Statistical Mechanics (4)

Def 4.1

Consider a gas inside a piston. Define dQ to be the thermal energy transferred from the surrounding to the system. …….(4.1.1)

Define dU, the change of internal energy of the gas to be

$$dU = dQ - PdV \qquad \text{…….(4.1.2)}$$

Define molar heat capacity of the gas at constant volume be

$$C_v = \frac{1}{\mu}\left(\frac{\partial Q}{\partial T}\right)_V \qquad \text{…….(4.1.3)}$$

where μ is the no. of mole of the gas. Define the molar heat capacity of the gas at constant pressure to be

$$C_P = \frac{1}{\mu}\left(\frac{\partial Q}{\partial T}\right)_P \qquad \text{…….(4.1.4)}$$

Define $\gamma = \dfrac{C_P}{C_V}$ …….(4.1.5)

Thm 4.2

Suppose a gas in a piston obey ideal gas law (i.e. $PV = \mu RT = NkT$) and that $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and that γ is a constant (independent of any variable), then it can be proven that if the gas undergo adiabatic process (i.e. $dQ=0$), then P, V must obey the following rule

$$PV^{\gamma} = \text{constant} \qquad \text{…….(4.2.1)}$$

Thm 4.3

It can be verified from experiment that for all kind of gas in piston,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \text{…….(4.3.1)}$$

This law is called the Joule's Law.

Def 4.4

If a gas is piston obey ideal gas law, it can be proven that

$$C_P - C_V = R \qquad \text{……….(4.4.1)}$$

Def 4.5

A process undergo by a gas in a piston is reversible iff

I. The process is very slow such that at each time in the process, the system is in equilibrium (settled down)
II. The work done by the system must equal to PdV (i.e. no energy dissipation due to friction, etc.)

Thm 4.6

Suppose function $f = f(x_1,..., x_n)$ is to be maximized under the constraint

$$\begin{cases} g_1(x_1,\ldots,x_n) = 0 \\ \quad\vdots \\ g_p(x_1,\ldots,x_n) = 0 \end{cases} \qquad \text{…….(4.6.1)}$$

Then the problem can be solved by solving the simultaneous equations:

$$\begin{cases} \dfrac{\partial f}{\partial x_j} + \lambda_1 \dfrac{\partial g_1}{\partial x_j} + \cdots + \lambda_p \dfrac{\partial g_p}{\partial x_j} = 0 \qquad \text{for } j = 1,\ldots,n \\ g_1(x_1,\ldots,x_n) = 0 \\ \quad\vdots \\ g_p(x_1,\ldots,x_n) = 0 \end{cases} \qquad \text{………..(4.6.2)}$$

which involve $n+p$ unknown: $x_1, \ldots, x_n; \lambda_1, \ldots, \lambda_p$ and $n+p$ equations.

Thm 4.7

If $\sum_i n_i$ identical distinguishable particle is to distribute along the energies, such that the no. of cell with energy ε_i is g_i and the no. of particle with energy ε_i is n_i, then the no. of way is given by

$$W(n_1,n_2,\ldots)=\frac{(N(n_1,n_2,\ldots))!}{n_1!n_2!\cdots}*g_1^{n_1}g_2^{n_2}\cdots \qquad \ldots\ldots(4.7.1)$$

where $N(n_1,n_2,\ldots)=\sum_i n_i$ …….(4.7.2)

Define the entropy $S(n_1,n_2,\ldots.) = k\ln W(n_1,n_2,\ldots)$ ……(4.7.3)

Let $n_i >> 1$ for all *i*, then using Stirling formula ($\ln n! = n\ln n - n \quad \text{for } n >> 1$), we can prove that

$$S(n_1,n_2,\ldots)=k[N(n_1,\ldots)\ln N(n_1,\ldots)-\sum_i n_i \ln n_i + \sum_i n_i \ln g_i] \qquad \ldots\ldots(4.7.4)$$

If *S* is to maximize under the constraint

$$g_1(n_1,n_2,\ldots)=\{\sum_i n_i\}-N_0 = 0$$
$$g_2(n_1,n_2,\ldots)=\{\sum_i n_i\}-E_0 = 0$$

……..(4.7.5) and (4.7.6)

then according to Thm 4.6,

$$\frac{1}{k}\frac{\partial S}{\partial n_j}-\alpha\frac{\partial g_1}{\partial n_j}-\beta\frac{\partial g_2}{\partial n_j}=0 \qquad \text{for } j=1,2,\ldots.. \qquad \ldots\ldots.(4.7.7)$$

which will lead to that

$$n_j = N_0 g_j e^{-\alpha}e^{-\beta\varepsilon_j} \qquad \text{for } j=1,2,\ldots.. \qquad \ldots\ldots(4.7.8)$$

Suppose after *S* is maximized under the two constraint (4.7.5), (4.7.6), suddenly the total internal energy is changed by *dU*. Let the change of no. of particle with energy ε_i is dn_i.

Since $U(n_1,n_2,\ldots)=\sum_i n_i\varepsilon_i$, then

$$dU=\sum_i \frac{\partial U}{\partial n_i}dn_i = \sum_i \varepsilon_i dn_i \qquad \ldots..(4.7.9)$$

From (4.7.7), we have

$$\frac{1}{k}\frac{\partial S}{\partial n_j}-\alpha-\beta\varepsilon_j=0 \qquad \text{for } j=1,2,\ldots.. \qquad \Rightarrow \sum_j(\frac{1}{k}\frac{\partial S}{\partial n_j}-\alpha-\beta\varepsilon_j)dn_j=0$$

Let the total no. of particle is not changed:

$$\Rightarrow \frac{1}{k} dS = \beta \sum_j \varepsilon_j dn_j = \beta dU = \beta dQ$$ (Assume no volume change)

By comparing with the formula $dS = \frac{dQ}{T}$, we have $\beta k = \frac{1}{T}$ or

$$\beta = \frac{1}{kT} \qquad \text{.........(4.7.10)}$$

<u>Thm 4.8</u>

If $\sum_i n_i$ identical indistinguishable particles is to distribute along the energies, such that the no. of cell with energy ε_i is g_i and the no. of particles with energy ε_i is n_i, then the no. of way is given by ......(4.8.0)

$$W(n_1, n_2, \ldots) = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \qquad \text{........(4.8.1)}$$

Let n_i>>1 for all I, and use Stirling formula, we can prove that

$$S(n_1, n_2, \ldots) = k \sum_i [(n_i + g_i - 1)\ln(n_i + g_i - 1) - n_i \ln n_i - (g_i - 1) - \ln(g_i - 1)!] \qquad \text{.....(4.8.2)}$$

If S is to maximize under the constraint $g_1(n_1, n_2, \ldots) = \{\sum_i n_i \varepsilon_i\} - E_o = 0$, then according to Thm 4.6

$$\frac{1}{k}\frac{\partial S}{\partial n_j} - \beta \frac{\partial g_1}{\partial n_j} = 0 \qquad \text{for } j=1,2,\ldots \qquad \text{......(4.8.3)}$$

which lead to $n_j = \frac{g_j - 1}{e^{\beta \varepsilon_j} - 1} \approx \frac{g_j}{e^{\beta \varepsilon_j} - 1}$ (if g_i>>1) ....(4.8.4)

<u>Thm 4.9</u>

Assume in a cubic box of side L, and set the periodic boundary condition to photon:

$$\mathbf{k} = \frac{2\pi}{L}(n_1\mathbf{e}_x + n_2\mathbf{e}_y + n_3\mathbf{e}_z) \quad \text{.......(4.9.1)}$$

Let $\rho^2 = n_1^2 + n_2^2 + n_3^2$ ....(4.9.2)

Then the no. of photon between ρ and $\rho+d\rho$ is $2(4\pi\rho^2)d\rho$ ....(4.9.3)

where the factor 2 comes from that photon have two direction of polarization. Substitute (4.9.1), (4.9.2) into (4.9.3), we have the no. of photon between ν and $\nu+d\nu$ (ν is frequency) is $2(4\pi(\frac{L}{c})^3\nu^2)d\nu$ ....(4.9.4)

and the total energy of photons between ν and $\nu+d\nu$ is therefore by substitution into (4.8.4):

$$dE = \frac{h\nu(2)4\pi(\frac{L}{c})^3\nu^2 d\nu}{e^{\frac{h\nu}{kT}} - 1}$$

and so energy volume density of photon between ν and $\nu+d\nu$

$$\frac{dE}{L^3} = \frac{8\pi h\nu^3 d\nu}{c^3(e^{\frac{h\nu}{kT}} - 1)} \quad \text{(Planck Radiation Formula)} \quad \text{.........(4.9.5)}$$

By special mathematics technique (Appendix A of "Statistical Physics", by F. Mandl), it can be evaluate that

$$\int_o^\infty \frac{1}{L^3}\frac{dE}{d\nu}d\nu = aT^4 \quad \text{.......(4.9.6)} \quad \left(a = \frac{\pi^2 k^4}{15\hbar^3 c^3} = 7.56\times 10^{-16}\right)$$

According to the corpuscle picture of photon, rate of energy passing through a certain area should be linearly related with the energy volume density, therefore, we can infer the wall of the box, which is a blackbody and have the same temperature with the photons radiates as

$$R \propto T^4 = e\sigma T^4 \quad \text{(Stefan-Boltzmann Law)} \quad \text{.......(4.9.7)}$$

where R is the energy per unit area per unit time, $\sigma = \frac{ac}{4}$ is the Stefan constant, e is the emissivity. For perfect reflector, $e=0$, and for blackbody, $e=1$.

<u>Thm 4.11</u>

If $\sum_i n_i$ identical indistinguishable particles is to distribute along the energies, such that the no. of cell with energy ε_i is g_i and the no. of particle with energy ε_i is n_i, and that every cell can only accommodate 1 particle, then the no. of way is given by …..(4.11.0)

$$W(n_1,n_2,...)=\prod_i \frac{g_i!}{n_i!(g_i-n_i)!} \qquad \text{……(4.11.1)}$$

Let gi is large enough, such that both g_i, n_i and g_i-n_i are large enough to apply the Stirling formula

$$\begin{cases} \ln g_i! \approx g_i \ln g_i - g_i \\ \ln n_i! \approx n_i \ln n_i - n_i \\ \ln(g_i-n_i)! \approx (g_i-n_i)\ln(g_i-n_i)-(g_i-n_i) \end{cases} \qquad \text{…….(4.11.2)}$$

Then the entropy can be given by

$$S(n_1,....)=k\sum_i [g_i \ln g_i - g_i - n_i \ln n_i + n_i - (g_i-n_i)\ln(g_i-n_i)+(g_i-n_i)] \qquad \text{….(4.11.3}$$

)

If S is to maximize under the constraint

$$g_1(n_1,n_2,...)=\{\sum_i n_i\}-N_0 = 0$$
$$g_2(n_1,n_2,...)=\{\sum_i n_i\}-E_0 = 0 \qquad \text{……..(4.11.4) and (4.11.5)}$$

Then according to Thm 4.6,

$$\frac{1}{k}\frac{\partial S}{\partial n_j}-\alpha\frac{\partial g_1}{\partial n_j}-\beta\frac{\partial g_2}{\partial n_j}=0 \qquad \text{for } j=1,2,..... \qquad \text{…….(4.11.6)}$$

which will lead to that

$$n_j = \frac{g_j}{e^{\alpha}e^{\beta\varepsilon_i}+1} \qquad \text{…….(4.11.7)}$$

Thm 4.12

Since $\lambda \nu = c \Rightarrow \nu = c/\lambda \Rightarrow d\nu = -\frac{c}{\lambda^2} d\lambda$. So from (4.9.5), we have

$$\frac{dE}{L^3} = \frac{8\pi h(\frac{c^3}{\lambda^3})\frac{c}{\lambda^2}d\lambda}{c^3(e^{hc/\lambda kT}-1)} = \frac{8\pi hc d\lambda}{\lambda^5(e^{hc/\lambda kT}-1)} \qquad \text{…….(4.12.1)}$$

So the energy volume density of photon between ($\lambda,\lambda+d\lambda$) is given by (4.12.1). To find the value of λ where $\frac{1}{L^3}\frac{dE}{d\lambda}$ is maximum, we have

$$\frac{d}{d\lambda}(\frac{1}{L^3}\frac{dE}{d\lambda}) = 0 \qquad \text{……(4.12.2)}$$

From (4.12.2), we have λ_{max}, the value of λ where $\frac{1}{L^3}\frac{dE}{d\lambda}$ is maximum is given by

$$\lambda_{\max}T = 2.898\times10^{-3} \qquad \text{(Wien's displacement Law)} \qquad \text{……(4.12.3)}$$

<u>Thm 4.13</u>

When $\frac{1}{L^3}\frac{dE}{d\lambda}$ in (4.9.5) is plotted against ν, we have

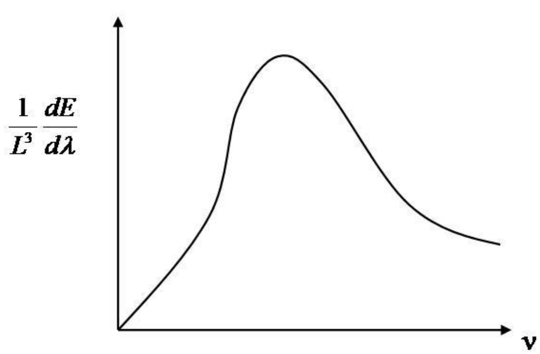


Figure 4.13.1

<u>Thm 4.14</u>

From formula (4.7.3), we know that $S = S(n_1, n_2, ...)$. If for every moment, *S* is to be maximized under the constraint (4.7.5) & (4.7.6), we have in (4.7.8) $n_i = n_i(N, E)$, where *N*, *E* is the total no. of particle and total energy respectively. Then $S = S(n_1(N,E), n_2(N,E), ...)$. Define the chemical potential

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_E \qquad \text{……(4.14.1)}$$

From (4.7.7), we have

$$\frac{1}{k}\frac{\partial S}{\partial n_i}(N,E) - \alpha - \beta\varepsilon_i = 0$$
$$\Rightarrow \frac{1}{k}\sum_i \frac{\partial S}{\partial n_i}(N,E)\frac{\partial n_i}{\partial N} = \sum_i (\alpha + \beta\varepsilon_i)\frac{\partial n_i}{\partial N}$$
$$\text{L.H.S.} = \frac{\partial S}{\partial N}$$

Consider the functions $f_1(N,E) = \sum_i n_i(N,E) = N \Rightarrow \frac{\partial f_i}{\partial N} = \sum_i \frac{\partial n_i}{\partial N} = 1$.

$$f_2(N,E) = \sum_i n_i(N,E)\varepsilon_i = E \Rightarrow \frac{\partial f_i}{\partial E} = 0$$
$$\therefore \text{R.H.S.} = \alpha$$

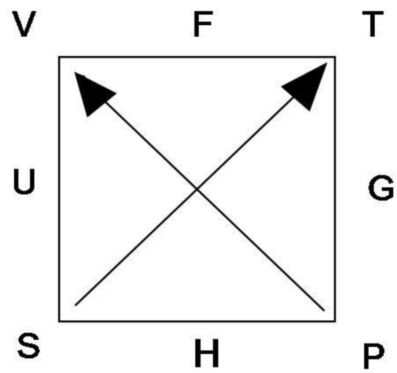
$$\Rightarrow \alpha = \frac{1}{k}\frac{\partial S}{\partial N} = -\frac{\mu}{kT} \qquad \text{……..(4.14.2)}$$

Thm 4.15

Suppose two variables out of four variables: *T*, *V*, *S*, *P* are independent variables. Suppose, there exist a *U*, such that *U* can be written as the function of any two independent variables out of *T*, *V*, *S*, *P* and that if we take *S*, *V* as the two independent variable, we will have

$$dU = TdS - PdV \qquad \text{…….(4.15.1)}$$

Then we can prove the “Maxwell relations”:



$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \text{.....(4.15.2a)} \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{........(4.15.2b)}$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \qquad \text{……(4.15.2c)} \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \text{.....(4.15.2d)}$$

Proof:

Firstly, define the function H (enthalpy), F (Helmhotz's free energy) and G (Gibb's free energy) by

$H=U+PV$ ……(4.15.3)
$F=U-TS$ ……(4.15.4)
$G=U-TS+PV$ ……(4.15.5)

Then take the total differentiation dH, dF and dG, and make use of (4.15.1), we will get

$dH=TdS+VdP$ …..(4.15.6a)
$dF=-SdT-PdV$ ……(4.15.6b)
$dG=-SdT+VdP$ ……(4.15.6c)

Let us repeat (4.15.1) here

$dU=TdS-PdV$ ……(4.15.6d)

Then from (4.15.6a) to (4.15.6d), we will be able to prove the Maxwell's relations (4.15.2a) to (4.15.2d) easily.

Thm 4.16

Suppose $\sum_i n_i$ identical distinguishable particle is to distribute along a series of cells, such that the *i*th cell has n_i particles. Suppose a particle in the *i*th cell will possess a energy ε_i, then the no. of way is given by

$$W(n_1, n_2, \ldots) = \frac{(N(n_1, n_2, \ldots))!}{n_1! n_2! \cdots} \qquad \ldots\ldots(4.16.1)$$

where $N(n_1, n_2, \ldots) = \sum_i n_i$ ....(4.16.2)

Define the entropy $S(n_1, n_2, \ldots.) = k \ln W(n_1, n_2, \ldots)$ ......(4.16.3)

Let $n_i >> 1$ for all *i*, then using Stirling formula ($\ln n! = n \ln n - n \quad$ for $n >> 1$), we can prove that

$$S(n_1, n_2, \ldots) = k[N(n_1, \ldots) \ln N(n_1, \ldots) - \sum_i n_i \ln n_i] \qquad \ldots\ldots(4.16.4)$$

If S is to maximize under the constraint

$$g_1(n_1, n_2, \ldots) = \{\sum_i n_i\} - N_0 = 0$$
$$g_2(n_1, n_2, \ldots) = \{\sum_i n_i\} - E_0 = 0 \qquad \ldots\ldots..(4.16.5) \text{ and } (4.16.6)$$

then according to Thm 4.6,

$$\frac{1}{k}\frac{\partial S}{\partial n_j} - \alpha \frac{\partial g_1}{\partial n_j} - \beta \frac{\partial g_2}{\partial n_j} = 0 \qquad \text{for } j=1,2,\ldots.. \qquad \ldots\ldots.(4.16.7)$$

which will lead to that

$$n_j = N_0 e^{-\alpha} e^{-\beta \varepsilon_j} \qquad \text{for } j=1,2,\ldots.. \qquad \ldots\ldots(4.7.8)$$

<u>Thm 4.17</u>

From (4.15.4), we have $F=U-TS$. Let us assume every thing in Thm 4.16 still valid. Then

$$
\begin{aligned}
F &= \sum_i n_i\varepsilon_i - Tk[N\ln N - \sum_i n_i \ln n_i] \\
&= \sum_i n_i\varepsilon_i - Tk[N\ln N - \sum_i n_i \ln(Ne^{-\alpha}e^{-\beta\varepsilon_i})] \\
&= \sum_i n_i\varepsilon_i - Tk[N\ln N - \sum_i n_i (\ln N - \alpha - \beta\varepsilon_i)] \\
&= \sum_i n_i\varepsilon_i - Tk[N\ln N - N\ln N + N\alpha + \beta\sum_i n_i\varepsilon_i] \\
&= -TkN\alpha
\end{aligned}
$$

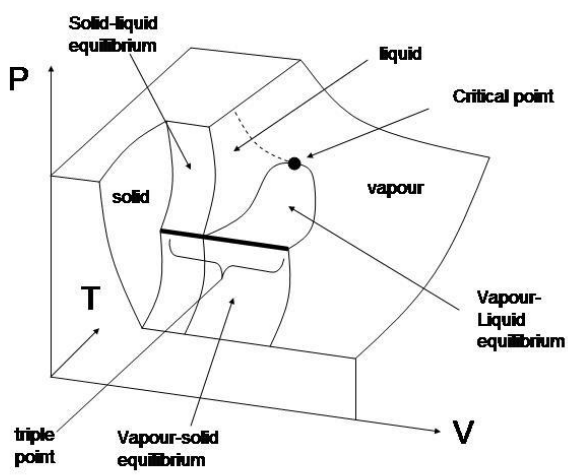
As $\sum_i Ne^{-\alpha}e^{-\beta\varepsilon_i} = N \Rightarrow e^{-\alpha}(\sum_i e^{-\beta\varepsilon_i}) = 1$. Define the partition function

$$Z = \sum_i e^{-\beta\varepsilon_i} \qquad \text{……(4.17.1)}$$

$$\Rightarrow e^{\alpha} = Z \Rightarrow \alpha = \ln Z$$
$$\Rightarrow F = -TkN\ln Z \qquad \text{……(4.17.2)}$$

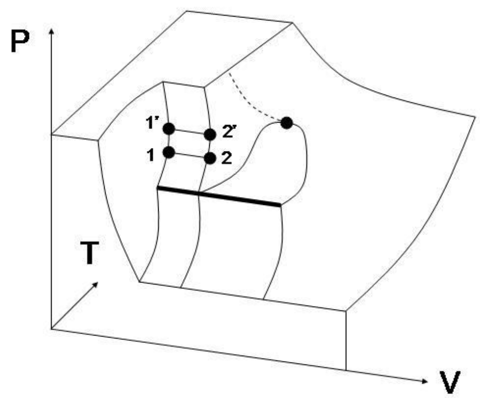
<u>Thm 4.18</u>

A typical *PVT* system



Critical point $(\frac{\partial P}{\partial V})_T = (\frac{\partial}{\partial V}(\frac{\partial P}{\partial V})_T)_T = 0$

<u>Thm 4.19</u>



Let G_1, G_2 be the Gibb's free energy at point 1 & 2 respectively. When the system moves along the dashes line from 1 to 2, P & T keep constant. So the change in Gibb's energy from (4.15.5) is

$$dG=dU-TdS+PdV$$
$$=dQ-TdS \qquad \text{.......(4.19.0a)}$$

$\therefore G_1 = G_2$. Similariy $G_{1'} = G_{2'} \Rightarrow G_{1'} - G_1 = G_{2'} - G_2$ ....(4.19.0b)

From (4.15.6c),

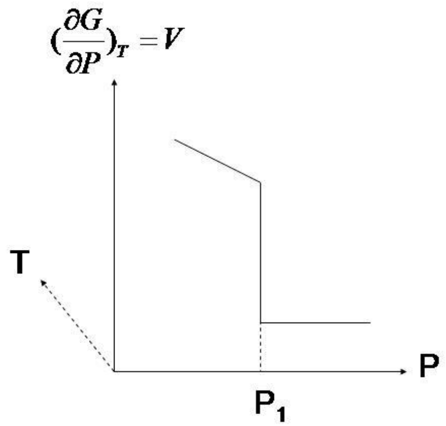
$$G_{1'} - G_1 = -S_1(T_{1'} - T_1) + V_1(P_{1'} - P_1) \qquad \text{......(4.19.0c)}$$
$$G_{2'} - G_2 = -S_2(T_{2'} - T_2) + V_2(P_{2'} - P_2) \qquad \text{.......(4.19.0d)}$$

Where S_1, V_1, S_2, V_2 are entropy and volume at point 1 & 2 respectively.

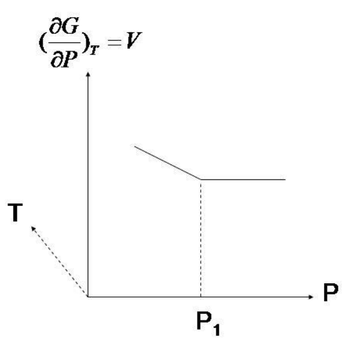
$$\Rightarrow -S_1 dT + V_1 dP = -S_2 dT + V_2 dP$$
$$\Rightarrow (V_2 - V_1) dP = (S_2 - S_1) dT$$
$$\Rightarrow \frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} \qquad \text{(Clausius-Clapeyron Equation)} \qquad \text{.......(4.19.1)}$$

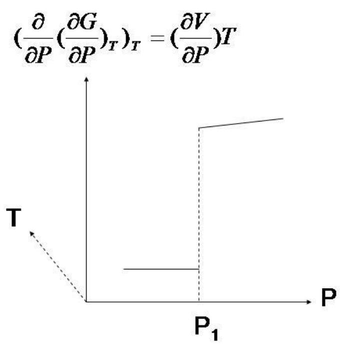
<u>Thm 4.20</u>

In Thm 4.19, $(\frac{\partial G}{\partial P})_T = V$ is discontinuous at a pressure (namely P_1):



Suppose now $(\frac{\partial G}{\partial P})_T = V$ is continuous at P_1, but $(\frac{\partial}{\partial P}(\frac{\partial G}{\partial P})_T)_T = (\frac{\partial V}{\partial P})T$ is discontinuous at P_1, i.e.





Then

$$\lim_{P\to P_1^-} d(V) = \lim_{P\to P_1^-}(\frac{\partial V}{\partial T})_P dT + \lim_{P\to P_1^-}(\frac{\partial V}{\partial P})_T dP \qquad \text{……(4.20.0a)}$$

$$\lim_{P\to P_1^+} d(V) = \lim_{P\to P_1^+}(\frac{\partial V}{\partial T})_P dT + \lim_{P\to P_1^+}(\frac{\partial V}{\partial P})_T dP \qquad \text{……(4.20.0b)}$$

As $\lim_{P\to P_1^-} d(V) = \lim_{P\to P_1^+} d(V)$, we have

$$(\lim_{P\to P_1^-}(\frac{\partial V}{\partial T})_P - \lim_{P\to P_1^+}(\frac{\partial V}{\partial T})_P)dT = (\lim_{P\to P_1^-}(\frac{\partial V}{\partial P})_T - \lim_{P\to P_1^+}(\frac{\partial V}{\partial P})_T)dP$$

$$\frac{dP}{dT}=-\frac{\lim\limits_{P\to P_1^-}(\frac{\partial V}{\partial T})_P-\lim\limits_{P\to P_1^+}(\frac{\partial V}{\partial T})_P}{\lim\limits_{P\to P_1^-}(\frac{\partial V}{\partial P})_T-\lim\limits_{P\to P_1^+}(\frac{\partial V}{\partial P})_T} \qquad \ldots\ldots(4.20.1)$$

Suppose $(\frac{\partial G}{\partial T})_P=-S$ is continuous at T_1 but $(\frac{\partial}{\partial T}(\frac{\partial G}{\partial T})_P)_P=-(\frac{\partial S}{\partial T})_P$ is discontinuous at T_1, then similar to the above argument,

$$\frac{dP}{dT}=\frac{\lim\limits_{T\to T_1^-}(\frac{\partial S}{\partial T})_P-\lim\limits_{T\to T_1^+}(\frac{\partial S}{\partial T})_P}{\lim\limits_{T\to T_1^-}(\frac{\partial V}{\partial T})_P-\lim\limits_{T\to T_1^+}(\frac{\partial V}{\partial T})_P} \qquad \ldots\ldots(4.20.2)$$

<u>Thm 4.21</u>

Consider the W given in (4.8.1). Suppose for all i, $g_i >> n_i$, then

$$W=\prod_i\frac{(g_i+n_i-1)(g_i+n_i-2)\cdots(g_i)}{n_i!}\approx\prod_i\frac{(g_i)^{n_i}}{n_i!} \qquad \ldots\ldots(4.21.1)$$

Consider the W given in (4.11.1). Suppose for all i, $g_i >> n_i$, then

$$W=\prod_i\frac{(g_i)!(g_i-1)!\cdots(g_i-n_i+1)!}{n_i!}\approx\prod_i\frac{(g_i)^{n_i}}{n_i!} \qquad \ldots\ldots(4.21.2)$$

$\therefore$ For Bose-Einstein & Fermi-Dirac System, if $g_i >> n_i$ for all i , …..(4.21.3) we can use treatment similar to the Maxwell Boltzmann System as in Thm. 4.7.

<u>Thm 4.22</u>

Assume we are talking about the system described in Thm 4.16,

$$-\frac{\partial}{\partial\beta}\ln Z=-\frac{1}{Z}\frac{\partial Z}{\partial\beta}=-\frac{1}{Z}\frac{\partial}{\partial\beta}(\sum_i e^{-\beta\varepsilon_i}) \quad \text{(From (4.17.1))} \quad =-\frac{1}{Z}\sum_i-\varepsilon_i e^{-\beta\varepsilon_i}=\frac{1}{Z}\sum_i\varepsilon_i e^{-\beta\varepsilon_i}$$

By definition $U=\sum_i n_i\varepsilon_i=\sum_i Ne^{-\alpha}e^{-\beta\varepsilon_i}\varepsilon_i$. Also, $\sum_i Ne^{-\alpha}e^{-\beta\varepsilon_i}=N$

$$\Rightarrow e^{-\alpha}Z=1\Rightarrow U=N\frac{1}{Z}\sum_i e^{-\beta\varepsilon_i}\varepsilon_i=-N\frac{\partial}{\partial\beta}\ln Z \qquad \ldots\ldots(4.22.1)$$

<u>Thm 4.23</u>

Assume we are still talking about the system described in Thm 4.16. Suppose each cell is formed by a point in the phase space $\bigotimes_{i=1}^{n_{ph}}\{\xi_i : \xi_i \in \Re\}$ such that the cell at $\{\xi_i\}_{i=1}^{n_{ph}}$ possess an energy

$$\varepsilon = \sum_{i=1}^{n_{ph}} A_i \xi_i^2 \qquad \text{……(4.23.1)}$$

Then the partition function will be given by (4.17.1)

$$Z = \sum_j e^{-\beta(\sum_{i=1}^{n_{ph}} A_i \xi_{i,j}^2)}$$

Let in the phase space $\bigotimes_{i=1}^{n_{ph}}\{\xi_{i,1} : \xi_{i,1} \in (\xi_i, \xi_i + \Delta\xi_i)\}$, the no. of state is given by $g(\xi_1,\ldots,\xi_{n_{ph}})\Delta\xi_1 \cdots \Delta\xi_{n_{ph}}$, then

$$Z = \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} e^{-\beta(\sum_{i=1}^{n_{ph}} A_i \xi_i^2)} g(\xi_1,\ldots,\xi_{n_{ph}}) d\xi_1 \cdots d\xi_{n_{ph}}$$

Suppose $g(\xi_1,\ldots,\xi_{n_{ph}})$ is a constant, independent of $\xi_1,\ldots,\xi_{n_{ph}}$, then

$$Z = g\prod_{i=1}^{n_{ph}} \int_{-\infty}^{+\infty} e^{-\beta A_i \xi_i^2} d\xi_i = g\prod_{i=1}^{n_{ph}} \left(\frac{\pi}{\beta A_i}\right)^{1/2} = g\beta^{-n_{ph}/2} \prod_{i=1}^{n_{ph}} \left(\frac{\pi}{A_i}\right)^{1/2}$$

$$\Rightarrow \frac{\partial Z}{\partial \beta} = -\frac{n_{ph}}{2}\frac{1}{\beta} Z$$

From (4.22.1),

$$U = -N\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{N}{Z}\left(-\frac{n_{ph}}{2\beta}\right)Z = \frac{1}{2} N n_{ph} kT \qquad \text{……(4.23.2)}$$