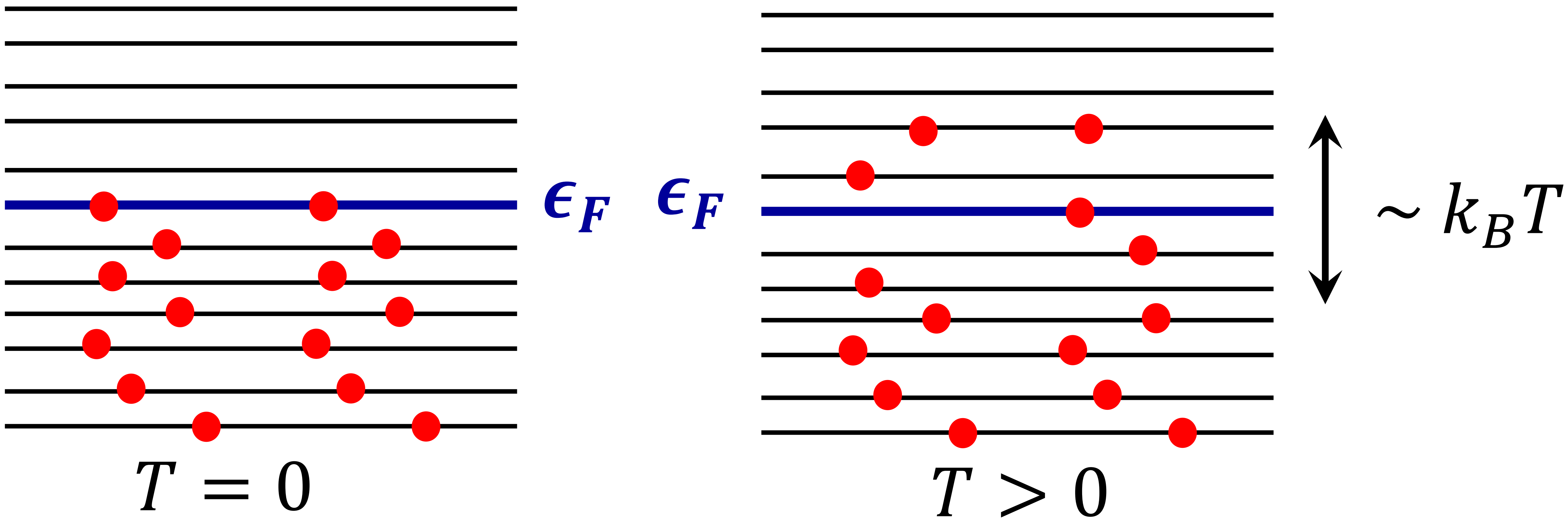
Non-zero temperature behaviour of free electron gas

Chemical potential and Specific heat

At $T = 0$, electrons of a non-interacting electron gas system fill-up the single-particle energy levels up to the Fermi energy level ϵ_F.



At $T > 0$, electrons near the Fermi level get excited and occupy energy levels above ϵ_F.

At some non-zero T, the spreading of electron energy spectrum about ϵ_F is $\sim k_B T$.

Only the electrons near ϵ_F can be excited by thermal energy. These electrons give rise to electronic specific heat of electron gas system.

Metals can be approximated as electron gas system, in this context, experimental observations nicely match with theoretical electron gas model of metals.

Average nos. of electrons in s-th single-particle state,

$$n_s = \frac{2}{\exp[\beta(\epsilon_s - \mu)] + 1}$$

Note that, each single particle state can accommodate two electrons

For macroscopically large system size, the single-particle energy levels form a continuum. ϵ_s is to described by a continuous variable ϵ

Here, the Fermi function can be expressed as,

$$F(\epsilon) = \frac{1}{\exp[\beta(\epsilon - \mu)] + 1} \qquad \text{---------------------- (1)}$$

Here, the Fermi function describes the probability of an electron to be found at energy level ϵ

In continuous energy spectrum, it is logical to ask about nos. of particles in energy interval ϵ to $\epsilon + d\epsilon$

If $\rho(\epsilon)$ is the density of states, then, nos. of electrons within energy interval ϵ to $\epsilon + d\epsilon$ is,

$$n(\epsilon)d\epsilon = 2 \times F(\epsilon)\rho(\epsilon)d\epsilon = 2 \times \frac{\rho(\epsilon)}{\exp[\beta(\epsilon - \mu)] + 1}d\epsilon \qquad \text{---------------} \; (2)$$

If N be the total nos. of electrons in the system, then,

$$N = \int_0^\infty n(\epsilon)d\epsilon = 2\int_0^\infty F(\epsilon)\rho(\epsilon)d\epsilon = 2\int_0^\infty \frac{\rho(\epsilon)}{\exp[\beta(\epsilon - \mu)] + 1}d\epsilon \qquad \text{---------------} \; (3)$$

Total average energy of the system,

$$\bar{E} = \int_0^\infty \epsilon \; n(\epsilon)d\epsilon = 2\int_0^\infty F(\epsilon)\rho(\epsilon)\epsilon \; d\epsilon = 2\int_0^\infty \frac{\epsilon\rho(\epsilon)}{\exp[\beta(\epsilon - \mu)] + 1}d\epsilon \qquad \text{---------} \; (4)$$

The specific heat is defined as,

$$C_V = \frac{\partial \bar{E}}{\partial T} \qquad \text{-------------------} \; (5)$$

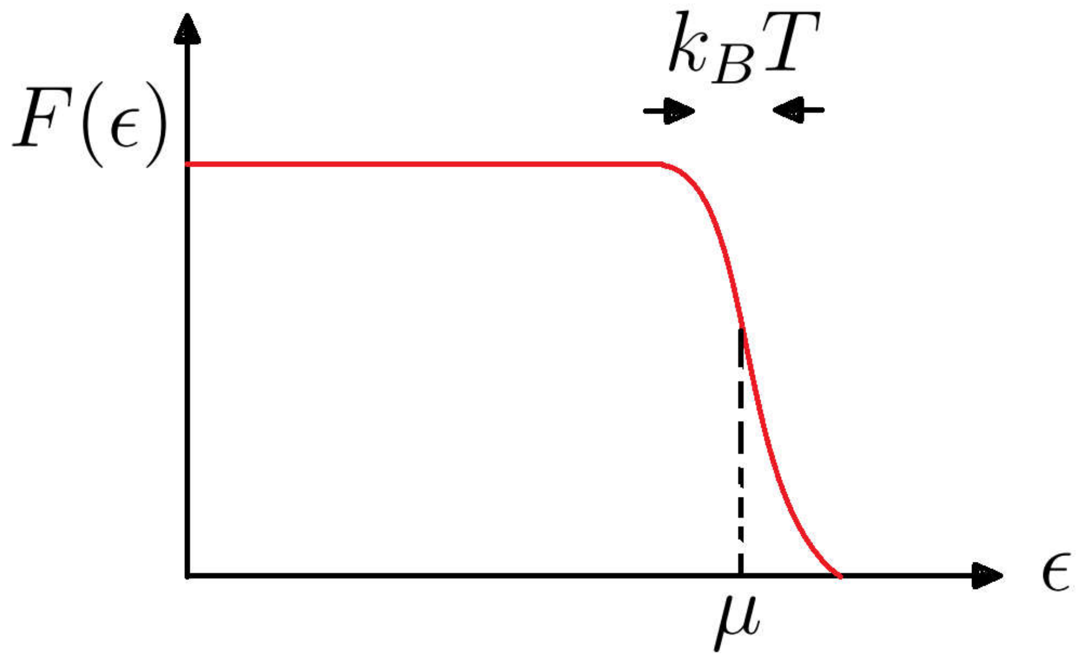
Temperature dependency of chemical potential μ can be established from relation (3) and to find out the temperature dependent electronic specific heat one has to calculate $\bar{E}$ from equation (4).

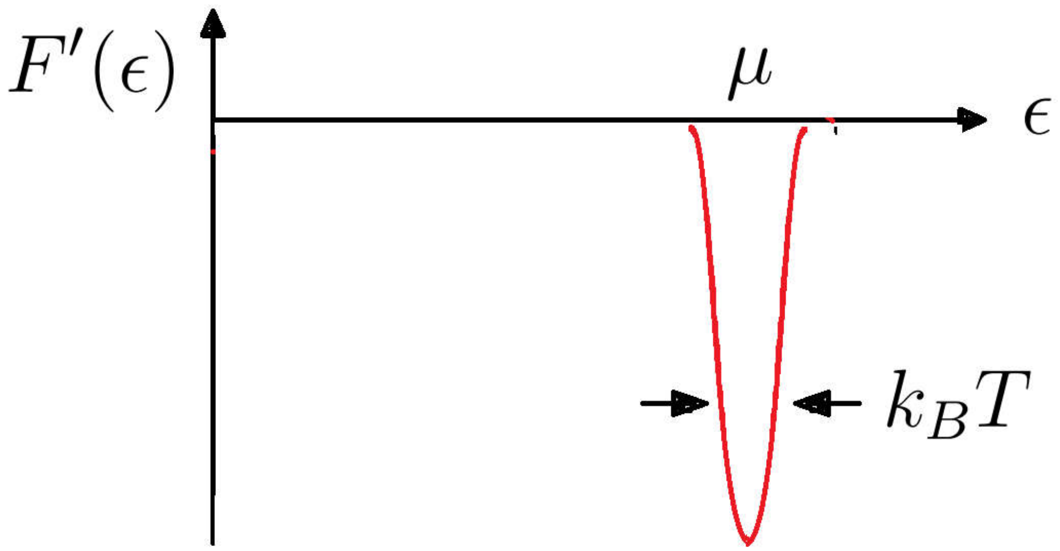
That means we have to perform the integrations given in (3) and (4).

Both these two integrals are in a general form of,

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\; d\epsilon \qquad \text{-------------------- (6)}$$

The Fermi function $F(\epsilon)$ is rapidly decreasing function about $\epsilon \approx \mu$





At room temperature or below the room temperature, for metals (electron gas system) a valid approximation is,

$$\beta\mu = \frac{\mu}{k_B T} \gg 1 \qquad \text{------------------- (7)}$$

This is to be the situation for rapid fall of Fermi function $F(\epsilon)$

The integral in form of (6), have rapidly varying function $F(\epsilon)$ and a slowly varying function $\varphi(\epsilon)$.

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\ d\epsilon \qquad \text{------------------- (6, repeat)}$$

Let define an integral function,

$$\psi(\epsilon) = \int_0^\epsilon \varphi(\epsilon')\ d\epsilon' \qquad \text{------------------- (8)}$$

Integrating by parts of expression (6)

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\ d\epsilon = [F(\epsilon)\psi(\epsilon)]_0^\infty - \int_0^\infty F'(\epsilon)\psi(\epsilon)\ d\epsilon \qquad \text{------------------- (9)}$$

By definition of $\psi(\epsilon)$ in (8) gives $\psi(0) = 0$ and the Fermi function vanishes for large ϵ. Therefore, the first term of the RHS expression of (9) vanishes.

So from (9),

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\ d\epsilon = -\int_0^\infty F'(\epsilon)\psi(\epsilon)\ d\epsilon \qquad \text{------------------- (10)}$$

$F'(\epsilon)$ is appreciable only within a narrow range of $\sim k_B T$ about $\epsilon \approx \mu$ and $\psi(\epsilon)$ is a slowly varying function. So, $\psi(\epsilon)$ can be expanded about $\epsilon \approx \mu$ to evaluate the integral (10)

$$\psi(\epsilon) = \sum_{m=0}^{\infty} \frac{1}{m!}\left[\frac{d^m\psi(\epsilon)}{d\epsilon^m}\right]_\mu (\epsilon-\mu)^m \qquad \text{------------------- (11)}$$

Combining expressions (10) and (11);

$$\Rightarrow \quad \int_0^\infty F(\epsilon)\varphi(\epsilon)\ d\epsilon = -\sum_{m=0}^{\infty} \frac{1}{m!}\left[\frac{d^m\psi(\epsilon)}{d\epsilon^m}\right]_\mu \int_0^\infty F'(\epsilon)(\epsilon-\mu)^m\ d\epsilon \qquad \text{--------- (12)}$$

Now,

$$F(\epsilon) = \frac{1}{\exp[\beta(\epsilon-\mu)]+1} \quad \Rightarrow \quad F'(\epsilon) = -\frac{\beta\exp[\beta(\epsilon-\mu)]}{(\exp[\beta(\epsilon-\mu)]+1)^2} \qquad \text{----------} \ (13)$$

We want to evaluate the RHS integral of (12),

$$\int_0^\infty F'(\epsilon)(\epsilon-\mu)^m \, d\epsilon = -\int_0^\infty \frac{\beta\exp[\beta(\epsilon-\mu)]}{(\exp[\beta(\epsilon-\mu)]+1)^2}(\epsilon-\mu)^m \, d\epsilon \qquad \text{----------} \ (14)$$

Let,

$$x = \beta(\epsilon-\mu)$$

Then,

$$\int_0^\infty F'(\epsilon)(\epsilon-\mu)^m \, d\epsilon = -\beta^{-m}\int_{-\beta\mu}^\infty \frac{x^m e^x}{(e^x+1)^2} \, dx \qquad \text{------------------} \ (15)$$

The function $F'(\epsilon)$ has sharp dip of width $\sim k_B T$ about $\epsilon \approx \mu$. Therefore, integral (14) or (15) can be evaluated within narrow range of the variable x. The integration range of x may be assumed to be $\sim few\ times\ of\ -k_B T\ to \sim few\ times\ of\ +k_B\, T$

In the above approximation of integration range, it is valid to consider the lower limit of RHS integral of (15) to be infinity. Because, $\beta\mu \gg 1$.

So, expression (15) becomes,

$$\int_0^\infty F'(\epsilon)(\epsilon-\mu)^m \, d\epsilon = -\beta^{-m}\int_{-\beta\mu}^\infty \frac{x^m e^x}{(e^x+1)^2}\, dx \approx -\beta^{-m}\int_{-\infty}^\infty \frac{x^m e^x}{(e^x+1)^2}\, dx \quad \text{----- (16)}$$

Now define,

$$I_m = \int_{-\infty}^\infty \frac{x^m e^x}{(e^x+1)^2}\, dx \quad \text{-------------------- (17)}$$

Note that

$$\frac{e^x}{(e^x+1)^2} = \frac{1}{(e^x+1)(e^{-x}+1)} \rightarrow \text{ even function}$$

Therefore, we can see from (17), only the even ordered terms will survive;

$$I_m = 0 \quad \text{if} \quad m \quad \text{is odd}$$

From the definition (17), it is easy to evaluate the value of I_0

$$I_0 = \int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2}\, dx \;=\; \int_{-\infty}^{\infty} \frac{d(e^x+1)}{(e^x+1)^2} \;=\; -\left[\frac{1}{e^x+1}\right]_{-\infty}^{\infty} \;=\; 1 \qquad \text{---------- (18)}$$

For even value of m (since, for odd m values, it is zero),

$$I_m = \int_{-\infty}^{\infty} \frac{x^m e^x}{(e^x+1)^2}\, dx \;=\; 2\int_{0}^{\infty} \frac{x^m e^x}{(e^x+1)^2}\, dx \qquad \text{-------------------- (19)}$$

Now,

$$\int_{0}^{\infty} \frac{x^m e^x}{(e^x+1)^2}\, dx = -\underbrace{\left[\frac{x^m}{e^x+1}\right]_{0}^{\infty}}_{0} + m\int_{0}^{\infty} \frac{x^{m-1}}{e^x+1}\, dx \qquad \text{--------------- (20)}$$

Therefore,

$$I_m = 2m\int_{0}^{\infty} \frac{x^{m-1}}{e^x+1}\, dx \qquad \text{-------------------- (21)}$$

Rewrite equation (16),

$$\int_0^\infty F'(\epsilon)(\epsilon-\mu)^m \, d\epsilon = -\beta^{-m}\int_{-\infty}^{\infty} \frac{x^m e^x}{(e^x+1)^2} \, dx \;=\; -(k_B T)^m I_m \qquad \text{------------ (22)}$$

We can approximate the expansion of (12) up to $m = 2$ since it contains increasing powers of the small valued factor $k_B T$

$I_0 = 1$ is already calculated. We have to calculate I_2

From (21);

$$I_2 = 4\int_0^\infty \frac{x}{e^x+1} \, dx \qquad \text{------------------- (23)}$$

The integrand,

$$\frac{x}{e^x+1} = xe^{-x}(1+e^{-x})^{-1} = xe^{-x}[1-e^{-x}+e^{-2x}-e^{-3x}+\ldots\ldots] = x\sum_{n=1}^{\infty}(-1)^{n+1}e^{-nx}$$

Therefore, from (23)

$$I_2 = 4\sum_{n=1}^{\infty}(-1)^{n+1}\int_0^{\infty} xe^{-nx}\, dx \quad \text{-------------------- (24)}$$

Now,

$$\int_0^{\infty} xe^{-nx}\, dx = \frac{1}{n^2}\int_0^{\infty} ye^{-y}\, dy = \frac{1}{n^2}\Gamma(2) = \frac{1}{n^2} \quad \text{-------------------- (25)}$$

So, from (24) and (25),

$$I_2 = 4\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n^2} = 4 \times \frac{\pi^2}{12} = \frac{\pi^2}{3} \quad \text{-------------------- (26)}$$

Now recall few previous equations

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\ d\epsilon = -\sum_{m=0}^{\infty} \frac{1}{m!}\left[\frac{d^m\psi(\epsilon)}{d\epsilon^m}\right]_\mu \int_0^\infty F'(\epsilon)(\epsilon-\mu)^m\ d\epsilon \quad \text{---------- (12, repeat)}$$

$$\int_0^\infty F'(\epsilon)(\epsilon-\mu)^m\ d\epsilon = -\beta^{-m}\int_{-\infty}^{\infty} \frac{x^m e^x}{(e^x+1)^2}\ dx \ = \ -(k_B T)^m I_m \quad \text{------ (22, repeat)}$$

We have considered expansion of (12) up to $m = 2$

Already obtained in (18) and (26) : $I_0 = 1$ and $I_2 = \pi^2/3$. Note, for odd values of m, $I_m = 0$

Therefore, form (12) and (22),

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\ d\epsilon \approx \psi(\mu) + \frac{\pi^2}{6}(k_B T)^2\psi''(\mu) \quad \text{--------------- (27)}$$

It is defined in (8) that,

$$\psi(\epsilon) = \int_0^{\epsilon} \varphi(\epsilon') \ d\epsilon' \quad \text{------------------- (8, repeat)}$$

Therefore, (27) can be re-expressed as,

$$\int_0^{\infty} F(\epsilon)\varphi(\epsilon) \ d\epsilon \ = \ \int_0^{\mu} \varphi(\epsilon) \ d\epsilon + \frac{\pi^2}{6}(k_B T)^2 \varphi'(\mu) \quad \text{-------------- (28)}$$

Recall expression (3),

$$N = \int_0^{\infty} n(\epsilon) d\epsilon = 2\int_0^{\infty} F(\epsilon)\rho(\epsilon) d\epsilon \quad \text{------------------- (3, repeat)}$$

From (3) and with the help of (28),

$$N \ = \ 2\int_0^{\mu} \rho(\epsilon) \ d\epsilon + \frac{\pi^2}{3}(k_B T)^2 \rho'(\mu) \quad \text{-------------- (29)}$$

Or,

$$N \ = \ 2\int_0^{\mu_0} \rho(\epsilon) \ d\epsilon + 2\int_{\mu_0}^{\mu} \rho(\epsilon) \ d\epsilon + \frac{\pi^2}{3}(k_B T)^2 \rho'(\mu) \quad \text{-------------- (30)}$$

Remember that at $T = 0$, the fermi function can be represented as,

$$F(\epsilon) = \begin{cases} 1 & \text{if } \epsilon < \mu_0 \\ 0 & \text{if } \epsilon > \mu_0 \end{cases} \quad \text{--------------- (31)}$$

That means the first RHS term of (30) : $2\int_0^{\mu_0} \rho(\epsilon)\ d\epsilon\ =\ N$ -------------- (32)

Since $\rho(\epsilon)$ is a slowly varying function, the second term can be approximated as

$$\int_{\mu_0}^{\mu} \rho(\epsilon)\ d\epsilon\ \approx\ \rho(\mu_0)(\mu - \mu_0) \quad \text{-------------- (33)}$$

For the third term of (30), we retain only the zeroth order term as it is multiplied with a small factor $(k_B T)^2$. The higher order terms of ρ' expansion would give rise to more smaller terms.

Therefore, considering these approximations, re-express (30)

$$N = N + 2\rho(\mu_0)(\mu - \mu_0) + \frac{\pi^2}{3}(k_B T)^2 \rho'(\mu_0) \quad \text{-------------- (34)}$$

$$\Rightarrow \quad \mu(T) = \mu_0 - \frac{\pi^2}{6}(k_B T)^2 \frac{\rho'(\mu_0)}{\rho(\mu_0)} \qquad \text{---------------} \ (35)$$

For free electron gas,

$$\rho(\epsilon) \sim \epsilon^{1/2} \qquad \text{---------------} \ (36)$$

Therefore,

$$\frac{\rho'(\mu_0)}{\rho(\mu_0)} = \frac{1}{2\mu_0} \qquad \text{---------------} \ (37)$$

Now, from expression (35)

$$\boxed{\mu(T) = \mu_0 \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\mu_0} \right)^2 + \ldots\ldots \right]} \qquad \text{---------------} \ (38)$$

Higher order smaller correction terms of $\mu(T)$ can be obtained if we consider higher order terms in the expansion of (12).

Recall expression (4),

$$\bar{E} = \int_0^\infty \epsilon\ n(\epsilon) d\epsilon = 2\int_0^\infty F(\epsilon)\rho(\epsilon)\epsilon\ d\epsilon$$ ------------ (4, repeat)

It is already mentioned that the integral of (4) has the form of (6),

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\ d\epsilon$$ ------------------- (6, repeat)

Where, $F(\epsilon) = \dfrac{1}{\exp[\beta(\epsilon-\mu)]+1}$ is a rapidly varying function about $\epsilon \approx \mu$.

and $\varphi(\epsilon) = \epsilon\rho(\epsilon)$ which is a smoothly varying function

It has been derived in (28) that,

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\ d\epsilon\ = \int_0^\mu \varphi(\epsilon)\ d\epsilon + \frac{\pi^2}{6}(k_B T)^2 \varphi'(\mu)$$ --------------- (28, repeat)

Therefore, integration of (4) can be evaluated with the help of (28);

$$\bar{E} = 2\int_0^{\mu} \epsilon\rho(\epsilon)\ d\epsilon + \frac{\pi^2}{3}(k_B T)^2 \left[\frac{d}{d\epsilon}(\epsilon\rho(\epsilon))\right]_{\mu} \quad \text{--------------- (39)}$$

Now,

$$\int_0^{\mu} \epsilon\rho(\epsilon)\ d\epsilon \;=\; \underbrace{\int_0^{\mu_0} \epsilon\rho(\epsilon)\ d\epsilon}_{Term-1} + \underbrace{\int_{\mu_0}^{\mu} \epsilon\rho(\epsilon)\ d\epsilon}_{Term-2} \;\approx\; \bar{E}_0 + 2\mu_0\rho(\mu_0)(\mu-\mu_0) \quad \text{------ (40)}$$

In (40), the first term is the total energy at $T = 0$ and the second term is approximated as it is slowly varying function and μ is very close to μ_0.

In (39), the second term can be approximated only with the leading order as it is already multiplied with small factor of $(k_B T)^2$.

$$\Rightarrow \quad \left[\frac{d}{d\epsilon}(\epsilon\rho(\epsilon))\right]_{\mu} \;\approx\; \rho(\mu_0) + \mu_0\rho'(\mu_0) \quad \text{--------------- (41)}$$

With the help of (40) and (41), on can re-express (39) as;

$$\bar{E} = \bar{E}_0 + 2\mu_0\rho(\mu_0)(\mu - \mu_0) + \frac{\pi^2}{3}(k_B T)^2[\rho(\mu_0) + \mu_0\rho'(\mu_0)]$$ --------------- (42)

It is established in (35),

$$(\mu - \mu_0) = -\frac{\pi^2}{6}(k_B T)^2\frac{\rho'(\mu_0)}{\rho(\mu_0)}$$ --------------- (43)

Therefore, from (42),

$$\bar{E} = \bar{E}_0 + \frac{\pi^2}{3}(k_B T)^2\rho(\mu_0)$$ --------------- (44)

Electronic specific heat of the electron gas system,

$$C_V = \frac{\partial \bar{E}}{\partial T} = \frac{2\pi^2}{3}k_B^2\rho(\mu_0)T$$ --------------- (45)

Density of states of free electron gas,

$$\rho(\epsilon)d\epsilon = \frac{V}{4\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\epsilon^{1/2}d\epsilon \quad \Rightarrow \quad \rho(\mu_0) = \frac{V}{4\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\mu_0^{1/2}$$ ---------- (46)

Zero temperature chemical potential or the Fermi energy,

$$\mu_0 = \frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{2/3}$$ --------------- (47)

Ealuating V from (46) and (47);

$$\rho(\mu_0) = \frac{3N}{4\mu_0}$$ ------------------ (48)

Therefore, from (45), we get the expression of specific heat of N-particle free electron gas

$$C_V = N\left(\frac{\pi^2 k_B^2}{2\mu_0}\right)T$$ ------------------ (49)