Grand potential for Fermi-Dirac and Bose-Einstein Masatsugu Sei Suzuki Department of Physics (Date: November 01 19, 2018)

Using the grand potential for both the fermions and bosons, we the thermodynamic properties are derived here. The energy dispersion of particles is assumed to be quadratic with momentum like free particles such as electron. The expression of the grand potential for fermion is very similar to that of bosons except for the distribution function. In spite of such a fact, the discussion will be done below separately, partly because of avoiding possible confusion. The book of Landau and Lifshitz, Statistical Physics is very useful for our understanding the concepts.

1. Grand potential for fermions

The partition function:

$$Z_G = \prod_i \sum_{n_i=0}^{1} \exp[-\beta n_i (\varepsilon_i - \mu)] = \prod_i \{1 + \exp[-\beta (\varepsilon_i - \mu)]\}$$

The grand potential

$$\Phi_G = -k_B T \ln Z_G$$

= $-k_B T \sum_i \ln \{1 + \exp[-\beta(\varepsilon_i - \mu)]\}$

The average number

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln Z_G}{\partial \mu}$$

= $-\frac{1}{\beta} \frac{\partial}{\partial \mu} \sum_i \ln\{1 + \exp[-\beta(\varepsilon_i - \mu)]\}$
= $\sum_i \frac{1}{\exp[\beta(\varepsilon_i - \mu)] + 1}$
= $\sum_i \langle n_i \rangle$

$$\langle n_i \rangle = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] + 1}$$

(Fermi-Dirac distribution function)

The entropy

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu},$$

,

The number:

$$N = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}$$

The pressure

$$P = - \left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}$$

Then the grand potential can be calculated as follows.

$$\Phi_G = -k_B T \sum_{k} \ln[1 + e^{-\beta(\varepsilon_k - \mu)}]$$

= $-k_B T \frac{gV}{(2\pi)^3} \int d^3 k \ln[1 + e^{-\beta(\varepsilon_k - \mu)}]$
= $-k_B T \frac{gV}{(2\pi)^3} 4\pi \int_0^\infty k^2 dk \ln[1 + e^{-\beta(\varepsilon_k - \mu)}]$

We use the following relation

$$\varepsilon_k = \varepsilon = \frac{\hbar^2}{2m}k^2, \qquad k = \left(\frac{2m}{\hbar^2}\right)^{1/2}\sqrt{\varepsilon}, \qquad dk = \frac{1}{2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\frac{1}{\sqrt{\varepsilon}}$$

Thus we have

$$\Phi_{G} = -k_{B}T \frac{gV}{(2\pi)^{3}} \frac{4\pi}{2} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \sqrt{\varepsilon} d\varepsilon \ln[1 + e^{-\beta(\varepsilon-\mu)}]$$
$$= -k_{B}T \frac{gV}{4\pi^{2}} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \sqrt{\varepsilon} d\varepsilon \ln[1 + e^{-\beta(\varepsilon-\mu)}]$$

The integration by parts gives

$$\Phi_G = -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} + 1} d\varepsilon$$

The pressure P is

$$P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = \frac{2}{3} \frac{gm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} + 1} d\varepsilon$$

We note that $\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = \frac{\Phi_G}{V}$, since Φ_G is proportional to *V*. So we have the relation

$$P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = -\frac{\Phi_G}{V}$$

or

$$\Phi_G = -PV. \tag{1}$$

The number N is obtained as

$$\begin{split} N &= -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V} \\ &= \frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \varepsilon^{3/2} \frac{\partial}{\partial \mu} \frac{1}{1 + e^{\beta(\varepsilon - \mu)}} d\varepsilon \\ &= -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \varepsilon^{3/2} \frac{\partial}{\partial \varepsilon} \frac{1}{1 + e^{\beta(\varepsilon - \mu)}} d\varepsilon \\ &= \frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \frac{3}{2} \int_0^\infty \frac{\sqrt{\varepsilon}d\varepsilon}{1 + e^{\beta(\varepsilon - \mu)}} \\ &= \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\sqrt{\varepsilon}d\varepsilon}{1 + e^{\beta(\varepsilon - \mu)}} \end{split}$$

or directly, we get N from the definition as

$$N = \sum_{k} \langle n_{k} \rangle$$
$$= \frac{gV}{(2\pi)^{3}} 4\pi \int_{0}^{\infty} k^{2} dk \frac{1}{e^{\beta(\varepsilon_{k}-\mu)} + 1}$$
$$= \frac{gV}{4\pi^{2}} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1}$$
$$= \frac{gVm^{3/2}}{\sqrt{2}\pi^{2}\hbar^{3}} \int_{0}^{\infty} \frac{\sqrt{\varepsilon} d\varepsilon}{1 + e^{\beta(\varepsilon-\mu)}}$$

We also calculate the energy U as

$$U = \sum_{k} \varepsilon_{k} \langle n_{k} \rangle$$

= $\frac{gV}{(2\pi)^{3}} 4\pi \int_{0}^{\infty} k^{2} dk \frac{\varepsilon_{k}}{e^{\beta(\varepsilon_{k}-\mu)} + 1}$
= $\frac{gV}{4\pi^{2}} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1}$
= $\frac{gVm^{3/2}}{\sqrt{2}\pi^{2}\hbar^{3}} \int_{0}^{\infty} \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1}$

So U is related to the grand potential as

$$\Phi_G = -\frac{2}{3}U.$$
 (2)

From Eqs.(1) and (2), we get the relation

$$PV = \frac{2}{3}U.$$

3. Grand potential for bosons The partition function:

$$Z_G = \prod_i \sum_{n_i=0}^{\infty} \exp[-\beta n_i (\varepsilon_i - \mu)] = \prod_i \{1 - \exp[-\beta (\varepsilon_i - \mu)]^{-1}\}$$

The grand potential

$$\Phi_G = -k_B T \ln Z_G$$

= $k_B T \sum_i \ln \{1 - \exp[-\beta(\varepsilon_i - \mu)]\}$

The average number

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln Z_G}{\partial \mu}$$

= $-\frac{1}{\beta} \frac{\partial}{\partial \mu} \sum_i \ln\{1 - \exp[-\beta(\varepsilon_i - \mu)]\}$
= $\sum_i \frac{1}{\exp[\beta(\varepsilon_i - \mu)] - 1}$
= $\sum_i \langle n_i \rangle$

$$\langle n_i \rangle = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] - 1}$$

(Bose-Einstein distribution function)

The entropy

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu},$$

The number:

$$N = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}$$

The pressure

$$P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}$$

We now calculate the grand potential

$$\Phi_{G} = k_{B}T \sum_{k} \ln[1 - e^{-\beta(\varepsilon_{k} - \mu)}]$$

= $k_{B}T \frac{gV}{(2\pi)^{3}} \int d^{3}k \ln[1 - e^{-\beta(\varepsilon_{k} - \mu)}]$
= $k_{B}T \frac{gV}{(2\pi)^{3}} 4\pi \int_{0}^{\infty} k^{2} dk \ln[1 - e^{-\beta(\varepsilon_{k} - \mu)}]$

where g = 2 for spin 1/2 particle. We use the following dispersion relation

$$\varepsilon_k = \varepsilon = \frac{\hbar^2}{2m}k^2, \qquad k = \left(\frac{2m}{\hbar^2}\right)^{1/2}\sqrt{\varepsilon}, \qquad dk = \frac{1}{2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\frac{1}{\sqrt{\varepsilon}}$$

So we have

$$\Phi_{G} = k_{B}T \frac{gV}{(2\pi)^{3}} \frac{4\pi}{2} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \sqrt{\varepsilon} d\varepsilon \ln[1 - e^{-\beta(\varepsilon - \mu)}]$$
$$= k_{B}T \frac{gV}{4\pi^{2}} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \sqrt{\varepsilon} d\varepsilon \ln[1 - e^{-\beta(\varepsilon - \mu)}]$$

The integration by parts gives

$$\Phi_G = -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} - 1} d\varepsilon$$

The pressure P is

$$P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = \frac{2}{3} \frac{gm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} - 1} d\varepsilon$$

Note that $\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = \frac{\Phi_G}{V}$, since Φ_G is proportional to V. So we have the relation

$$P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = -\frac{\Phi_G}{V}$$

or

$$\Phi_G = -PV.$$

The number N is

$$N = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}$$

$$= \frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \varepsilon^{3/2} \frac{\partial}{\partial \mu} \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} d\varepsilon$$

$$= -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \varepsilon^{3/2} \frac{\partial}{\partial \varepsilon} \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} d\varepsilon$$

$$= \frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \frac{3}{2} \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$$

$$= \frac{gVm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$$

or simply, we get N from

$$N = \sum_{k} \langle n_{k} \rangle$$

= $\frac{gV}{(2\pi)^{3}} 4\pi \int_{0}^{\infty} k^{2} dk \frac{1}{e^{\beta(\varepsilon_{k}-\mu)} - 1}$
= $\frac{gV}{4\pi^{2}} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$
= $\frac{gVm^{3/2}}{\sqrt{2}\pi^{2}\hbar^{3}} \int_{0}^{\infty} \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$

We also calculate the energy E as

$$U = \sum_{k} \varepsilon_{k} \langle n_{k} \rangle$$
$$= \frac{gV}{(2\pi)^{3}} 4\pi \int_{0}^{\infty} k^{2} dk \frac{\varepsilon_{k}}{e^{\beta(\varepsilon_{k}-\mu)} - 1}$$
$$= \frac{gV}{4\pi^{2}} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$$
$$= \frac{gVm^{3/2}}{\sqrt{2}\pi^{2}\hbar^{3}} \int_{0}^{\infty} \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$$

So U is related to the grand potential as

$$\Phi_G = -\frac{2}{3}U.$$

We get the relation

$$PV = \frac{2}{3}U.$$

3. Scaling relation for fermion and boson

This result is exact, and so must hold valid in the limiting case of a Boltzmann gas also. In fact, on substituting the Boltzmann value $E = \frac{3}{2}Nk_BT$, we obtain the Boyle law. We consider the pressure *P*.

$$P = \frac{2}{3} \frac{gm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} \pm 1} d\varepsilon$$
(1)

for the positive sign for fermion and the minus sign for boson. From Eq.(1), substituting $\beta \varepsilon = x$, we obtain

$$\begin{split} \Phi_{G} &= -PV \\ &= -\frac{2}{3} \frac{Vgm^{3/2}}{\sqrt{2}\pi^{2}\hbar^{3}} (k_{B}T)^{5/2} \int_{0}^{\infty} \frac{x^{3/2}}{e^{x-\beta\mu} \pm 1} dx \\ &= VT^{5/2} f(\frac{\mu}{T}) \\ &= VT^{5/2} f(\frac{\mu}{T}) \end{split}$$

where f is a function of a single variable. The entropy S is obtained as

$$\begin{split} S &= -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} \\ &= -V \frac{5}{2} T^{3/2} f(\frac{\mu}{T}) + V T^{5/2} \frac{\mu}{T^2} f'(\frac{\mu}{T}) \\ &= -V \frac{5}{2} T^{3/2} f(\frac{\mu}{T}) + V T^{3/2} \frac{\mu}{T} f'(\frac{\mu}{T}) \\ &= V T^{3/2} [-\frac{5}{2} f(\frac{\mu}{T}) + \frac{\mu}{T} f'(\frac{\mu}{T})] \\ &= V T^{3/2} g_S(\frac{\mu}{T}) \end{split}$$

where $g_s(x) = -\frac{5}{2}f(x) + xf'(x)$. The number N is obtained as

$$N = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V} = -VT^{5/2}\frac{1}{T}f'(\frac{\mu}{T}) = -VT^{3/2}f'(\frac{\mu}{T}) = VT^{3/2}g_N(\frac{\mu}{T})$$

where

$$g_N(x) = -f'(x)$$

Then we have

$$\frac{S}{N} = \phi(\frac{\mu}{T})$$

where

$$\phi(x) = \frac{g_S(x)}{g_N(x)}$$

In an adiabatic process (S = constant), $\frac{\mu}{T}$ remains constant. Since

$$\frac{N}{VT^{3/2}} = g_N(\frac{\mu}{T})$$

we have

$$VT^{3/2}$$
 =constant

From the relation

$$\frac{P}{T^{5/2}} = f(\frac{\mu}{T})$$

we also have

$$\frac{P}{T^{5/2}}$$
=constant.

Thus we have

$$PV^{5/3} \propto T^{\frac{5}{2}} (T^{-3/2})^{5/3} = \text{constant}$$

4. Approximation for fermion and boson

$$E = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}d\varepsilon}{\frac{1}{z}e^{\beta\varepsilon}\pm 1}$$
$$P = \frac{2}{3} \frac{gm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}}{\frac{1}{z}e^{\beta\varepsilon}\pm 1} d\varepsilon$$
$$N = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{1/2}d\varepsilon}{\frac{1}{z}e^{\beta\varepsilon}\pm 1}$$

We now expand the integrand as a power of z,

$$\frac{\varepsilon^{n}}{\frac{1}{z}e^{\beta\varepsilon}\pm 1} = z\varepsilon^{n}e^{-\beta\varepsilon}\left(1\pm ze^{-\beta\varepsilon}+z^{2}e^{-2\beta\varepsilon}-z^{3}e^{-3\beta\varepsilon}+\ldots\right)$$
$$= z\varepsilon^{n}e^{-\beta\varepsilon}\pm z^{2}\varepsilon^{n}e^{-2\beta\varepsilon}+z^{3}\varepsilon^{n}e^{-3\beta\varepsilon}-z^{4}\varepsilon^{n}e^{-4\beta\varepsilon}+\ldots)$$

Using the Laplace transformation for the term with n = 3/2, we have

$$\int_{0}^{\infty} \frac{\varepsilon^{3/2}}{\frac{1}{z}} d\varepsilon = \frac{3\sqrt{\pi}}{4\beta^{5/2}} \left(z \pm \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} \pm \frac{z^3}{4^{5/2}} + \dots \right)$$
$$\int_{0}^{\infty} \frac{\varepsilon^{1/2}}{\frac{1}{z}} e^{\beta\varepsilon} \pm 1} d\varepsilon = \frac{\sqrt{\pi}}{2\beta^{3/2}} \left(z \pm \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} \pm \frac{z^3}{4^{5/2}} + \dots \right)$$

Thus we have the approximation for U and N as follows.

$$U = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \frac{3\sqrt{\pi}}{4\beta^{5/2}} \left(z \pm \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} \pm \frac{z^4}{4^{5/2}} + \ldots\right)$$
$$N = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \frac{\sqrt{\pi}}{2\beta^{3/2}} \left(z \pm \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} \pm \frac{z^4}{4^{5/2}} + \ldots\right)$$

and

$$P = \frac{2}{3} \frac{gm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \frac{3\sqrt{\pi}}{4\beta^{5/2}} \left(z \pm \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} \pm \frac{z^4}{4^{5/2}} + \dots\right)$$

REFERENCE

L.D. Landau and E.M. Lifshitz, Statistical Physics (Pergamon Press, 1980).

APPENDIX-I

Grand potential

$$\Phi_G = -k_B T \ln Z_G, \qquad PV = k_B T \ln Z_G$$

$$\Phi_G = -PV = F - \mu N = U - ST - \mu N$$

$$U - \mu N = -T^2 \frac{\partial}{\partial T} \left(\frac{\Phi_G}{T} \right)_{V,\mu}$$

$$d\Phi_{G} = dU - d(ST) - d(\mu N)$$

= TdS - PdV + \mu dN - SdT - TdS - \mu dN - Nd\mu
= -PdV - SdT - Nd\mu

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu}, \qquad P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}, \qquad N = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}$$

APPENDIX-IICalculation of Φ_G (fermion) using the Sommerfeld expansionUsing the formula for fermions,

$$\Phi_G = -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} + 1} d\varepsilon$$

$$N = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_{0}^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon \qquad (\text{at } T = 0 \text{ K})$$

we get the ratio

$$\begin{split} \frac{\Phi_G}{N} &= -\frac{2}{3} \frac{\int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1}}{\int_0^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon} \\ &= (-\frac{2}{3}) \frac{\frac{2}{5} \mu^{5/2} [1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mu}\right)^2]}{\frac{2}{3} \varepsilon_F^{3/2}} \\ &= -\frac{2}{5} \frac{\mu^{5/2}}{\varepsilon_F^{3/2}} [1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mu}\right)^2] \\ &\approx -\frac{2}{5} \varepsilon_F [1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\varepsilon_F}\right)^2] \end{split}$$

$$\Phi_G = -\frac{2}{5} N \varepsilon_F \left[1 + \frac{5}{8} \left(\frac{k_B T}{\varepsilon_F}\right)^2\right]$$

where we use the Sommerfeld expansion

$$\int_{0}^{\infty} \frac{\varphi(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} = \int_{0}^{\mu} \varphi(\varepsilon)f(\varepsilon)d\varepsilon + \frac{\pi^{2}}{6}(k_{B}T)^{2}\varphi'(\mu)$$

The entropy S is obtained by

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} = Nk_B \left(\frac{\pi^2 k_B T}{2\varepsilon_F}\right)$$