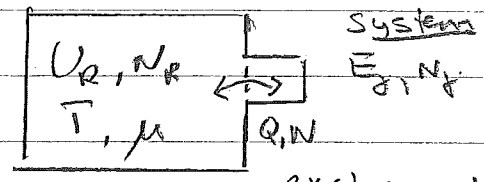
Phys 301 Fall 2019

Lecture #9 Gibbs Factor



total U, N fixed

$U = U_R + E_j$

$N = N_R + N_j$

$$\tilde{P}_j = \text{Const}' \, \Omega_R(U - E_j, N - N_j)$$

reservoir multiplicity

expand as before

$$\ln(\Omega_R) = \frac{1}{k} S_R(U - E_j, N - N_j)$$

$$= S(U,N) + \left(\frac{\partial S}{\partial U}\right)_{V,N}(-E_j) + \left(\frac{\partial S}{\partial N}\right)_{U,V}(-N_j)$$

$$= S(U,N) - \frac{1}{T}(E_j - \mu N_j)$$

giving

$$\tilde{P}_j = \text{Const}' \exp\left[-\beta(E_j - \mu N_j)\right]$$

Grand partition function

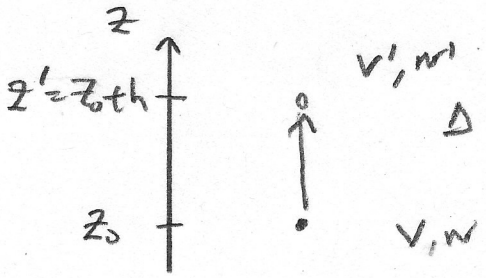
$$\boxed{Z = \sum_j e^{-\beta(E_j - \mu N_j)}}$$

generalize to multiple molecular species e.g.

$\mu_A N_j^A + \mu_B N_j^B$

Chemical Potential (refer to Bairlein)

① law of atmosphere



$\Delta PE = mgh$ energy required to move molecule $z_0 \to z' = z_0 + h$

$$\frac{\tilde{p}'}{\tilde{p}} = e^{-mgh/kT}$$ Boltzmann factor

$$Z = \left(\frac{V}{\ell_Q^3}\right)^N \frac{1}{N!} \qquad Z' = \left(\frac{V'}{\ell_Q^3}\right)^{N'} \frac{1}{N'!} \left(e^{-\frac{mgh}{kT}}\right)^{N'}$$

$$F = -kT \ln Z = -kTN \ln\left(\frac{V}{\ell_Q^3}\right) + kT \ln N!$$

$$\mu = \frac{\partial F}{\partial N} = -kT \ln\left(\frac{V}{\ell_Q^3}\right) + kT \underbrace{\frac{d}{dN} \ln N!}_{\frac{d}{dN}(N \ln N - N) = \ln N}$$

$$= -kT \ln\left(\frac{V}{N\ell_Q^3}\right)$$

similarly,

$$F' = -kTN' \ln\left(\frac{V}{\ell_Q^3}\right) + kT \ln N'! + kTN'\left(\frac{mgh}{kT}\right)$$

$$\mu' = \frac{\partial F'}{\partial N'} = -kT \ln\left(\frac{V'}{N'} \frac{1}{\ell_Q^3}\right) + kT\left(\frac{mgh}{kT}\right)$$

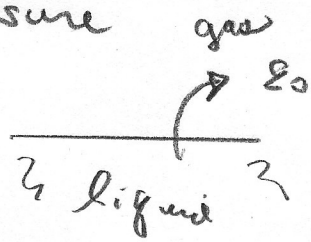
$\mu' = \mu$ in equilibrium,

$$\ln\left(\frac{V'/N'}{V/N}\right) = +\frac{mgh}{kT}$$

ideal gas law $\frac{V}{N} = \frac{kT}{p}$, $\frac{V'}{N'} = \frac{kT}{p'}$

$$\frac{p'}{p} = e^{-mgh/kT}$$

② Vapor pressure



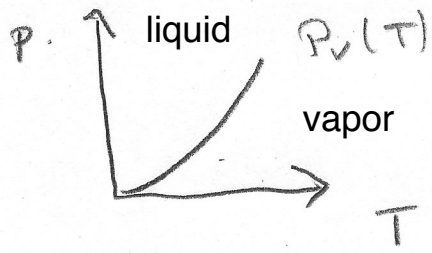
energy needed to move molecule out of liquid

in liquid, $\frac{V}{N} = v_0$ volume of molecule

in gas, $\frac{V'}{N'} = \frac{kT}{p'}$ p' pressure of gas

identical argument gives $\mu_{liquid} = \mu_{gas}$ along vapor pressure curve

$$\frac{\ln\left(\frac{V'}{N'}\right)}{\ln\left(V/N\right)} = \frac{\varepsilon_0}{kT}$$



along vapor pressure curve, chemical potentials are equal

$$\left(\frac{P_v}{kT/V_0}\right) = e^{-\varepsilon_0/kT}$$

$$P_v(T) = \left(\frac{kT}{V_0}\right) e^{-\varepsilon_0/kT}$$

Compare to

$$P_v(T) = \left(\frac{P_0}{e^{L/kT_0}}\right) e^{-L/NkT}$$

We can interpret specific heat of fusion per molecule $\frac{L}{N} = \varepsilon_0$

Example: Co poisoning

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

$\ln Z = N\left[\ln V - \ln N - \ln V_Q + 1\right]$ ideal gas

$Z_{int} = 1$

$\frac{\partial}{\partial N} \ln Z = [\;] - 1 = \ln\left(\frac{V}{N V_Q}\right)$

and E.O.S., $\frac{V}{N} = \left(\frac{kT}{p}\right)$ where p is partial pressure $= 0.2$ atm

$4\,Fe^{2+}$ binding sites on hemoglobin.

Each site has 3 states:

state	energy (eV)	
empty	0	
O_2 bound	-0.7	$\equiv \varepsilon$
CO bound	-0.85	$\equiv \varepsilon'$ more tightly bound

$$Z = 1 + e^{-\beta(\varepsilon-\mu)} + e^{-\beta(\varepsilon'-\mu')}$$

Chemical potential for O_2 we are told

$\mu = -0.6$eV $\qquad \varepsilon - \mu = -0.7 + 0.6 = -0.1$eV

at body temp. $T = 310$ K,

$$e^{-\beta(\varepsilon-\mu)} \simeq 42$$

$$\tilde{P}_{O_2} = \frac{42}{Z}$$

Chemical potential for O_2 @37°C (310K)

See (P) 6.48.

$$\mu = -kT \ln\left(\frac{V}{N V_Q} Z_{int}\right)$$

$$l_Q = \sqrt{\frac{2\delta}{m}}\, l_Q^{N_2} = \sqrt{\frac{28}{32}}\, 0.019\ nm = 0.0178\ nm$$

$P = 0.2$ atm partial pressure

$$\frac{kT}{P} = \frac{(1.38\times10^{-23}\ \frac{Nm}{K})(310K)}{0.2\times10^{5}\ \frac{N}{m^2}} = 2.14\times10^{-25}\ m^3$$

$$Z_{int} = \frac{kT}{2\varepsilon} \qquad \varepsilon = 1.8\times10^{-4} \text{ (from book)}$$

sym. factor

$$Z_{int} = \frac{(8.6\times10^{-5}\ \frac{eV}{K})(310)}{(2)(1.8\times10^{-4})} = 74$$

$$\ln\left(\frac{V}{N}\frac{Z_{int}}{V_Q}\right) = \ln\left(\frac{2.14\times10^{-25}}{(1.78\times10^{-11})^3}\, 74\right) = 21.8$$

$$\mu = -(8.6\times10^{-5})\ \frac{eV}{K}(310K)\, 21.8 = -0.57$$

Schroeder says $\mu \approx -0.6$

Chemical potential depends on partial pressure as $\mu = -kT \ln\left(\frac{kT}{p}\right) = kT \ln\left(\frac{p}{kT}\right)$

factor $e^{\beta\mu} = \frac{p}{kT}$

so for C.O. at 1% of O_2,

$$\frac{\tilde{P}_{CO}}{\tilde{P}_{O_2}} = \left(\frac{1}{100}\right) \frac{e^{-\beta\varepsilon'}}{e^{-\beta\varepsilon}} = \frac{1}{100} e^{-\beta(\varepsilon'-\varepsilon)}$$

ratio of partial pressures

$$= \frac{1}{100} e^{\beta(0.15)} = 2.75$$

then $\tilde{P}_{CO} = \frac{1}{z}(42)(2.75) = \frac{116}{z}$

w/o any CO, O_2 saturation is

$$\frac{42}{1+42} = \underline{\underline{98\%}}$$

with CO at partial pressure of 1% (O_2)

$$\frac{42}{1+42+116} = \underline{\underline{27\%}}$$

interesting aside O_2 blood monitor measures fraction of hemoglobin binding sites occupied so cannot measure CO poisoning.

Quantum Statistics:

Bosons (integer spin) No Pauli Exclusion

Fermions ($\frac{1}{2}$ integer spin) Pauli-exclusion

Pauli exclusion – maximum of 1 fermion in a quantum state.

$$\tilde{P}(n) = \frac{1}{Z} e^{-n(\varepsilon-\mu)\beta}$$

Fermions: $Z = 1 + e^{-(\varepsilon-\mu)\beta}$

Bosons: $Z = 1 + y + y^2 + \cdots$ where $y = e^{-(\varepsilon-\mu)\beta}$

$$= \frac{1}{1-y} = \frac{1}{1-e^{-(\varepsilon-\mu)\beta}}$$

<u>Distribution Functions</u> Average number of particles in state of energy ε.

Fermions (Fermi-Dirac)

$$\bar{n}_{FD} = \sum n\tilde{P}(n) = 0\,\tilde{P}(0) + 1\,\tilde{P}(1) = \frac{e^{-(\varepsilon-\mu)\beta}}{1+e^{-(\varepsilon-\mu)\beta}}$$

$$= \frac{1}{e^{(\varepsilon-\mu)\beta}+1}$$

Bose Einstein

$$\bar{n}_{BE} = \sum n \tilde{P}_n = \frac{1}{Z}\sum_{n=0}^{\infty} n\, e^{-n(\varepsilon-\mu)\beta}$$

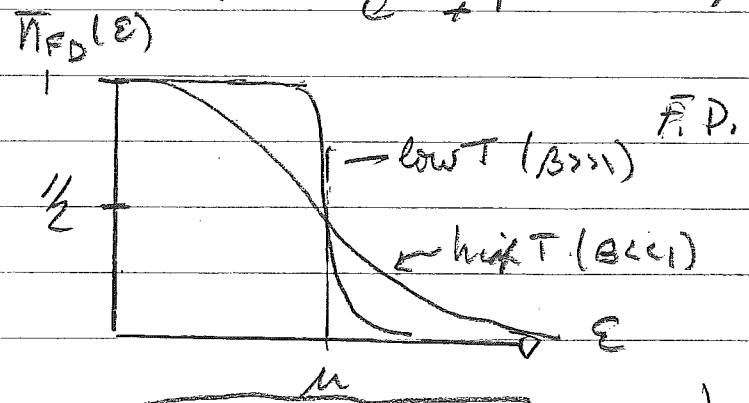
$$= -\frac{1}{Z}\frac{\partial Z}{\partial x} \quad \text{where } x \equiv (\varepsilon-\mu)\beta$$

$$Z = \frac{1}{1-e^{-x}} \qquad \frac{\partial Z}{\partial x} = \frac{(-1)e^{-x}}{(1-e^{-x})^2}$$

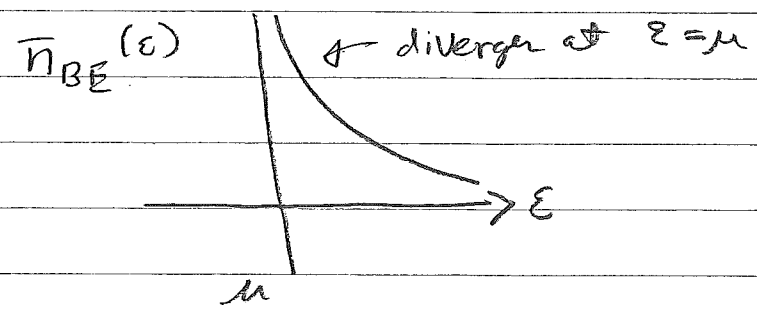
$$\bar{n}_{BE} = \frac{e^{-x}}{1-e^{-x}} = \frac{1}{e^{x}-1} = \frac{1}{e^{\beta(\varepsilon-\mu)}-1}$$

We see that they are both

$$\bar{n} = \frac{1}{e^{x} \mp 1} \quad \begin{matrix} - \text{ for B.E.} \\ + \text{ for F.D.} \end{matrix}$$



$$\boxed{\bar{n}_{FD}(\mu) = \tfrac{1}{2}} = \frac{1}{e^{0}+1}$$



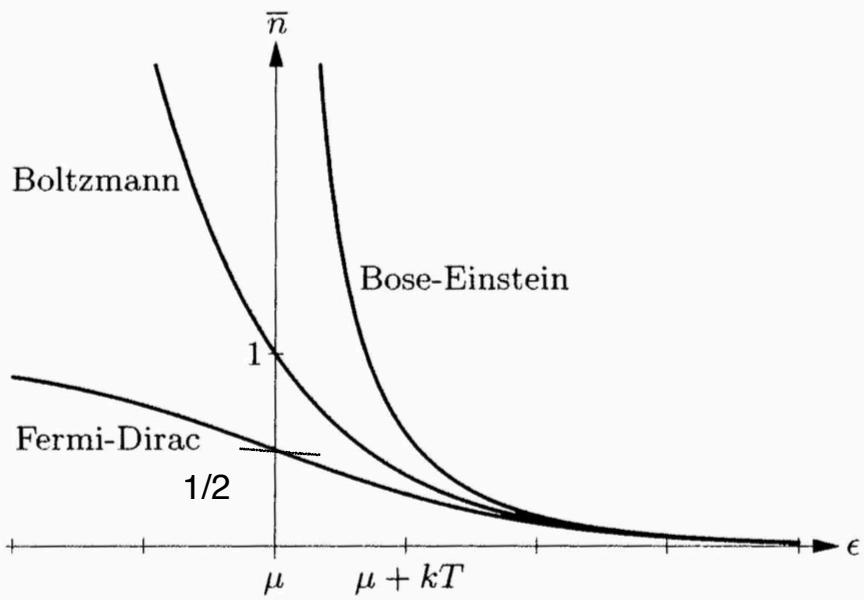


Figure 7.7. Comparison of the Fermi-Dirac, Bose-Einstein, and Boltzmann distributions, all for the same value of μ. When $(\epsilon - \mu)/kT \gg 1$, the three distributions become equal.

In limit $x = (\varepsilon - \mu)\beta \gg 1$

Both distributions become equal to the Boltzmann distribution,

$$\bar{n}_{Boltz} = e^{-x} = e^{-(\varepsilon-\mu)\beta}$$

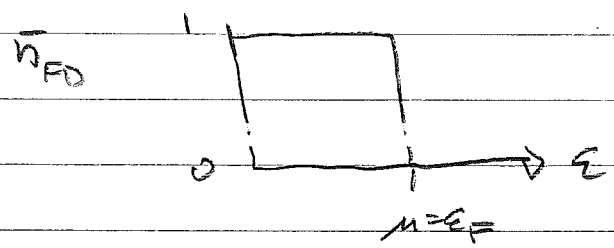
Degenerate Fermi Gas

for room temp electrons, $l_Q = 4.3\,nm$

In a metal with ~ 1 conducting electron per atom,

$$\frac{V}{N} \sim (0.2\,nm)^3 \ll l_Q^3$$ Need Quantum statistics

At $T=0$, all states are occupied up to Fermi energy



keep in mind that μ(T) so μ(0) = ε_F

Review of Density of States

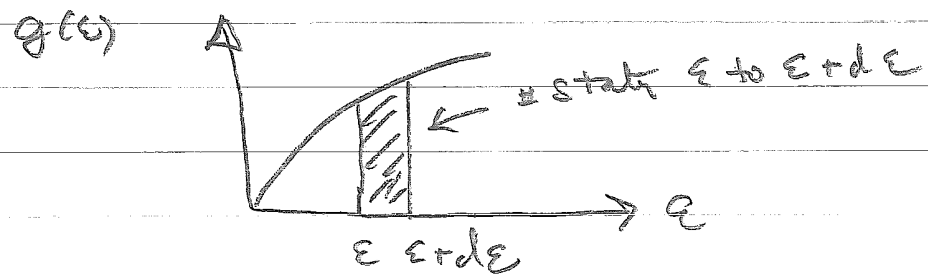
phase space quantized as $\left(\frac{d^3\vec{r}\, d^3p}{h^3}\right)$

$\boxed{\varepsilon = p^2/2m}$ $\quad \frac{d\varepsilon}{dp} = p/m$

$$p^2 dp = \sqrt{2m\varepsilon}\, m\, d\varepsilon$$

$$g(\varepsilon)\, d\varepsilon = \frac{V}{h^3}(2j+1)\, 4\pi p^2 dp$$

$$= (2j+1)\frac{V}{h^3}\frac{\pi}{4}(8m)^{3/2}\sqrt{\varepsilon}\, d\varepsilon$$



Example 1 Single molecule translational partition function –

$$Z^{(1)}_{tr} = \frac{V}{h^3}\int d^3p\, e^{-\beta p^2/2m} = \frac{V}{\ell_Q^3} \qquad \ell_Q = \left(\frac{h^2\beta}{2\pi m}\right)^{1/2}$$

giving $\quad Z_{IG} = \frac{1}{N!}\left(\frac{V}{\ell_Q^3} Z_{int}\right)^N$

IG ideal gas

$$Z_{int} = Z_e Z_{rot}$$

Electron density of states

$$g(\varepsilon) = (2j+1)\frac{\pi}{4h^3}(8m)^{3/2} V\sqrt{\varepsilon} = (2j+1) C V \sqrt{\varepsilon}$$

↑ multiplicity factor = 2 for e^-

$$C = \frac{\pi}{4h^3}(8m)^{3/2} = \frac{1}{\ell_Q^3}\left(\frac{h^2\beta}{2\pi m}\right)^{3/2}\frac{\pi}{4h^3}(8m)^{3/2}$$

$$\boxed{C = \frac{2}{\sqrt{\pi}}\frac{\beta^{3/2}}{\ell_Q^3}}$$

$g(\varepsilon)=2CV\sqrt{\varepsilon}$

But note C is independent of β

at $T=0$ for electron gas

$$N = \int_0^{\varepsilon_F} g(\varepsilon)\,d\varepsilon = 2CV\int_0^{\varepsilon_F}\varepsilon^{1/2}\,d\varepsilon = \frac{4}{3}CV\varepsilon_F^{3/2}$$

$$= \frac{4}{3}\frac{\pi}{4h^3}(8m)^{3/2} V\,\varepsilon_F^{3/2} = \frac{\pi}{3h^3}V(8m\varepsilon_F)^{3/2}$$

$$\boxed{\varepsilon_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}}$$ Fermi Energy

At non-zero temperature

$$N = \int g(\varepsilon)\,\bar{n}_{FD}(\varepsilon)\,d\varepsilon$$

$$= \int_0^\infty 2CV\sqrt{\varepsilon}\left(\frac{1}{e^{\beta(\varepsilon-\mu)}+1}\right)d\varepsilon$$

define μ by N

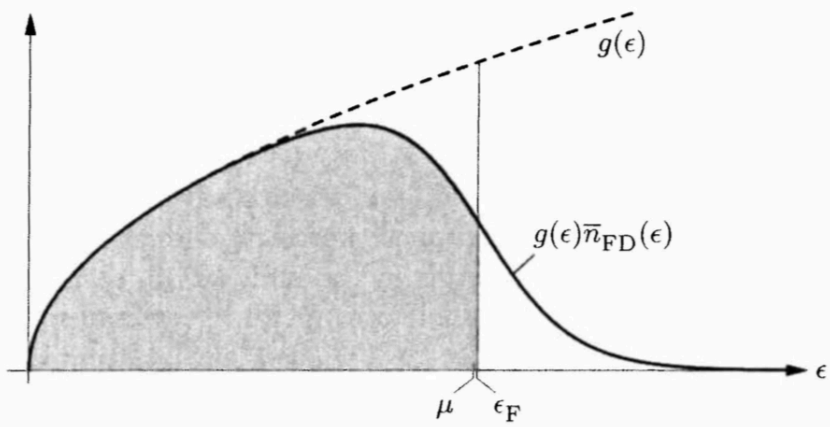


Figure 7.14. At nonzero T, the number of fermions per unit energy is given by the density of states times the Fermi-Dirac distribution. Because increasing the temperature does not change the total number of fermions, the two lightly shaded areas must be equal. Since $g(\epsilon)$ is greater above ϵ_{F} than below, this means that the chemical potential decreases as T increases. This graph is drawn for $T/T_{\mathrm{F}} = 0.1$; at this temperature μ is about 1% less than ϵ_{F}.

Electron gas energy

$$U = \int_0^\infty \varepsilon\, g(\varepsilon)\, \bar{n}_{FD}(\varepsilon)\, d\varepsilon$$

at $T=0$

$$U = \int_0^{\varepsilon_{FD}} \varepsilon^{3/2}\, 2CV\, d\varepsilon = \frac{4}{5} CV \varepsilon_F^{5/2}$$

$$CV = \frac{3}{4} N \frac{1}{\varepsilon_F^{3/2}}, \quad \boxed{U = \frac{3}{5} N \varepsilon_F} \qquad \underline{T=0}$$

Pressure $\quad P = -\dfrac{\partial U}{\partial V}$

$$\frac{\partial \varepsilon_F}{\partial V} = \frac{h^2}{8m}\left(\frac{3}{\pi} N^{2/3}\right) \frac{\partial}{\partial V} V^{-2/3}$$

$$= -\frac{2}{3} \frac{\varepsilon_F}{V}$$

$$P = N \frac{3}{5}\left(\frac{2}{3}\right) \frac{\varepsilon_F}{V} = \frac{2}{5} \frac{N}{V} \varepsilon_F$$

$$\boxed{P = \frac{2}{3} \frac{U}{V}}$$ degeneracy pressure

Example 2

Counting of electrons in "electron gas"

$$N = \int g(\varepsilon)\, \bar{n}_{FD}(\varepsilon)\, d\varepsilon$$

$\uparrow\ 2j+1 = 2(\frac{1}{2})+1 = 2$ spin "up, down"

$$\bar{n}_{FD} = \sum_{n=0}^{1} n \tilde{P}_n = \left[e^{\beta(\varepsilon-\mu)} + 1 \right]^{-1}$$

at $T=0$ $\quad \bar{n}_{FD}(\varepsilon) = \begin{cases} 1 & \varepsilon < \varepsilon_F \\ 0 & \varepsilon > \varepsilon_F \end{cases}$

$$N = \int_0^{\varepsilon_F} g(\varepsilon)\, d\varepsilon$$

$$= 2CV \int_0^{\varepsilon_F} \varepsilon^{1/2}\, d\varepsilon = \frac{4}{3} C V \varepsilon_F^{3/2}$$

$$C = \frac{\pi}{4h^3}(8m)^{3/2} \qquad \varepsilon_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}$$

$$U = \frac{3}{5} N \varepsilon_F \quad (T=0)$$

$$P = \frac{2}{3}\frac{U}{V} \quad (T=0)$$ degeneracy pressure

Semiclassical Energy U (Baierlein, ch 8)

quantum effects and the chemical potential

Do both BE, FD at same time as

$$\bar{n} = \frac{1}{e^{x} + q} \qquad x = \beta(\varepsilon - \mu) \qquad q = \begin{cases} +1 & \text{F.D.} \\ -1 & \text{BE.} \end{cases}$$

expand for $y \equiv e^{x} = e^{\beta(\varepsilon-\mu)} \gg 1$

$$\frac{1}{y+q} = \frac{1}{y}\left(1 + \frac{q}{y}\right)^{-1} \cong \frac{1}{y}\left(1 - \frac{q}{y}\right) = \frac{1}{y} - \frac{q}{y^2}$$

$$\bar{n}(\varepsilon) \cong e^{-x} - q\, e^{-2x} = e^{-\beta\varepsilon} e^{\mu\beta} - q\, e^{-2\beta\varepsilon} e^{2\mu\beta}$$

$$U = \int_0^\infty g(\varepsilon)\, \varepsilon\, \bar{n}(\varepsilon)\, d\varepsilon$$

$$= (2j+1) \frac{V}{\ell_Q^3} \beta^{3/2} \frac{2}{\sqrt{\pi}} \left[e^{\mu\beta} \int_0^\infty \varepsilon^{3/2} e^{-\beta\varepsilon} d\varepsilon - q\, e^{2\mu\beta} \int_0^\infty \varepsilon^{3/2} e^{-2\beta\varepsilon} d\varepsilon \right]$$

$\omega \equiv \beta\varepsilon$

$$[\;] = \left(\frac{1}{\beta}\right)^{3/2+1} \left\{ e^{\mu\beta} \int_0^\infty \omega^{3/2} e^{-\omega} d\omega - q\, e^{2\mu\beta} \int_0^\infty \omega^{3/2} e^{-2\omega} d\omega \right\}$$

$$= \left(\frac{1}{\beta}\right)^{3/2+1} \left\{ e^{\mu\beta} \frac{3\sqrt{\pi}}{4} - q\, e^{2\mu\beta} \frac{3}{16}\sqrt{\frac{\pi}{2}} \right\}$$

$$\boxed{U = \frac{(2j+1)}{\beta} \frac{V}{\ell_Q^3} \left(\frac{3}{2}\right) \left[e^{\mu\beta} - \frac{q}{4\sqrt{2}} e^{2\mu\beta} \right]}$$

Similar calculation gives N in terms of μ

$$N = \int_0^\infty g(\varepsilon)\,\bar{n}(\varepsilon)\,d\varepsilon$$

$$= (2j+1)\frac{V}{\ell_Q^3}\beta^{3/2}\frac{2}{\sqrt{\pi}}\left[e^{\mu\beta}\int_0^\infty \varepsilon^{1/2}e^{-\beta\varepsilon}\,d\varepsilon - q\,e^{2\mu\beta}\int_0^\infty \varepsilon^{1/2}e^{-2\beta\varepsilon}\,d\varepsilon\right]$$

$$= (2j+1)\frac{V}{\ell_Q^3}\frac{2}{\sqrt{\pi}}\left[e^{\mu\beta}\underbrace{\int_0^\infty w^{1/2}e^{-w}\,dw}_{\sqrt{\pi}/2} - q\,e^{2\mu\beta}\underbrace{\int_0^\infty w^{1/2}e^{-2w}\,dw}_{\frac{1}{4}\sqrt{\frac{\pi}{2}}}\right]$$

$$\boxed{N = (2j+1)\frac{V}{\ell_Q^3}\left[e^{\mu\beta} - \frac{q}{2\sqrt{2}}e^{2\mu\beta}\right]}$$

solve for chemical potential

In semi-classical approximation

$$\frac{\ell_Q^3}{V} \ll 1 \quad \text{so} \quad e^{\mu\beta} \ll 1$$

To first order, $e^{\mu\beta} \cong \frac{N}{(2j+1)}\frac{\ell_Q^3}{V}$

giving for U,

$$U = N\frac{3}{2}\left(\frac{1}{\beta}\right) \quad \boxed{=(3/2)NkT}$$

To second order, let $e^{\mu\beta} \equiv y$, $c = \frac{N}{(2j+1)}\frac{\ell_Q^3}{V}$

$$y - \frac{q}{2\sqrt{2}}y^2 = c$$

$y \cong c$ first order

$y \approx c + \frac{q}{2\sqrt{2}}c^2$ second order

Then U to second order is

$$U = \left(\frac{2j+1}{\beta}\right) \frac{V}{l_Q^3} \left(\frac{3}{2}\right) \left[y - \frac{q}{4\sqrt{2}} y^2 \right]$$

$$[\ ] = c + \frac{q}{2\sqrt{2}} c^2 - \frac{q}{4\sqrt{2}} \left(c + \frac{q}{2\sqrt{2}} c^2 \right)^2$$

$$\cong c + c^2 \frac{q}{2\sqrt{2}} \left(1 - \frac{1}{2}\right) = c + c^2 \frac{q}{4\sqrt{2}}$$

$$U = \frac{2j+1}{\beta} \frac{V}{l_Q^3} \left(\frac{3}{2}\right) \left(\frac{N}{2j+1} \frac{l_Q^3}{V}\right) \left[1 + c \frac{q}{4\sqrt{2}} \right]$$

$$\boxed{U = \frac{3}{2} NRT \left[1 + \frac{q}{4\sqrt{2}} \frac{N}{V} \frac{l_Q^3}{(2j+1)} \right]}$$

with $q = -1$ BE, $+1$ F.D. and $l_Q^3 \propto \left(\frac{1}{T}\right)^{3/2}$

So when Quantum effects become important U is no longer simply proportional to T.

Also, semiclassical ideal gas chemical potential.

recall we had $\mu = \frac{\partial F}{\partial N} = -kT \ln\left(\frac{V}{N l_Q^3}\right) = -kT \ln\left(\frac{1}{c}\right)$

Now $y \cong c + \frac{q}{2\sqrt{2}} c^2$ $\quad q = \pm 1 \begin{cases} + & \text{F.D.} \\ - & \text{B.E.} \end{cases}$

with $c = \frac{N l_Q^3}{V} \ll 1$ $\quad y = e^{\mu\beta}$; $\quad l_Q = \frac{h}{\sqrt{2\pi m k T}}$

$$e^{-\mu\beta} = \frac{1}{y} = \frac{1}{c}\left(\frac{1}{1+\frac{q}{2\sqrt{2}}c}\right) \cong \frac{1}{c}\left(1 - \frac{q}{2\sqrt{2}}c\right)$$

$$\mu = -kT\left[\ln\frac{1}{c} + \ln\left(1 - \frac{q}{2\sqrt{2}}c\right)\right]$$

with $\ln(1-x) \approx -x$

$$\mu = -kT\left[\ln\left(\frac{1}{c}\right) - \frac{q}{2\sqrt{2}}c\right]$$

$$= -kT\ln\left(\frac{1}{c}\right) + kT\frac{q}{2\sqrt{2}}c$$

$$\text{extra} = \pm\frac{c}{2\sqrt{2}}$$

$\mu \begin{cases} \text{more negative} & \text{B.E.} \\ \text{less negative} & \text{F.D.} \end{cases}$ $\quad \begin{cases} \text{more} \\ \text{less} \end{cases}$ energy needed to remove molecule

Chemical potential in quantum statistics

From thermodynamics $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

Thermodynamic quantities related to partition function Z as $\left(\beta \equiv \frac{1}{kT}\right)$

$$U = -\frac{\partial}{\partial \beta} \ln Z$$

$$F = -\frac{1}{\beta} \ln Z$$

$$\frac{S}{k} = \beta (U - F) = \beta \left(-\frac{\partial \ln Z}{\partial \beta}\right) + \ln Z$$

Classical <u>monatomic</u> gas, single molecule

$$Z_{tr}^{(1)} = \frac{V}{h^3} \int_0^\infty 4\pi p^2 dp \, e^{-\beta p^2/2m}$$

$$= \frac{V}{h^3} \int g(\varepsilon) e^{-\beta \varepsilon} d\varepsilon$$

$$g(\varepsilon) = C V \sqrt{\varepsilon} \qquad C = \frac{\pi}{4h^3} (8m)^{3/2}$$

$$Z_{tr}^{(1)} = \frac{V}{l_Q^3}$$

Z for N molecules $Z = \frac{1}{N!} \left(\frac{V}{l_Q^3}\right)^N$

$$F = -kT \ln Z = -kT \ln \frac{V}{l_Q^3} + kT \ln N!$$

$$\ln N! = N \ln N - N$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -kT \ln\left(\frac{V}{l_Q^3}\right) + kT N = -kT \ln\left(\frac{V}{N l_Q^3}\right)$$

In quantum case

$$Z_{FD}(\varepsilon) = 1 + e^{-\beta(\varepsilon-\mu)}$$

$$Z_{BE}(\varepsilon) = \frac{1}{1 - e^{-\beta(\varepsilon-\mu)}}$$

Single particle with energy ε

$$\bar{n}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} \pm 1}$$

$+$ F.D.
$-$ B.E.

$$N = \int_0^\infty g(\varepsilon)\, \bar{n}(\varepsilon)\, d\varepsilon$$

for non-relativistic particle (e.g. electrons in metal)

$$\varepsilon = p^2/2m$$

$$g(\varepsilon) = (2j+1)\, c V \sqrt{\varepsilon} \qquad c = \frac{\pi}{4h^3}(8m)^{3/2}$$

$\mu(T)$ defined by integral to get N.