Chapter 13

The Nature of Thermodynamics

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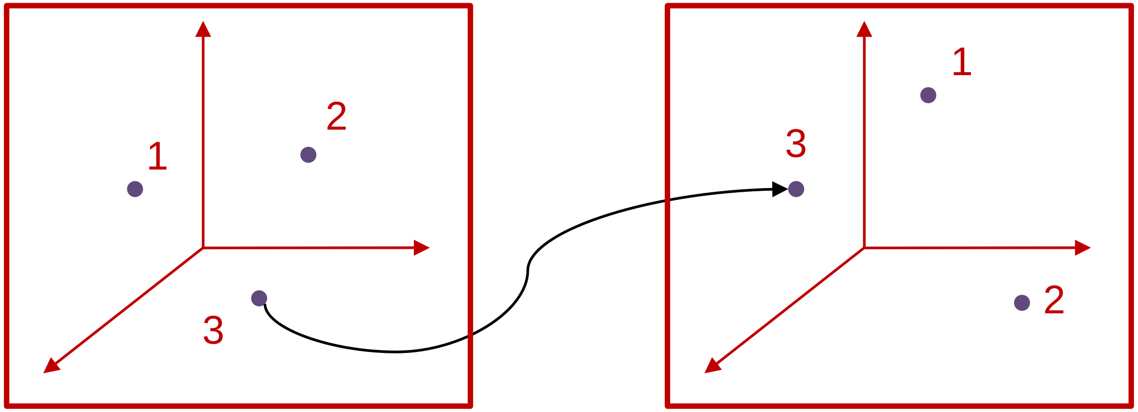
- Distinguishability : Classical Statistics

  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.

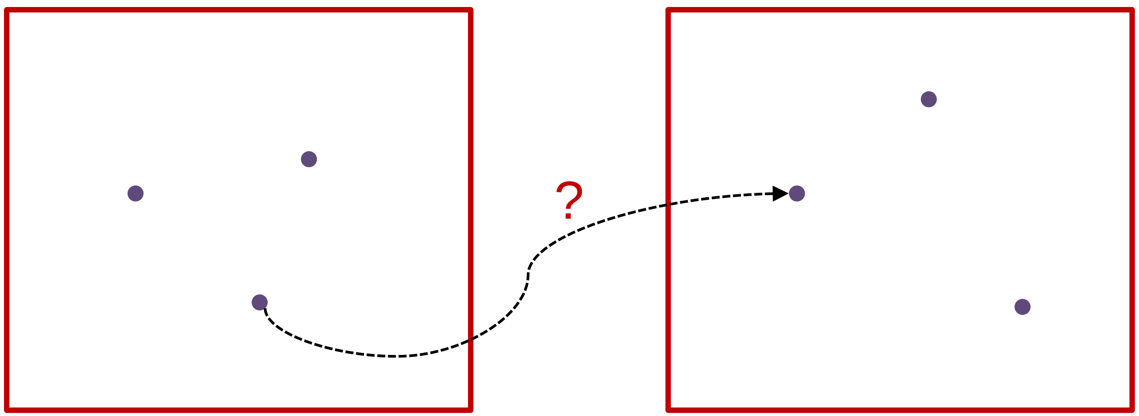


State at t = 0 State at t > 0

13.1 Boltzmann Statistics

- 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.



State at t = 0 State at t > 0

13.1 Boltzmann Statistics

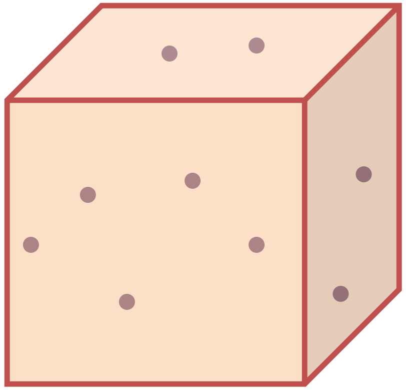
- Boltzmann statistics

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.

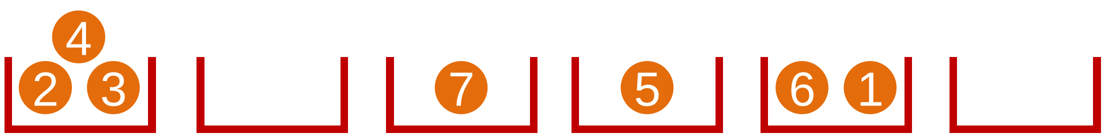


$$\left.\begin{aligned} \sum N_i &= N \\ \sum N_i \epsilon_i &= E \end{aligned}\right\} \text{two constraints of the system}$$

13.1 Boltzmann Statistics

- 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 $g_i = 6$

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

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

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

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

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

- Boltzmann distributions

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

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

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

$\rightarrow$ 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,

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

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

Then, number distribution becomes

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

Boltzmann distribution function

# of particles per each quantum state for the equilibrium configuration

- Physical relation of constant β

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

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

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

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

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

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

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

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

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

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

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

Partition function has information of degeneracy and energy level.

There are two consequences of partition function.

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

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

- Distribution function

From previous results, the number distributions N_i

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

Then, the Boltzmann distribution function is defined as below.

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

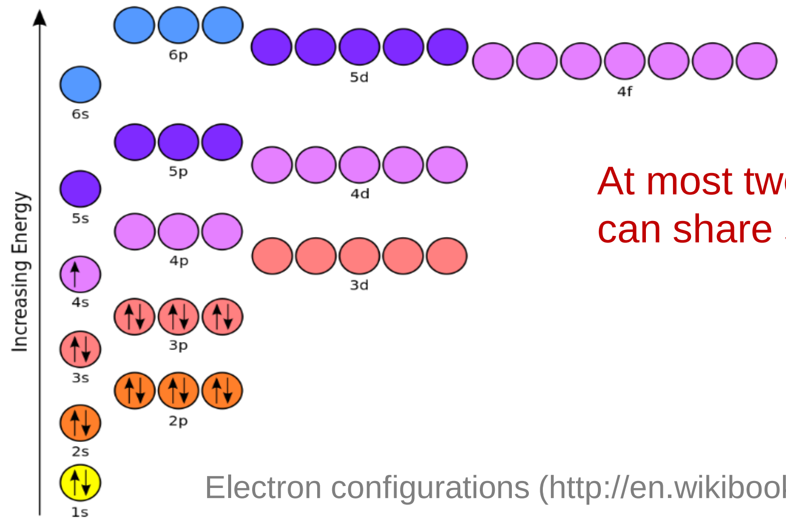
13.4 Fermi-Dirac Distribution

- 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 electrons, positrons, protons, and neutrons.



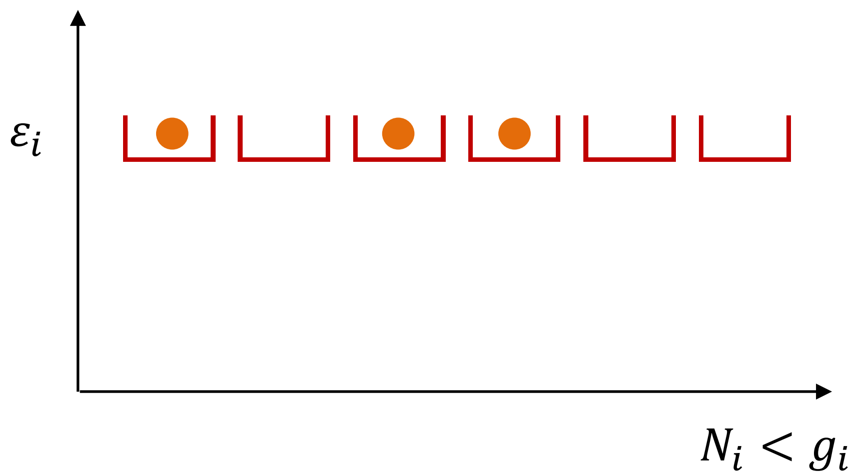
At most two electrons(with different spins) can share same orbitals

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

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, $\ln(N!) = N ln(N) - N$

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

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

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

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

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

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

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

13.4 Fermi-Dirac Distribution

- 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.

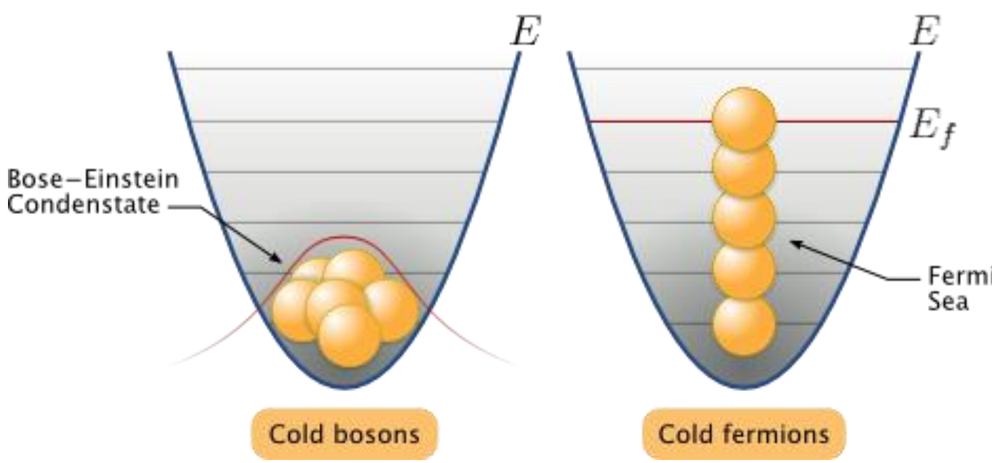
$$f(\epsilon_i) \equiv \frac{N_i}{g_i} = \frac{1}{e^{-\alpha-\beta\epsilon_i}+1} = \frac{1}{e^{(\epsilon_i-\mu)/kT}+1}$$

- Boson

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

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

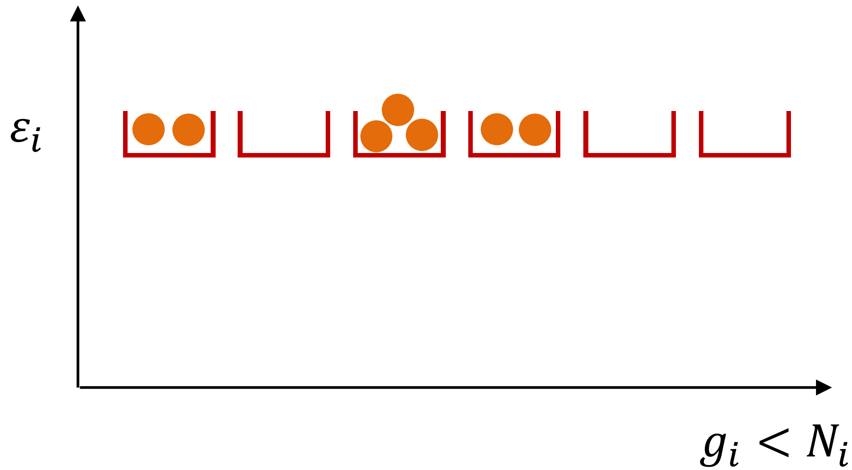
  3) Photon is the most notable example of Boson.



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.



Ex) seven particles for j^{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 j^{th} energy level is undetermined yet

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

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

13.5 Bose-Einstein Distribution

Applying method of Lagrange multipliers to Bose-Einstein distributions,

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

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

Then, number distribution becomes

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

- 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 j, 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 at 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 j^{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

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

- 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.

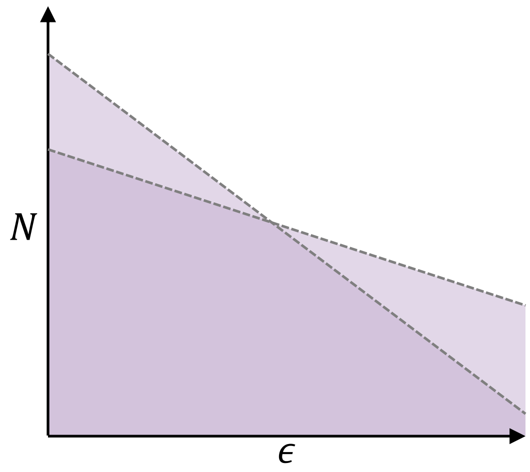
$$dU = \delta Q - \delta W = TdS - PdV$$

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

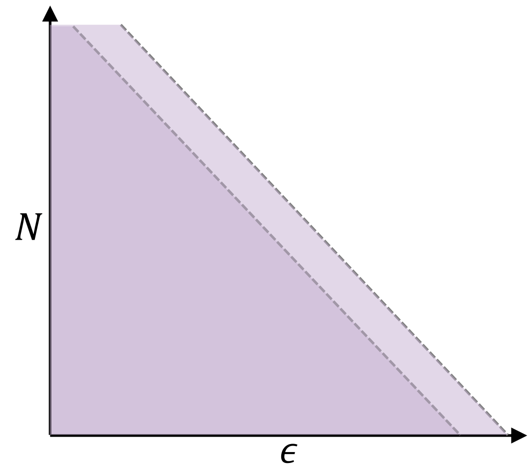
$$\sum N_i d\epsilon_i = -PdV \qquad \sum \epsilon_i dN_i = TdS$$

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,

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

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

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

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

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

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

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

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

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

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

13.8 Comparison of the Distributions

- Number distributions for identical indistinguishable particles

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