) - \sum N_i \ln(N_i) + \sum N_i)}{\partial N_i} + \alpha \frac{\partial(\sum N_i)}{\partial N_i} + \beta \frac{\partial(\sum N_i \epsilon_i)}{\partial N_i} = 0$$

$$\Rightarrow \ln(g_i) - \ln(N_i) - \frac{N_i}{N_i} + 1 + \alpha + \beta\epsilon_i = 0$$

Then, number distribution becomes

$$\ln\left(\frac{N_i}{g_i}\right) = \alpha + \beta\epsilon_i \longrightarrow N_i/g_i = e^{\alpha+\beta\varepsilon_i} = f_i(\varepsilon_i)$$

Boltzmann distribution function

# of particles per each quantum state for the equilibrium configuration

13.3 Boltzmann Distributions

- Physical relation of constant β

$$\sum N_i \ln g_i - \sum N_i \ln N_i + \alpha \sum N_i + \beta \sum N_i \varepsilon_i = 0$$

$$\sum N_i \ln g_i - \sum N_i \ln N_i = -\alpha N - \beta U$$

$$\ln(w_B) = \ln(N!) + \sum [N_i \ln(g_i) - N_i \ln(N_i) + N_i]$$

$$= \ln(N!) + \sum \left[N_i \ln\left(N_i e^{-\alpha-\beta\epsilon_i}\right) - N_i \ln(N_i) + N_i\right]$$

$$= \ln(N!) + \sum [N_i \ln(N_i) - \alpha N_i - \beta N_i \epsilon_i - N_i \ln(N_i) + N_i]$$

$$= \mathbf{ln}(\boldsymbol{N}!) + \boldsymbol{N} - \boldsymbol{\alpha}\mathbf{N} - \boldsymbol{\beta}\mathbf{U}$$

13.3 Boltzmann Distributions

Using the statistical definition of entropy,

$$S = k\ln(w_B) = k\ln(N!) + k(1-\alpha)\mathrm{N} - k\beta\mathrm{U} = S_0 - k\beta\mathrm{U}$$

In classical thermodynamics,

$$dS(U,V) = \frac{1}{T}dU + \frac{P}{T}dV = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV \rightarrow \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

From the previous result, $S = k\ln(N!) + k(1-\alpha)\mathrm{N} - k\beta\mathrm{U} = S_0 - k\beta\mathrm{U}$

$$\left(\frac{\partial S}{\partial U}\right)_V = -k\beta$$

Comparing these two results, the constant β becomes

$$\beta = -\frac{1}{kT}$$

13.3 Boltzmann Distributions

$$N_i = g_i e^{\alpha+\beta\varepsilon_j} = g_i e^{\alpha} e^{-\varepsilon_i/kT}$$

For the value of e^{α},

$$N = \sum_i N_i = e^{\alpha} \sum_i g_j e^{-\varepsilon_i/kT}$$

$$e^{\alpha} = \frac{N}{\sum g_i e^{-\varepsilon_i/kT}}$$

And hence,

$$f_i = \frac{N_i}{g_i} = \frac{N e^{-\varepsilon_i/kT}}{\sum g_i e^{-\varepsilon_i/kT}}$$ (Boltzmann distribution)

Partition function Z

- Partition function

Partition function is defined to

$$Z \equiv \sum_{i=1}^{\infty} g_i e^{\beta \epsilon_i}$$

Partition function has information of degeneracy and energy level.

There are two consequences of partition function.

1) $N = \sum_{i=1}^{\infty} N_i = \sum_{i=1}^{\infty} g_i e^{\alpha + \beta \epsilon_i} = e^{\alpha} Z \qquad e^{\alpha} = \frac{N}{Z}$

2) $E = \sum_{i=1}^{\infty} N_i \epsilon_i = \sum_{i=1}^{\infty} g_i \epsilon_i e^{\alpha + \beta \epsilon_i} = e^{\alpha} \left(\frac{\partial Z}{\partial \beta}\right)_V = \frac{N}{Z} \left(\frac{\partial Z}{\partial \beta}\right)_V = N \left(\frac{\partial \ln(Z)}{\partial \beta}\right)_V$

- Distribution function

From previous results, the number distributions N_i

$$N_i = g_i e^{\alpha} e^{\beta \epsilon_i} = g_i \frac{N}{Z} e^{-\frac{\epsilon_i}{kT}}$$

Then, the Boltzmann distribution function is defined as below.

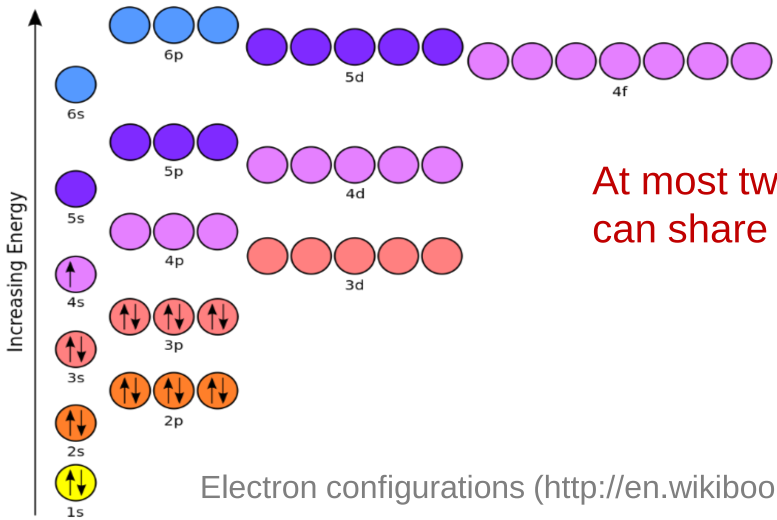
$$f(\epsilon_i) \equiv \frac{N_i}{g_i} = \frac{N e^{-\frac{\epsilon_i}{kT}}}{Z}$$

- Fermion

  1) Fermion is indistinguishable particle which obeys Pauli's exclusion principle.

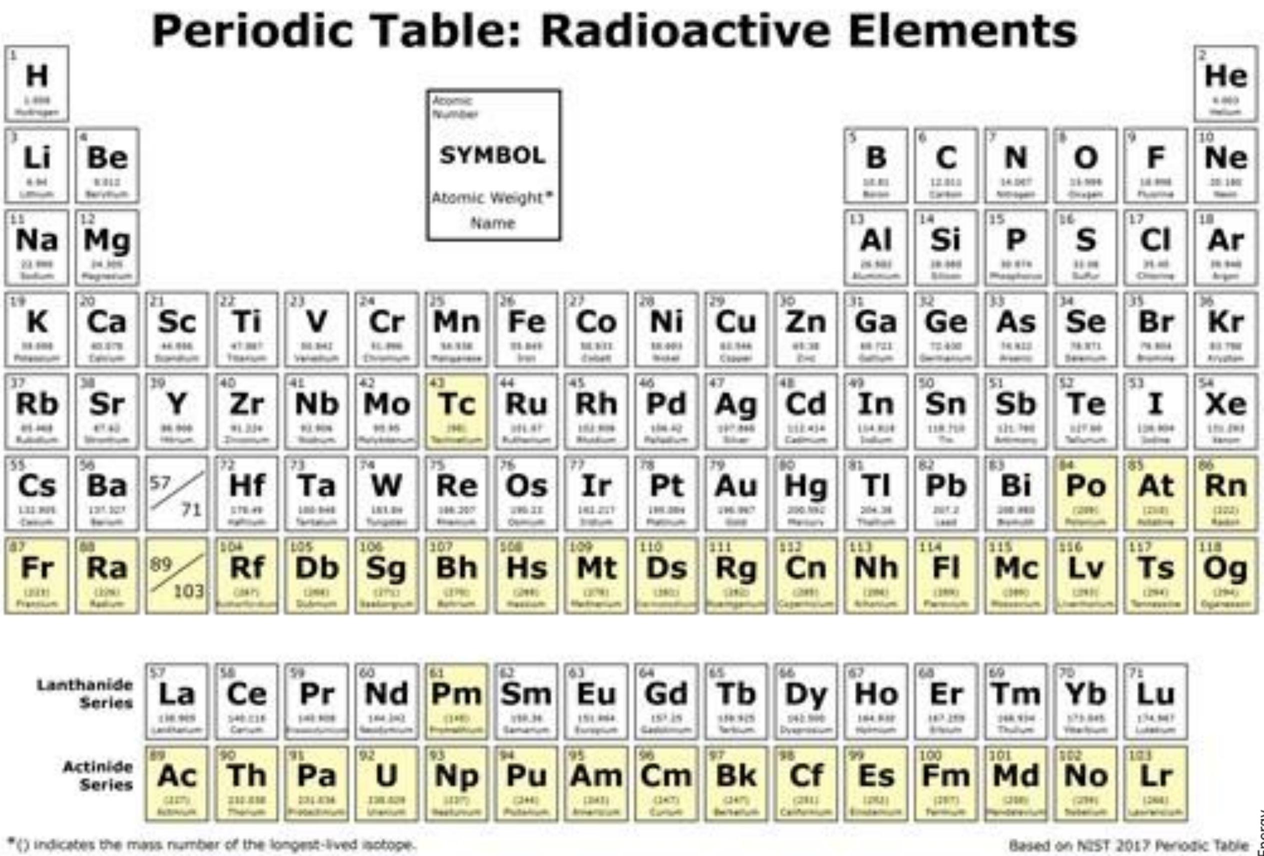
  2) Pauli's exclusion principle means that no quantum state can accept more than one particle.

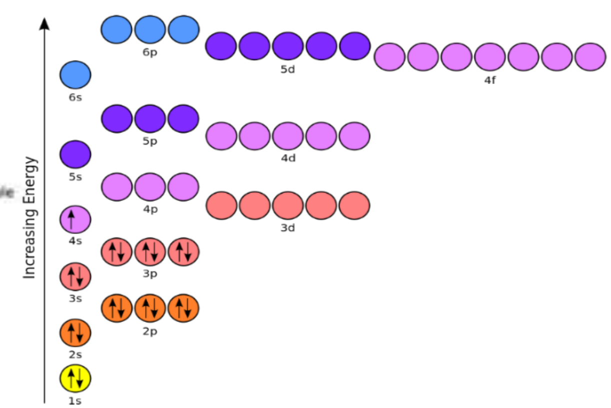
  3) Examples of fermions are electron, positron, proton, neutron, and neutrino.



At most two electrons (with different spins) can share the same orbitals

Electron configurations (http://en.wikibooks.org)

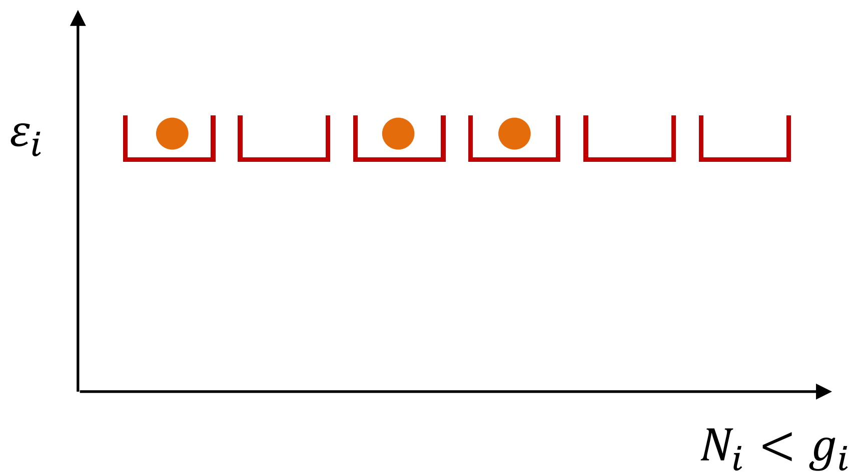

Periodic Table: Radioactive Elements
Atomic Number
SYMBOL
Atomic Weight*
Name
1 H
2 He
3 Li 4 Be
5 B 6 C 7 N 8 O 9 F 10 Ne
11 Na 12 Mg
13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
19 K 20 Ca 21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
37 Rb 38 Sr 39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
55 Cs 56 Ba 57 71 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
87 Fr 88 Ra 89 103 104 Rf 105 Db 106 Sg 107 Bh 108 Hs 109 Mt 110 Ds 111 Rg 112 Cn 113 Nh 114 Fl 115 Mc 116 Lv 117 Ts 118 Og
Lanthanide Series
57 La 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu
Actinide Series
89 Ac 90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr
*() indicates the mass number of the longest-lived isotope.
Based on NIST 2017 Periodic Table


Increasing Energy
1s
2s
2p
3s
3p
4s
3d
5s
4p
4d
5p
6s
6p
5d
4f

13.4 Fermi-Dirac Distribution

- Number of rearrangement

  Distribution of n_i particles among g_i state boxes.



Ex) three particles for i^{th} energy level of $g_i = 6$

$$w_{FD} = \prod {}_{g_i}C_{N_i} = \prod \frac{g_i!}{(g_i - N_i)!\,N_i!}$$

- Fermi-Dirac distributions

From Stirling's approximation, $\ln(N!) = N\ln(N) - N$

$$\ln(w_{FD}) = \sum[\ln(g_i!) - \ln(N_i!) - \ln((g_i - N_i)!)]$$

$$= \sum[g_i \ln(g_i) - g_i - N_i \ln(N_i) + N_i - (g_i - N_i)\ln(g_i - N_i) + (g_i - N_i)]$$

N_i for j^{th} energy level is undetermined yet.

→ Method of Lagrange multiplier is used to obtain most probable macro state under two constraints, $\sum N_i = N$, $\sum N_i\epsilon_i = E$

$$\frac{\partial(\ln(w_{FD}))}{\partial N_i} + \alpha\frac{\partial(\sum N_i - N)}{\partial N_i} + \beta\frac{\partial(\sum N_i\epsilon_i - E)}{\partial N_i} = 0$$

13.4 Fermi-Dirac Distribution

Applying method of Lagrange multipliers to Fermi-Dirac distributions,

$$\frac{\partial(\sum[g_i \ln(g_i) - N_i \ln(N_i) - (g_i - N_i)\ln(g_i - N_i)])}{\partial N_i} + \alpha \frac{\partial(\sum N_i)}{\partial N_i} + \beta \frac{\partial(\sum N_i \epsilon_i)}{\partial N_i} = 0$$

$$\Rightarrow \quad -\ln(N_i) - \frac{N_i}{N_i} + \ln(g_i - N_i) + \frac{g_i - N_i}{g_i - N_i} + \alpha + \beta\epsilon_i = 0$$

Then, number distribution becomes

$$\ln\left(\frac{g_i}{N_i} - 1\right) = -\alpha - \beta\epsilon_i \longrightarrow N_i = g_i \frac{1}{e^{-\alpha-\beta\epsilon_i} + 1}$$

- Distribution function

Provisionally, we associated α with the chemical potential μ divided by kT, and reserve for later the physical interpretation of this connection.

$$\alpha = \frac{\mu}{kT}$$

Then, the Fermi-Dirac distribution function is defined as below.

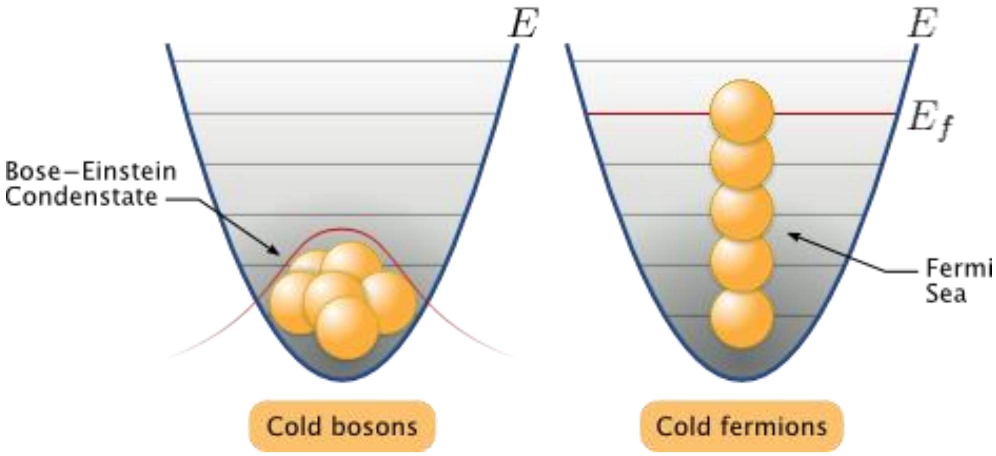
$$f(\epsilon_i) \equiv \frac{N_i}{g_i} = \frac{1}{e^{-\alpha-\beta\epsilon_i} + 1} = \frac{1}{e^{(\epsilon_i-\mu)/kT} + 1}$$

- Boson

1) Boson is indistinguishable particle not obeying Pauli's exclusion principle.

2) Thus, one micro-state can be occupied by several Bosons.

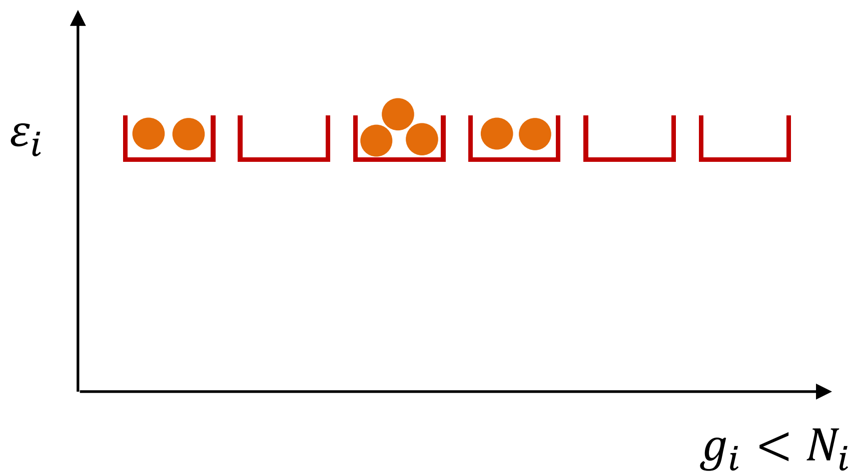
3) Photon is the most notable example of Boson.



Difference between fermions and bosons
(http://quantum-bits.org/)

- Number of rearrangement

  Rearrangement of $N_i + g_i - 1$ symbols into $g_i - 1$ partitions (degeneracy) and N_i particles.



$N_i + g_i - 1$ symbols

$g_i - 1$ partitions

Ex) seven particles for i^{th} energy level of $g_i = 6$

$$w_{BE} = \prod {}_{N_i+g_i-1}C_{g_i-1} = \prod \frac{(N_i + g_i - 1)!}{N_i!\,(g_i - 1)!}$$

13.5 Bose-Einstein Distribution

- Bose-Einstein distributions

From Stirling's approximation, $\ln(N!) = N\ln(N) - N$

$$\ln(w_{BE}) = \sum[\ln((N_i+g_i-1)!) - \ln(N_i!) - \ln((g_i-1)!)]$$

$$= \sum[(N_i+g_i-1)\ln(N_i+g_i-1) - N_i\ln(N_i) - (g_i-1)\ln(g_i-1)]$$

N_i for i^{th} energy level is undetermined yet

→ Method of Lagrange multiplier is used to obtain the most probable macro state under two constraints,
$\sum N_i = N$, $\sum N_i\epsilon_i = E$

$$\frac{\partial(\ln(w_{BE}))}{\partial N_i} + \alpha\frac{\partial(\sum N_i - N)}{\partial N_i} + \beta\frac{\partial(\sum N_i\epsilon_i - E)}{\partial N_i} = 0$$

Applying method of Lagrange multipliers to Bose-Einstein distributions,

$$\frac{\partial(\sum[(N_i+g_i-1)\ln(N_i+g_i-1)-\sum N_i\ln(N_i)])}{\partial N_i}+\alpha\frac{\partial(\sum N_i)}{\partial N_i}+\beta\frac{\partial(\sum N_i\epsilon_i)}{\partial N_i}=0$$

$$\Rightarrow \ln(N_i+g_i-1)+\frac{g_i+N_i-1}{g_i+N_i-1}-\ln(N_i)-\frac{N_i}{N_i}+\alpha+\beta\epsilon_i=0$$

Then, number distribution becomes

$$\ln\left(\frac{N_i+g_i-1}{N_i}\right)=-\alpha-\beta\epsilon_i \longrightarrow N_i=g_i\frac{1}{e^{-\alpha-\beta\epsilon}-1}$$

- Distribution function

$$N_i = g_i \frac{1}{e^{-\alpha-\beta\epsilon} - 1} \qquad \left(\alpha = \frac{\mu}{kT}, \beta = -\frac{1}{kT}\right)$$

Then, the Bose-Einstein distribution function is defined as below.

$$f(\epsilon_i) \equiv \frac{N_i}{g_i} = \frac{1}{e^{-\alpha-\beta\epsilon_i} - 1} = \frac{1}{e^{(\epsilon_i-\mu)/kT} - 1}$$

- Maxwell-Boltzmann Statistics

For dilute system, $N_i \ll g_i$ for all i, which is called dilute gas.

$$w_{BE} = \prod \frac{(g_i + N_i - 1)!}{N_i!\,(g_i - 1)!} = \prod \frac{(g_i + N_i - 1)\cdot(g_i + N_i - 2)\cdots(g_i + 1)\cdot(g_i)}{N_i!} \approx \prod \frac{{g_i}^{N_i}}{N_i!}$$

$$w_{FD} = \prod \frac{(g_i)!}{N_i!\,(g_i - N_i)!} = \prod \frac{(g_i)\cdot(g_i - 1)\cdots(g_i - N_i + 2)\cdot(g_i - N_i + 1)}{N_i!} \approx \prod \frac{{g_i}^{N_i}}{N_i!}$$

Therefore, both Fermion and Boson follow Maxwell-Boltzmann statistics for dilute gas.

$$w_{MB} = \prod \frac{{g_i}^{N_i}}{N_i!}$$

- Maxwell-Boltzmann distributions

From Stirling's approximation, $\ln(N!) = N\ln(N) - N$

$$\ln(w_{MB}) = \sum[N_i \ln(g_i) - \ln(N_i!)] = \sum[N_i \ln(g_i) - N_i \ln(N_i) + N_i]$$

N_i for i^{th} energy level is undetermined yet.

→ Method of Lagrange multiplier is used to obtain the most probable macro state under two constraints,

$\sum N_i = N, \sum N_i \epsilon_i = E$

$$\frac{\partial(\ln(w_{MB}))}{\partial N_i} + \alpha\frac{\partial(\sum N_i - N)}{\partial N_i} + \beta\frac{\partial(\sum N_i\epsilon_i - E)}{\partial N_i} = 0$$

Applying method of Lagrange multipliers to Maxwell-Boltzmann distributions,

$$\frac{\partial(\ln(\sum[N_i \ln(g_i) - N_i \ln(N_i) + N_i]))}{\partial N_i} + \alpha \frac{\partial(\sum N_i)}{\partial N_i} + \beta \frac{\partial(\sum N_i \epsilon_i)}{\partial N_i} = 0$$

$$\Rightarrow \ln(g_i) - \ln(N_i) - \frac{N_i}{N_i} + 1 + \alpha + \beta\epsilon_i = 0$$

Then, number distribution becomes

$$\ln\left(\frac{g_i}{N_i}\right) = -\alpha - \beta\epsilon_i \longrightarrow N_i = g_i e^{\alpha+\beta\epsilon_i}$$

$$f(\epsilon_i) \equiv \frac{N_i}{g_i} = \frac{1}{e^{-\alpha-\beta\epsilon_i} + 0}$$

- Distribution function

$$N_i = g_i e^{-\alpha-\beta\epsilon} \qquad \left(\alpha = \frac{\mu}{kT}, \qquad \beta = -\frac{1}{kT}\right)$$

Then, the Maxwell-Boltzmann distribution function is defined as below.

$$f(\epsilon_i) \equiv \frac{N_i}{g_i} = e^{\alpha+\beta\epsilon_i} = e^{-\frac{(\epsilon_i-\mu)}{kT}} = \frac{N}{Z} e^{-\epsilon_i/kT} \qquad (e^{\frac{\mu}{kT}} = \frac{N}{Z})$$

- Energy transition

$$U = \sum N_i \epsilon_i$$

$$dU = \sum N_i d\epsilon_i + \sum \epsilon_i dN_i = \sum N_i \frac{d\epsilon_i(V)}{dV} dV + \sum \epsilon_i dN_i$$

This statistical expression can be matched with classical expression.

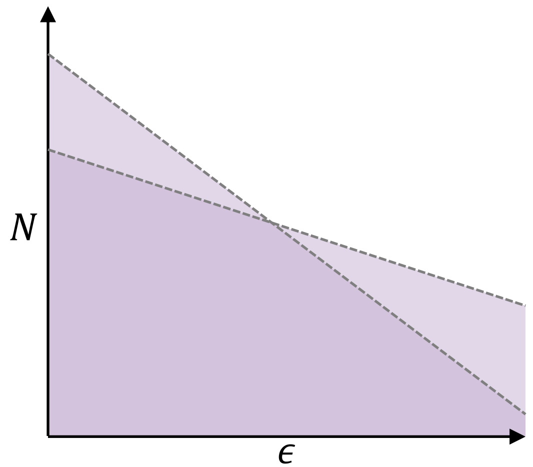
$$dU = \delta Q - \delta W = TdS - PdV$$

$$\sum N_i \frac{d\epsilon_i(V)}{dV} dV + \sum \epsilon_i dN_i = -PdV + TdS$$

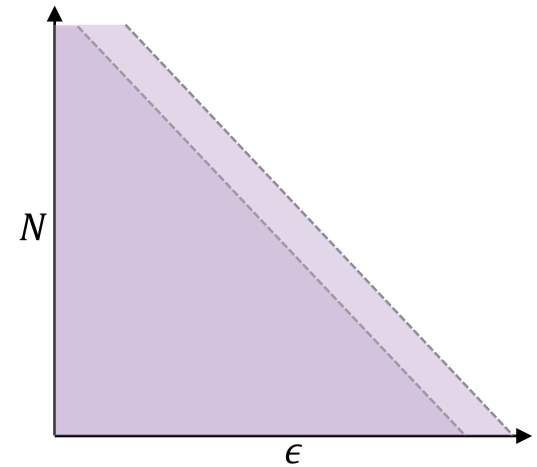
$$\sum N_i d\epsilon_i = -PdV \qquad \sum \epsilon_i dN_i = TdS$$

Heat transfer to the system : particles are re-distributed so that particles are shifted from lower to higher energy level.

Isentropic process with work done : the energy levels are shifted to higher values with no re-distribution.



Heat transfer



Work done

- Physical relations of constant α

For a dilute gas,

$$S = k\ln(w_{MB}) = k\sum\left[N_i \ln\left(\frac{g_i}{N_i}\right) + N_i\right] = k\sum[N_i \ln(e^{-\alpha-\beta\epsilon_i}) + N_i]$$

$$= k\sum\left[N_i\left(\ln\left(\frac{Z}{N}\right) + 1\right) - \frac{1}{kT}N_i\epsilon_i\right]$$

$$(\because e^{\alpha} = \frac{N}{Z}, \beta = -\frac{1}{kT})$$

$$\longrightarrow \quad S = Nk\left(\ln\left(\frac{Z}{N}\right) + 1\right) + \frac{U}{T}$$

In classical thermodynamics,

$$dF(U,V,N) = -SdT - PdV + \mu dN \rightarrow \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu$$

From the previous result, $S = Nk\left(\ln\left(\frac{Z}{N}\right) + 1\right) + \frac{U}{T}$

$$F = U - TS = -NkT\left(\ln\left(\frac{Z}{N}\right) + 1\right)$$

$$\left(\frac{\partial F}{\partial N}\right)_{V,T} = -kT\left(\ln\left(\frac{Z}{N}\right) + 1\right) + \frac{NkT}{N}$$

$$\Rightarrow \quad \mu = -kT\left(\ln\left(\frac{Z}{N}\right)\right)$$

Recalling that $\frac{N}{Z} = e^{\alpha}$, constant α is associated with chemical potential and temperature as it is previously introduced.

$$\alpha = \ln\left(\frac{N}{Z}\right) = \frac{\mu}{kT}$$

- Number distributions for identical indistinguishable particles

$$\frac{N_i}{g_i} = \frac{1}{e^{(\epsilon_i - \mu)/kT} + a} \qquad a = \begin{cases} +1 & \text{for FD statistics} \\ -1 & \text{for BE statistics} \\ 0 & \text{for MB statistics} \end{cases}$$