3. Statistical mechanics of a system of one kind of particles, non-interacting

the molecular partition function
the nature of alpha and beta
interpretation of heat and work
interpretation of entropy

Consider an ISOLATED SYSTEM (no flow of matter or energy to/from surroundings)

i.e. (1) FIXED NUMBER of particles

(2) FIXED TOTAL ENERGY E

Constraints:

$$(1) \quad \sum N_i = N$$

$$(2) \quad \sum N_i \epsilon_i = E$$

ϵ_i are single-particle energy levels

- What is the most probable distribution?

the distribution that maximizes t (no. of configurations or system quantum states) subject to above constraints.

The number of configurations are:

BOLTZONS $$t = \frac{N!}{\prod_i N_i!} \prod_i \left(g_i^{N_i}\right)$$

corrected BOLTZONS $$t = \prod_i \left(\frac{g_i^{N_i}}{N_i!}\right)$$

i.e. divided by $N!$ to correct for distinguishability

FERMIONS $$t = \prod_i \left(\frac{g_i!}{N_i!(g_i - N_i)!}\right)$$

BOSONS $$t = \prod_i \left[\frac{(g_i + N_i - 1)!}{(g_i - 1)!\, N_i!}\right]$$

To find the most probable distribution we need to maximize t or $\ln t$ subject to the constraints (1) and (2)

To find the most probable distribution (continued):

Steps:

(1) Stirling's approximation for large N

$$N! \simeq (2\pi N)^{1/2} N^N e^{-N}$$

$$\ln N! \simeq N \ln N - N \quad \text{neglect } \tfrac{1}{2}\ln(2\pi N)$$

(2) How to find an extremum for a function of n independent variables?

$$f(x_1, x_2, \cdots x_n)$$

$$\frac{\partial f(x_1, x_2, \cdots x_n)}{\partial x_i} = 0 \qquad i = 1, 2, \cdots n \quad \text{n equations to solve}$$

defines a point which is an extremum

i.e. we need to do

$$\frac{\partial t}{\partial N_i} = 0 \quad \text{for each } N_i$$

However, not all our variables N_i are independent, but are constrained by some conditions. Normally, can do it in a straightforward way by solving constraint equations for any two variables in terms of the others and plug into $f(x_1, x_2, \cdots x_n)$ then solve for $(n-2)$ such equations of the type $\frac{\partial f}{\partial x_i} = 0$. Instead:

Easier and more elegant method of Lagrange multipliers

There are two constants α and β such that the solution of the $n+2$ equations

$$\frac{\partial f(x_1,x_2,\cdots x_n)}{\partial x_i} + \alpha\,\frac{\partial g}{\partial x_i}(x_1,x_2,\cdots x_n) + \beta\,\frac{\partial h}{\partial x_i}(x_1,x_2\cdots x_n) = 0$$

for $i=1,2,\cdots n$

$$g(x_1,x_2,\cdots x_n)=0$$

$$h(x_1,x_2,\cdots x_n)=0$$

The constants α and β are known as **Lagrange multipliers**

Apply this method to our problem:
Set up the equations using multipliers α and $-\beta$

(1) $N-\sum_i N_i=0$

(2) $E-\sum_i N_i\epsilon_i=0$

(3)-(...)

$$\frac{\partial \ln t}{\partial N_i} + \alpha\underbrace{\frac{\partial N}{\partial N_i}}_{1} - \beta\underbrace{\frac{\partial E}{\partial N_i}}_{\epsilon_i} = 0$$

for $i=1,2,\cdots n$
one equation for each

FERMIONS:

$$t_{FD} = \prod_i\left[\frac{g_i!}{N_i!(g_i-N_i)!}\right]$$

use Stirling's approx

$$\ln t_{FD} = \sum_i\left[g_i\ln g_i - N_i\ln N_i - (g_i-N_i)\ln(g_i-N_i)\right]$$

$$= \sum_i\left[-g_i\ln\left(\frac{g_i-N_i}{g_i}\right) + N_i\ln\left(\frac{g_i-N_i}{N_i}\right)\right]$$

BOSONS:

$$t_{BE} = \prod_i \frac{(g_i + N_i - 1)!}{(g_i - 1)!\, N_i!}$$

$$\ln t_{BE} = \sum_i \left[g_i \ln \frac{g_i + N_i}{g_i} \quad + N_i \ln \frac{g_i + N_i}{N_i} \right]$$

using also $g_i - 1 \approx g_i$ for g_i large

CORRECTED BOLTZONS:

$$t_{CB} = \prod_i \left(\frac{g_i^{N_i}}{N_i!} \right)$$

$$\ln t_{CB} = \sum_i \left[N_i \ln \frac{g_i}{N_i} \quad + N_i \right]$$

Now derivatives with respect to N_i are evaluated:

$$\frac{\partial \ln t_{FD}}{\partial N_i} = \frac{\partial}{\partial N_i} \left[g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln (g_i - N_i) \right]$$

$$= -\left[\ln N_i + \frac{N_i}{N_i} \right] - \left[\ln (g_i - N_i)(-1) - \frac{(g_i - N_i)}{(g_i - N_i)} \right]$$

$$= -\ln N_i - 1 + \ln (g_i - N_i) + 1$$

$$= \ln \left(\frac{g_i - N_i}{N_i} \right)$$

$$\frac{\partial \ln t_{BE}}{\partial N_i} = \ln \left(\frac{g_i + N_i}{N_i} \right)$$

$$\frac{\partial \ln t_{CB}}{\partial N_i} = \ln g_i - \frac{N_i}{N_i} - \ln N_i + 1 = \ln \frac{g_i}{N_i}$$

Now we are ready to solve the equations:

$$\frac{\partial \ln t}{\partial N_i} + \alpha \frac{\partial N}{\partial N_i} - \beta \frac{\partial E}{\partial N_i} = 0$$

FD: $\ln \left(\frac{g_i - N_i}{N_i} \right) + \alpha (1) - \beta (\epsilon_i) = 0$

$$\ln \frac{N_i}{g_i - N_i} = \alpha - \beta \epsilon_i$$

$$\frac{N_i}{g_i - N_i} = e^{\alpha} e^{-\beta\epsilon_i} \quad \text{or} \quad N_i = g_i e^{\alpha} e^{-\beta\epsilon_i} - N_i e^{\alpha} e^{-\beta\epsilon_i}$$

$$\frac{N_i}{g_i} = \frac{e^{\alpha} e^{-\beta\epsilon_i}}{1 + e^{\alpha} e^{-\beta\epsilon_i}} = \frac{1}{e^{-\alpha} e^{+\beta\epsilon_i} + 1}$$

$$N_{i_{FD}} = g_i \frac{1}{e^{-\alpha} e^{+\beta\epsilon_i} + 1}$$

BE: $$\frac{\partial \ln t_{BE}}{\partial N_i} + \alpha \frac{\partial N}{\partial N_i} - \beta \frac{\partial E}{\partial N_i} = 0$$

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

$$\frac{N_i}{g_i + N_i} = e^{\alpha} e^{-\beta\epsilon_i}$$

$$N_{i_{BE}} = g_i \frac{1}{e^{-\alpha} e^{+\beta\epsilon_i} - 1}$$

CB: $$\frac{\partial \ln t_{CB}}{\partial N_i} + \alpha \frac{\partial N}{\partial N_i} - \beta \frac{\partial E}{\partial N_i} = 0$$

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

$$N_{i_{CB}} = g_i \frac{1}{e^{-\alpha} e^{+\beta\epsilon_i}}$$ Boltzmann distribution law

SUMMARY

$$\boxed{N_i = \frac{g_i}{e^{-\alpha} e^{+\beta\epsilon_i} \underbrace{\overset{\leftarrow \text{FD}}{\underset{\text{BE}}{\pm 1}}}_{\substack{0 \\ \text{for CB}}}}}$$

FD and BE reduce to CB when $g_i >> N_i$ so that $e^{-\alpha} e^{+\beta\epsilon_i} >> 1$

These equations give N_i for the most probable distributions, which according to the fundamental assumption of statistical mechanics, has the same properties as an actual equilibrium distribution.

Now need to evaluate α and β by using the other two equations that we haven't used yet:

$$\sum_i N_i = N \text{ and } \sum_i N_i \epsilon_i = E$$

CORRECTED BOLTZONS:

$$N_{i_{CB}} = \frac{g_i}{e^{-\alpha} e^{+\beta\epsilon_i}} \qquad \sum_i N_{i_{CB}} = N = \sum_i g_i e^{+\alpha} e^{-\beta\epsilon_i}$$

$$\therefore \; e^{\alpha} = \frac{N}{\boxed{\sum_i g_i e^{-\beta\epsilon_i}}}$$

call this q

"molecular partition function"

$$q \equiv \sum_i g_i e^{-\beta\epsilon_i}$$

$$N_{i_{CB}} = \frac{N}{q} g_i e^{-\beta\epsilon_i} \quad \text{or} \quad \frac{N_{i_{CB}}}{N} = \frac{g_i e^{-\beta\epsilon_i}}{q}$$

Recall $P_i = \frac{N_i}{N}$ = probability of finding any one particle in level i

average $\langle f \rangle$ of any property $= \sum_i P_i f_i$

For example,

$$\langle \epsilon \rangle = \sum_i \frac{N_i}{N} \epsilon_i = \sum_i \left(\frac{g_i e^{-\beta\epsilon_i}}{\sum_i g_i e^{-\beta\epsilon_i}} \epsilon_i \right)$$

Note that $\left(\frac{\partial q}{\partial \beta}\right)_V = \sum_i -\epsilon_i g_i e^{-\beta\epsilon_i}$

constant volume

$$\therefore \; \langle \epsilon \rangle = -\frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -\left(\frac{\partial \ln q}{\partial \beta}\right)_V$$

$$E = \sum_i N_i \epsilon_i = \sum_i \frac{N}{q} g_i e^{-\beta\epsilon_i} \epsilon_i = N \langle \epsilon \rangle$$

← average energy per particle

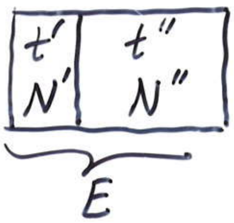
$$\therefore \; E = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V$$

- To determine the nature of α and β:

β 1. Consider two systems, each with its own set of particles and single-particle energy levels.

2. Allow exchange of energy

3. Solve 2 separate problems with two different α values α' and α'' and only one β



$$\sum N_i' = N' \qquad \sum N_j'' = N''$$

$$\sum N_i'\epsilon_i' + \sum N_j''\epsilon_j'' = E$$

$$t = t't'' \quad \text{total no. of configurations}$$

$$\frac{\partial \ln t}{\partial N_i'} + \alpha'\frac{\partial N'}{\partial N_i'} + \alpha''\underbrace{\boxed{\frac{\partial N''}{\partial N_i'}}}_{\text{zero}} - \beta\frac{\partial E}{\partial N_i'} = 0 \quad \text{for all } i$$

$$\frac{\partial \ln t}{\partial N_j''} + \alpha'\underbrace{\boxed{\frac{\partial N'}{\partial N_j''}}}_{\text{zero}} + \alpha''\frac{\partial N''}{\partial N_j''} - \beta\frac{\partial E}{\partial N_j''} = 0 \quad \text{for all } j$$

We end up with

$$\left.\begin{array}{ll} \dfrac{\partial \ln t'}{\partial N_i'} + \alpha' - \beta\epsilon_i' = 0 & \text{for all } i \\ \dfrac{\partial \ln t''}{\partial N_j''} + \alpha'' - \beta\epsilon_j'' = 0 & \text{for all } j \end{array}\right\} \text{These look the same as what we had before}$$

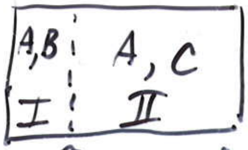
4. ∴ we will get the SAME form of distibution law for BOTH systems except

$$\begin{Bmatrix} \text{different everything} \\ \text{common } \beta \end{Bmatrix}$$

But we know that: Two systems in contact so they can exchange energy but otherwise are non-interacting can only have one thing in common: TEMPERATURE!

Therefore β must be a function of temperature alone.

α 1. Consider two systems, exchanging particles as well as energy



semi-permeable, can exchange energy and A particles.

2. $\sum N_{iA}^{I} + \sum N_{iA}^{II} = N_A$ L. multiplier α_A

$\sum N_{iB}^{I} = N_B \qquad \sum N_{iC}^{II} = N_C$

$\sum N_{iA}^{I} \epsilon_{iA}^{I} + \sum N_{iB}^{I} \epsilon_{iB}^{I} + \sum N_{iA}^{II} \epsilon_{iA}^{II} + \sum N_{iC}^{II} \epsilon_{iC}^{II} = E$

L. multiplier β

$\frac{\partial N_A}{\partial N_{iA}^{I}} = 1 \qquad \frac{\partial N_A}{\partial N_{iA}^{II}} = 1 \qquad \frac{\partial E}{\partial N_{iA}^{I}} = \epsilon_{iA}^{I}$ etc.

total number of configurations

$t = t_A^{I} t_A^{II} t_B^{I} t_C^{II}$ we end up with:

$$\frac{\partial \ln t_A^{I}}{\partial N_A^{I}} + \alpha_A - \beta \epsilon_{iA}^{I} = 0$$

$$\frac{\partial \ln t_A^{II}}{\partial N_A^{II}} + \alpha_A - \beta \epsilon_{iA}^{II} = 0$$

$$\frac{\partial \ln t_B^{I}}{\partial N_B^{I}} + \alpha_B - \beta \epsilon_{iB}^{I} = 0$$

$$\frac{\partial \ln t_C^{II}}{\partial N_C^{II}} + \alpha_C - \beta \epsilon_{iC}^{II} = 0$$

These are again the SAME FORM of distribution laws for each of A, B, C particles where
{different everything}
{common β
{common α_A }

But we know that two or more systems in contact so they can exchange energy and particles but otherwise non-interacting have one thing in common: CHEMICAL POTENTIAL

Therefore, α must be related to the chemical potential.

INTERPRETATION OF HEAT and WORK in molecular terms:

WORK done by a particle in the i^{th} quantum state, if parameter l is changed $= dw_i = -F_{il}\, dl$

FORCE $\quad F_{il} = -\left(\frac{\partial \epsilon_{il}}{\partial l}\right)$

F_l = total force for changing the parameter l $= \sum_i N_i F_{il}$

WORK done by a system on the surroundings if the change is carried out reversibly, is equal to

$$dW_{rev} = -F_l\, dl = -\sum_i N_i F_{il}\, dl$$

$$= -\sum_i N_i \underbrace{\left(\frac{-\partial \epsilon_{il}}{\partial l}\right) dl}_{-d\epsilon_i} = +\sum_i N_i\, d\epsilon_i$$

For an arbitrary small change imposed on the system:

$$dE = \sum_i N_i\, d\epsilon_i + \sum_i \epsilon_i\, dN_i$$

$\sum_i N_i\, d\epsilon_i$: change in energy levels by changing parameter l [associated with $+dW$] as seen above

$\sum_i \epsilon_i\, dN_i$: change in the distribution of particles among the energy levels is therefore associated with dQ_{rev}

since

$$dE = dQ + dW$$

The first law is assumed in pure mechanics.

Proof of $\beta = \frac{1}{kT}$

Evaluate β for a perfect gas using CB distribution:

$$\epsilon_{s_x s_y s_z} = \frac{h^2}{8m}\left(\frac{s_x^2}{X^2} + \frac{s_y^2}{Y^2} + \frac{s_z^2}{Z^2}\right)$$

quantum numbers s_x, s_y, s_z

X, Y, Z dimensions of box

$$q_{CB} = \sum_i g_i e^{-\beta \epsilon_i} = \sum_{s_x=1}^{\infty} \sum_{s_y=1}^{\infty} \sum_{s_z=1}^{\infty} e^{-\beta \epsilon_{s_x s_y s_z}}$$

(if allowing all possible values for $s_x\ s_y\ s_z$ $g_i = 1$)

$$= \sum_{s_x=1}^{\infty} \sum_{s_y=1}^{\infty} \sum_{s_z=1}^{\infty} e^{-\frac{\beta h^2}{8m}\frac{s_x^2}{X^2}} \cdot e^{-\frac{\beta h^2}{8m}\frac{s_y^2}{Y^2}} \cdot e^{-\frac{\beta h^2}{8m}\frac{s_z^2}{Z^2}}$$

$$= \left(\sum_{s_x=1}^{\infty} e^{-\frac{\beta h^2}{8m}\frac{s_x^2}{X^2}}\right) \cdot \left(\sum_{s_y=1}^{\infty} e^{-\frac{\beta h^2}{8m}\frac{s_y^2}{Y^2}}\right) \cdot \left(\sum_{s_z=1}^{\infty} e^{-\frac{\beta h^2}{8m}\frac{s_z^2}{Z^2}}\right)$$

The unrestricted sum over all s_x, s_y, s_z is the product of three separate sums.

→ $$q_{CB} = q_x \cdot q_y \cdot q_z$$

product of partition functions for the separate degrees of freedom!

For $\beta \frac{h^2}{8mX^2} << 1$ replace infinite discrete sum with an integral, start from zero for convenience.

$$q_x \approx \int_{s_x=0}^{\infty} e^{-\frac{\beta h^2}{8mX^2} s_x^2}\, ds_x = \left(\frac{2\pi m}{\beta h^2}\right)^{1/2} X$$

$$q_{CB} = \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} \underbrace{X \cdot Y \cdot Z}_{V} \longrightarrow$$

V volume

$$\ln q_{CB} = \frac{3}{2}\ln\frac{2\pi m}{\beta h^2} + \ln V = -\frac{3}{2}\ln\beta + \frac{3}{2}\ln\frac{2\pi m}{h^2} + \ln V$$

$$\frac{\partial \ln q_{CB}}{\partial \beta} = -\frac{3}{2}\frac{\partial \ln \beta}{\partial \beta} = -\frac{3}{2}\frac{1}{\beta}$$

$$\left(\frac{\partial \ln q_{CB}}{\partial \beta}\right)_V = -\frac{3}{2}\frac{1}{\beta}$$

$$\underbrace{E = -N\left(\frac{\partial \ln q_{CB}}{\partial \beta}\right)_V}_{\text{derived before}} = \frac{3}{2}\frac{N}{\beta}$$

Force in the x direction on the rectangular box is

$$F_X = \sum_i N_i \underbrace{F_{X_i}}_{\frac{-\partial \epsilon_i}{\partial X}} = \sum_i \left(\frac{N}{q} g_i e^{-\beta\epsilon_i}\right)\left(\frac{-\partial \epsilon_i}{\partial X}\right)$$

Since $q_{CB} = \sum_i g_i e^{-\beta\epsilon_i}$

$$\left(\frac{\partial q}{\partial X}\right)_{\beta, Y, Z} = \sum_i g_i e^{-\beta\epsilon_i} \cdot -\beta\frac{\partial \epsilon_i}{\partial X}$$

$$F_X = \frac{N}{q}\sum_i g_i e^{-\beta\epsilon_i} \cdot \frac{-\partial \epsilon_i}{\partial X} = \frac{N}{q} \cdot \frac{1}{\beta}\left(\frac{\partial q}{\partial X}\right)_{\beta, Y, Z} = \frac{N}{\beta}\left(\frac{\partial \ln q}{\partial X}\right)_{\beta, Y, Z}$$

but $\frac{\partial \ln q}{\partial X} = \frac{\partial \ln X}{\partial X}$

$= \frac{1}{X}$

from $\ln q_{CB} = \frac{3}{2}\ln\frac{2\pi m}{\beta h^2} + \ln X \cdot Y \cdot Z$

$\therefore F_X = \frac{N}{\beta}\frac{1}{X}$

Pressure = Force per unit area = $\frac{F_X}{YZ} = \frac{N}{\beta}\frac{1}{V}$

or $PV = \frac{N}{\beta}$ but $PV = NkT$ $\therefore \beta = 1/kT$

$\therefore E = \frac{3}{2}NkT$

Since this is the same dS that one can derive from Carnot cycles

$$\underset{\text{CLASSICAL THERMODYNAMICS}}{dS = \frac{dQ_{rev}}{T}}$$

then $S_{\text{STATISTICAL MECHANICS}}$ and $S_{\text{CLASSICAL THERMODYNAMICS}}$ can only differ by an additive constant for any one substance.

At ordinary temperatures there are a VERY LARGE NUMBER of levels accessible to the particles so that $S_{\text{STAT. MECH.}}$ is of the order of $\sim 10^{24} k$

At extremely low temperatures the particles will all be in the lowest single particle levels available to them (depending on whether they are fermions or bosons) and there may be only 1 or a very few configurations possible

$$\ln t \longrightarrow \underset{\text{or small}}{\text{zero}} \quad \text{at} \quad T \rightarrow 0 \text{ K}$$

Thus, at $\underline{T=0}$ $S_{\text{STAT. MECH.}} = 0$ only one configuration, $t = 1$

But the 3rd Law of THERMODYNAMICS says

$$S_{\text{THERMOD.}} = 0 \quad \text{at} \quad T = 0$$

Therefore the additive constant which relates $S_{\text{STATISTICAL MECHANICS}}$ with $S_{\text{THERMODYNAMICS}}$ is ZERO.

Let us now express all thermodynamic quantities in terms of q molecular partition function

$$q \equiv \sum_i g_i e^{-\beta\epsilon_i}$$

a function of T and V

CONSIDER A SYSTEM MADE UP OF <u>CORRECTED</u> <u>BOLTZONS</u>:

$$t_{CB} = \prod_i \frac{g_i^{N_i}}{N_i!}$$

$$\ln t_{CB} = \sum_i \left(N_i \ln \frac{g_i}{N_i} + N_i\right)$$

$$\frac{\partial \ln t_{CB}}{\partial N_i} + \alpha \frac{\partial N}{\partial N_i} - \beta \frac{\partial E}{\partial N_i} = 0$$

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

$$N_i = g_i e^{\alpha} e^{-\beta\epsilon_i}$$

$$\sum_i N_i = \sum_i g_i e^{\alpha} e^{-\beta\epsilon_i}$$

$$N = e^{\alpha} q \quad \text{or} \quad e^{\alpha} = \frac{N}{q}$$

$-\beta\epsilon_i$

$-\beta\epsilon_i$

$$E = \sum_i N_i \epsilon_i = \sum_i \left(\frac{N}{q} g_i e^{-\beta\epsilon_i}\right)\epsilon_i$$

$$q \equiv \sum_i g_i e^{-\beta\epsilon_i}$$

$$\left(\frac{\partial q}{\partial \beta}\right)_V = \sum_i g_i(-\epsilon_i)e^{-\beta\epsilon_i}$$

$$\left(\frac{\partial \ln q}{\partial \beta}\right)_V = \frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = \frac{-\sum_i g_i \epsilon_i e^{-\beta}}{q}$$

ϵ_i

$$E = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V$$

number of configurations corresponding to the most probable distribution

$$S_{\substack{FD\\BE}} = k \ln t_{\substack{FD\\BE}}$$

$$= k \sum_i \left[N_i \ln\left(\frac{g_i \mp N_i}{N_i}\right) \mp g_i \ln\left(\frac{g_i \mp N_i}{g_i}\right) \right]$$

INTERPRETATION of ENTROPY in molecular terms:

Define STATISTICAL MECHANICAL ENTROPY

$$S \equiv k \ln t$$

where t corresponds to the most probable distribution

For example, $S_{CB} = k \sum_i \left(N_i \ln \frac{g_i}{N_i} + N_i\right)$

for CORRECTED BOLTZONS

Consider an arbitrary reversible change in the system:

ϵ_i may change

E may change

but if reversible, the system remains in equilibrium during the change (i.e., it is always in the most probable distribution)

Since $t = t(N_1, N_2, N_3, \cdots)$ only a function of occupancy numbers

then $dS = k\, d(\ln t) = k \sum_i \frac{\partial(\ln t)}{\partial N_i} dN_i$

But $t_{\text{most probable}}$ already satisfies the equation

$$\frac{\partial(\ln t)}{\partial N_i} + \alpha - \beta\epsilon_i = 0 \quad \text{or}$$

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

$$\therefore \quad dS = k \sum_i (-\alpha + \beta\epsilon_i) dN_i$$

$$= -\alpha k \underbrace{\sum_i dN_i}_{\text{zero since sum of } N_i \text{ is constant} = N} + \beta k \sum_i \epsilon_i dN_i$$

$$= \beta k \underbrace{\sum_i \epsilon_i dN_i}_{dQ_{rev}}$$

NOW use $\beta = \frac{1}{kT}$

STATISTICAL MECHANICAL ENTROPY $dS = \frac{dQ_{rev}}{T}$

$$S \equiv k \ln t$$

$$= k\left\{ \sum_i \left(N_i \ln \frac{g_i}{N_i} + N_i \right) \right\}$$

$$N_i = g_i e^{\alpha} e^{-\beta\epsilon_i}$$

$$\frac{g_i}{N_i} = e^{-\alpha} e^{+\beta\epsilon_i}$$

$$= \frac{q}{N} e^{+\beta\epsilon_i}$$

$$\ln \frac{g_i}{N_i} = \ln\left(\frac{q}{N} e^{+\beta\epsilon_i} \right)$$

$$= k\left\{ \sum_i N_i \ln \frac{q}{N} + \sum_i N_i \beta\epsilon_i + \sum_i N_i \right\}$$

$$= k\left\{ \left(\ln \frac{q}{N}\right) \sum_i N_i + \beta \sum_i N_i \epsilon_i + \sum_i N_i \right\}$$

$$= k\left\{ \left(\ln \frac{q}{N}\right) \cdot N + \beta \cdot E + N \right\}$$

$$S = kN \ln \frac{q}{N} + \frac{E}{T} + kN$$

$$E - TS = ?$$

multiply above by T to get

$$TS = NkT \ln \frac{q}{N} + E + NkT$$

$$- NkT \ln \frac{q}{N} - NkT$$

$$A \equiv E - TS = - NkT \ln \frac{q}{N} - NkT$$

$$\mu \equiv \left(\frac{\partial A}{\partial N} \right)_{T,V} = -kT \ln \frac{q}{N} - NkT \underbrace{\frac{\partial \ln \frac{\boxed{q}}{N}}{\partial N}}_{-\frac{\partial \ln N}{\partial N} \text{ or } -\frac{1}{N}} - kT$$

q is not a function of N

$$= -kT \ln \frac{q}{N}$$

Recall $e^{\alpha} = \frac{N}{q}$ or $\alpha = \ln\frac{N}{q} = -\ln\frac{q}{N}$

$$\mu = -kT\ln\frac{q}{N} \quad \therefore \quad \boxed{\alpha = \frac{\mu}{kT}}$$

$$G \equiv N\mu$$

$$= -NkT\ln\frac{q}{N}$$

Summarizing, for a system of corrected boltzons

$$E = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V = \frac{N}{q}\sum_i g_i \epsilon_i e^{-\beta\epsilon_i}$$

$$S = kN\ln\left(\frac{q}{N}\right) + \frac{E}{T} + kN$$

$$A = E-TS = -NkT\ln\left(\frac{q}{N}\right) - NkT$$

$$G = -NkT\ln\left(\frac{q}{N}\right)$$

where $q \equiv \sum_i g_i e^{-\beta\epsilon_i}$

where ϵ_i are the energy levels of one molecule

g_i is the degeneracy of the ith level