PHYS 3014: Statistical Mechanics

Lecture Notes
Part 19

Fermi Gas : Non-degenerate Case

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Programme: B. Sc. Physics
Semester: VI

Thermodynamics of Ideal Fermi Gas

For Fermi gas, the fugacity or absolute activity $z\{= \exp(\frac{\mu}{KT})\}$ can have any value between 0 and ∞. i.e $0 \leq z < \infty$. Due to Pauli's exclusion principle the maximum number of particle occupying a single energy state is one. So there is no question of phenomenon like condensation of fermi gas. All values of μ occur in the system. μ is the mean energy required for addition of another particle to the system so μ must increase with particle number at fixed volume.

If Z is the grand partition function of the Fermi gas system, then we have

$$\frac{PV}{KT} = \ln Z = \sum_{\epsilon} \ln(1+ze^{-\beta\epsilon}) \quad ---(1)$$

where V is the volume of the system, P is the pressure and T is the temperature at equilibrium.

The no. of particles in the system

$$N(T, V, z) = \sum_{\epsilon} \bar{n}_{\epsilon} = \sum_{\epsilon} \frac{1}{z^{-1} e^{\beta\epsilon} + 1} \quad \text{---} \; (2)$$

For large volume V, the summation can be written in terms of integrals. So equations (1) and (2) can be written as

$$\frac{PV}{KT} = \int_0^\infty \ln\left(1 + z e^{-\beta\epsilon}\right) g(\epsilon)\, d\epsilon$$

$$= g \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \epsilon^{1/2} \ln\left(1 + z e^{-\beta\epsilon}\right) d\epsilon$$

where $g = 2S+1$

$= 2$ for electrons.

put $\beta\epsilon = x \Rightarrow \beta d\epsilon = dx$

$$\therefore \quad \frac{PV}{KT} = g\,\frac{2\pi V}{h^3}(2m)^{3/2}(KT)^{3/2}\int_0^\infty x^{1/2}\ln(1+z\,e^{-x})\,dx$$

or,
$$\frac{P}{KT} = g\,\frac{2\pi}{h^3}(2mKT)^{3/2}\left[\left\{\ln(1+z\,e^{-x})\cdot\frac{x^{3/2}}{3/2}\right\}_0^\infty - \int_0^\infty \frac{2}{3}x^{3/2}\frac{(-z\,e^{-x})\,dx}{(1+z\,e^{-x})}\right]$$

$$= g\,\frac{2\pi}{h^3}(2mKT)^{3/2}\,\frac{\sqrt{\pi}\;\frac{1}{2}}{\sqrt{\pi}\;\frac{3}{2}\cdot\frac{1}{2}}\int_0^\infty \frac{x^{3/2}\,dx}{(z^{-1}e^{x}+1)}$$

$$= g\,\frac{(2\pi mKT)^{3/2}}{h^3}\cdot\frac{1}{\Gamma 5/2}\int_0^\infty \frac{x^{5/2-1}\,dx}{(z^{-1}e^{x}+1)}$$

We can define Fermi-Dirac function

$$f_\nu(z) = \frac{1}{\Gamma\nu}\int_0^\infty \frac{x^{\nu-1}\,dx}{z^{-1}e^{x}+1} = z - \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} - \frac{z^4}{4^\nu} + \cdots \quad \text{---- (2A)}$$

$$\therefore \frac{P}{KT} = \frac{g}{\lambda^3} f_{5/2}(z) \quad \text{---} \ (3)$$

where g is the weight factor arising from the spin of fermions and λ is the mean thermal wavelength of the particles

$$\lambda = \frac{h}{\sqrt{2\pi m K T}}$$

and

$$N = \int_0^\infty g(\epsilon) \frac{d\epsilon}{z^{-1} e^{\beta\epsilon} + 1}$$

or,

$$N = g \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2} \, d}{z^{-1} e^{\beta\epsilon} + 1}$$

$$= g \frac{2\pi V}{h^3} (2m)^{3/2} (KT)^{3/2} \frac{\sqrt{\pi} \cdot \frac{1}{2}}{\frac{1}{2}\sqrt{\pi}} \int_0^\infty \frac{x^{3/2 - 1} \, dx}{z^{-1} e^{x} + 1}$$

or, $N = g\dfrac{(2\pi mKT)^{3/2}}{h^3} \cdot f_{3/2}(z)$

or, $N = \dfrac{g}{\lambda^3} f_{3/2}(z)$ - - - (4)

The internal energy of the Fermi gas is given by

$$U = -\left[\frac{\partial}{\partial \beta} \ln Z\right]_{z,V}$$

$$= KT^2\left[\frac{\partial}{\partial T} \ln Z\right]_{z,V}$$

$$= KT^2\left[\frac{\partial}{\partial T}\left(\frac{PV}{KT}\right)\right]_{z,V} \quad \text{using eqn (1)}$$

$$= KT^2\left[\frac{\partial}{\partial T}\left(\frac{gV}{\lambda^3} f_{5/2}(z)\right)\right]_{z,V} \quad \text{using eqn (3)}$$

or, $$U = KT^2 gV f_{5/2}(z) \cdot \left\{\frac{\partial}{\partial T}\left[\frac{(2\pi mKT)^{3/2}}{h^3}\right]\right\}_{V,z}$$

$$= KT \cdot gV f_{5/2}(z) \frac{3}{2} \cdot \frac{(2\pi mKT)^{3/2}}{h^3}$$

or, $$U = \frac{3}{2} KT \frac{gV}{\lambda^3} f_{5/2}(z) \quad \text{--- (5)}$$

or, $$U = \frac{3}{2} NKT \frac{f_{5/2}(z)}{f_{3/2}(z)} \quad \text{--- (6)}$$ using equ^n (4)

$\therefore$ $$\boxed{P = \frac{2}{3}\frac{U}{V}} \quad \text{-- (7)}$$ System satisfies the standard relationship. Holds for non-relativistic ideal gases.

or, $$PV = NKT \frac{f_{5/2}(z)}{f_{3/2}(z)} \quad \text{--- (8)}$$

For Fermi-Dirac function $f_\nu(z) = \frac{1}{\Gamma\nu}\int_0^\infty \frac{x^{\nu-1}dx}{z^{-1}e^x+1}$, $0 \le z < \infty$

$$\frac{\partial}{\partial z} f_\nu(z) = \frac{1}{z} f_{\nu-1}(z) \quad \text{--- (9)}$$

$\because$

$$z \frac{\partial}{\partial z} f_\nu(z) = \frac{1}{\Gamma\nu} \int_0^\infty \frac{z \cdot x^{\nu-1} z^{-2} e^x \, dx}{(z^{-1}e^x + 1)^2}$$

$$= \frac{1}{\Gamma\nu}\left[\left\{-\frac{x^{\nu-1}}{(z^{-1}e^x+1)}\right\}_0^\infty + (\nu-1)\int_0^\infty \frac{x^{\nu-1-1}\,dx}{z^{-1}e^x+1}\right]$$

$$= 0 + \frac{1}{\Gamma\nu-1}\int_0^\infty \frac{x^{(\nu-1)-1}\,dx}{z^{-1}e^x+1}$$

$$= f_{\nu-1}(z)$$ First term vanishes for $\nu > 1$.

and. $$\frac{\partial}{\partial T}\left[f_{3/2}(z)\right] = \frac{\partial}{\partial T}\left(\frac{N\lambda^3}{Vg}\right)$$ using eqn (4)

$$= -\frac{3}{2}\frac{1}{T} \cdot f_{3/2}(z)$$

$\therefore$ $$\frac{\partial z}{\partial T} \cdot \frac{\partial}{\partial z} f_{3/2}(z) = -\frac{3}{2T} f_{3/2}(z)$$

or, $$\frac{\partial z}{\partial T} \cdot \frac{1}{z} f_{1/2}(z) = -\frac{3}{2T} f_{3/2}(z) \Rightarrow \frac{\partial z}{\partial T} = -\frac{3}{2T} z \frac{f_{3/2}(z)}{f_{1/2}(z)} \quad \text{--- (10)}$$

The specific heat of Fermi gas is

$$C_V = \left[\frac{\partial U}{\partial T}\right]_{V,N}$$

$$= \frac{3}{2} NK \frac{\partial}{\partial T}\left[T \frac{f_{5/2}(z)}{f_{3/2}(z)}\right] \quad \text{using eqn } 6$$

or, $$\frac{C_V}{NK} = \frac{3}{2}\frac{f_{5/2}(z)}{f_{3/2}(z)} + \frac{3}{2}T \cdot \frac{\partial z}{\partial T} \cdot \frac{\partial}{\partial z}\left[\frac{f_{5/2}(z)}{f_{3/2}(z)}\right]$$

$$= \frac{3}{2}\frac{f_{5/2}(z)}{f_{3/2}(z)} + \frac{3}{2}T\left[-\frac{3}{2T} z \frac{f_{3/2}(z)}{f_{1/2}(z)}\right] \cdot \left[\frac{f_{3/2}(z) \cdot \frac{1}{z} f_{3/2}(z) - \frac{1}{z} f_{1/2}(z) f_{5/2}(z)}{[f_{3/2}(z)]^2}\right]$$

$$= \frac{3}{2}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4} z \frac{f_{3/2}(z)}{f_{1/2}(z)}\left[\frac{1}{z} - \frac{f_{1/2}(z) f_{5/2}(z)}{z (f_{3/2}(z))^2}\right] \quad \text{using eqn } 9 \text{ and } 10$$

or, $$\frac{C_V}{NK} = \frac{3}{2}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4}\frac{f_{3/2}(z)}{f_{1/2}(z)} + \frac{9}{4}\frac{f_{5/2}(z)}{f_{3/2}(z)}$$

or, $$\frac{C_V}{NK} = \frac{15}{4}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4}\frac{f_{3/2}(z)}{f_{1/2}(z)} \quad \text{---} \quad (11)$$

Helmholtz free energy of Fermi gas

$$F = N\mu - PV \qquad\qquad z = e^{\mu/KT}$$

$$= NKT\ln z - NKT\frac{f_{5/2}(z)}{f_{3/2}(z)} \qquad \text{using eqn (8)}$$

or, $$F = NKT\left[\ln z - \frac{f_{5/2}(z)}{f_{3/2}(z)}\right] \quad \text{---} \quad (12)$$

Entropy of the Fermi gas

$$S = \frac{U-F}{T} = \frac{3}{2}NK\frac{f_{5/2}(z)}{f_{3/2}(z)} - NK\left[\ln z - \frac{f_{5/2}(z)}{f_{3/2}(z)}\right]$$

or, $$S = NK\left[\frac{5}{2}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \ln z\right] \quad \text{---} \quad (13)$$

It has been observed that, the thermodynamic quantities associated with Fermi Gas depend on the absolute activity z of the system which intern depends on temperature T. For detailed studies, about these quantities require functional dependence of parameter z on $n = \frac{N}{V}$ and T under certain conditions.

Eqn. (4) reads $\frac{N}{V} = \frac{g}{\lambda^3} f_{3/2}(z)$

Non-degenerate Fermi Gas

If the density of the gas is very low or its temperature is very high, then

$$\frac{N}{V} \frac{\lambda^3}{g} << 1 \quad \text{classical limit}$$

and gas is said to be highly non-degenerate.

$$\therefore \quad f_{3/2}(z) = \frac{N\lambda^3}{vg} << 1 \quad \text{--- (14)}$$

$\therefore$ equ^n 2A implies that z itself is much smaller than unity $z << 1$

and $f_\nu(z) \simeq z$

Therefore, for non-degenerate Fermi gas, the thermo-dynamic quantities become

$$P = \frac{NKT}{V}$$

$$U = \frac{3}{2} NKT$$

$$\text{--- (15)}$$

$$C_V = \frac{3}{2} NK$$

$$F = NKT\left[\ln\left(\frac{N\lambda^3}{gV}\right) - 1\right] \qquad \because f_{3/2}(z) \simeq z = \frac{N\lambda^3}{Vg}$$

and $S = NK\left[\frac{5}{2} - \ln\left(\frac{N\lambda^3}{gV}\right)\right]$. Classical Ideal gas.

If z is small in comparison with unity ($z<1$) but not very small then z can be eliminated between equations (3) and (4). Then equation of state can assume form of virial expansion. (slightly degenerate)

$$\frac{PV}{NKT} = 1 + \frac{1}{2^{5/2}}\left(\frac{N\lambda^3}{Vg}\right) - \left(\frac{2}{3^{5/2}} - \frac{1}{2^3}\right)\left(\frac{N\lambda^3}{Vg}\right)^2 + \cdots \quad (16)$$

and therefore

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

$$= \frac{3}{2} NKT\left[1 + \frac{1}{2^{5/2}}\left(\frac{N\lambda^3}{Vg}\right) - \left(\frac{2}{3^{5/2}} - \frac{1}{2^3}\right)\left(\frac{N\lambda^3}{Vg}\right)^2 + \cdots\right] \quad (17)$$

The first term is the energy in the Boltzmann limit i.e classical limit where as other terms are the higher order correction terms due to deviation from classical behaviour.

The specific heat

$$C_V = \frac{3}{2}NK\left[1 - \frac{1}{2\times 2^{5/2}}\left(\frac{N\lambda^3}{Vg}\right) + 2\times\left(\frac{2}{3^{5/2}} - \frac{1}{2^3}\right)\left(\frac{N\lambda^3}{Vg}\right)^2 - \cdots\cdots\right]$$

$$= \frac{3}{2}NK\left[1 - 0.0884\left(\frac{N\lambda^3}{Vg}\right) + 0.0066\left(\frac{N\lambda^3}{Vg}\right)^2 - \cdots\right] \quad \cdots\cdots (18)$$

Therefore at finite temperatures, specific heat of gas is smaller than it's limiting value $\frac{3}{2}NK$. With decrease of temperature, specific heat of Fermi gas decreases monotonically.

The correction terms depend on quantity $\frac{N\lambda^3}{Vg}$. It will be small when

$$\frac{N\lambda^3}{Vg} << 1$$

i.e the gas must be sufficiently rarefied or temperature T should be high. At very high temperature, correction term will be very small and could be neglected leading to the classical behaviour.

When the temperature T and density $\frac{N}{V}$ are such that the quantity $\frac{N\lambda^3}{Vg}$ is of the order of unity, the gas is said to become degenerate.

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Thank You

For any questions/doubts/suggestions and submission of assignments

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