Density of states $g(\varepsilon)$

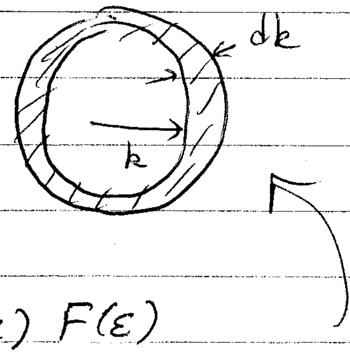
Often we want to sum a quantity that depends on $\vec{k}$ only through the energy ε_k, ie

$$\sum_{s} \sum_{\vec{k}} F(\varepsilon_k) = 2 \sum_{\vec{k}} F(\varepsilon_k) = \frac{V}{4\pi^3} \int d^3k \, F(\varepsilon_k)$$

↑ sum over spin states

Define $g(\varepsilon)$ as the number of states per unit energy per unit volume, ie

$$\frac{1}{V} \sum_{s} \sum_{\vec{k}} = \underset{\substack{\vec{k} \text{ such that} \\ \varepsilon \le \varepsilon_k \le \varepsilon + d\varepsilon}}{\frac{1}{4\pi^3} \int d^3k} = g(\varepsilon) \, d\varepsilon$$



Then $$\frac{1}{V} \sum_{s} \sum_{\vec{k}} F(\varepsilon_k) = \int d\varepsilon \, g(\varepsilon) \, F(\varepsilon)$$

When ε_k depends on $\vec{k}$ only through $|\vec{k}|$, ~~we can write~~ volume of integrale in $\vec{k}$-space is a spherical shell of width dk and we can write

$$\frac{1}{4\pi^3} \int d^3k = \frac{4\pi}{4\pi^3} \int dk \, k^2 = \frac{1}{\pi^2} \int dk \, k^2 = \int g(\varepsilon) \, d\varepsilon$$

$$\frac{1}{\pi^2} k^2 \, dk = g(\varepsilon) \, d\varepsilon$$

$$\boxed{g(\varepsilon) = \frac{1}{\pi^2} k^2 \frac{dk}{d\varepsilon}}$$

For free electrons $\varepsilon = \frac{\hbar^2 k^2}{2m}$

$$g(\varepsilon) = \frac{1}{\pi^2} \frac{2m\varepsilon}{\hbar^2} \frac{1}{(d\varepsilon/dk)}$$

$$= \frac{2m\varepsilon}{\pi^2\hbar^2} \frac{1}{\frac{2\hbar^2 k}{2m}} = \frac{2m\varepsilon}{\pi^2\hbar^2} \frac{k}{2\varepsilon}$$

$$= \frac{m}{\pi^2\hbar^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

$$\boxed{g(\varepsilon) = \frac{m}{\pi^2\hbar^3} \sqrt{2m\varepsilon}} \quad \propto \sqrt{\varepsilon}$$

~~Total energy~~

~~$\frac{E}{V} = \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)\, \varepsilon$~~

Write $g(\varepsilon) = C\sqrt{\varepsilon}$ where C is appropriate const

Density of electrons

$$n = \frac{1}{V} \sum_s \sum_{|\vec{k}|<k_F} 1 \qquad \text{count states}$$

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

so $C = \frac{3}{2} \frac{n}{\varepsilon_F^{3/2}}$

$$\boxed{g(\varepsilon) = \frac{3}{2} \frac{n}{\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}}}$$

Total energy

$$\frac{E}{V} = \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)\, \varepsilon = C \int_0^{\varepsilon_F} d\varepsilon\, \varepsilon^{3/2} = \frac{2}{5} C \varepsilon_F^{5/2}$$

$$= \frac{2}{5} \cdot \frac{3}{2} \frac{n}{\varepsilon_F^{3/2}} \varepsilon_F^{5/2}$$

$$\boxed{\frac{E}{V} = \frac{3}{5} n \varepsilon_F}$$ same as we found before

We will see that $g(\varepsilon)$, and in particular $g(\varepsilon_F)$ is a *very* important quantity in determining the behavior of conduction electrons in a metal

Pressure of conduction electrons in a metal

From thermodynamics

$$dE = TdS - p\,dV$$

at $T=0$

$$dE = -p\,dV$$

$$p = -\left(\frac{dE}{dV}\right)$$

Now $E = \frac{3}{5} V n \varepsilon_F = \frac{3}{5} N \varepsilon_F$

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} \quad \text{where} \quad k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3}$$

so $\varepsilon_F \propto V^{-2/3}$ for constant N

$E = \text{const}\ V^{-2/3}$ $\qquad$ $\text{const} = \frac{3}{5} N \frac{\hbar^2}{2m} (3\pi^2 N)^{2/3}$

$$-\frac{dE}{dV} = \frac{2}{3}\,\text{const}\ V^{-5/3} = \frac{2}{3}\,\text{const}\ \frac{V^{-2/3}}{V}$$

$$\boxed{p = \frac{2}{3}\frac{E}{V}} = \frac{2}{3}\frac{3}{5}\, n\varepsilon_F = \frac{2}{5}\, n\varepsilon_F$$

~~Bulk modulus~~ Compare to a classical ideal gas where

$p = n k_B T$ classical

we now have: $p = \frac{2}{5} n k_B T_F$ quantum where $\varepsilon_F = k_B T_F$

since $T_F \gg T$ for a metal

$p_{\text{quantum}} \gg p_{\text{classical}}$

Bulk modulus $\quad B \equiv 1/\kappa \quad , \quad \kappa$ = compressibility

$$B = -V\left(\frac{\partial p}{\partial V}\right)_N \leftarrow \text{derivative is at constant } N$$

$p = \frac{2}{3}\frac{E}{V}$ and $E = \text{const}\ V^{-2/3}$

$\Rightarrow p = \text{const}\ V^{-5/3}$

$$B = -V\left(\frac{\partial p}{\partial V}\right)_N = +V\,\frac{5}{3}\,\text{const}\ V^{-7/3} = \frac{5}{3}\,\text{const}\ V^{-5/3}$$

$$= \frac{5}{3} p = \frac{5}{3}\cdot\frac{2}{3}\frac{E}{V} = \frac{10}{9}\frac{E}{V} = \frac{10}{9}\frac{3}{5}\, n\varepsilon_F = \frac{2}{3}\, n\varepsilon_F$$

$$\boxed{B = \frac{2}{3} n \varepsilon_F} \quad \text{at } T=0$$

$$= \left[\frac{6.15}{(r_s/a_0)}\right]^5 \times 10^{10} \text{ dynes/cm}^2$$

metal	B - theory	B - expt	($\times 10^{10}$ dynes/cm^2)
Li	23.9	11.5	
Na	9.25	6.42	
Cu	63.8	134.3	
Ag	34.5	99.9	

Our free electron model gives correct order of magnitude. Note that our calculation gives only the contribution to B from the conduction electrons, whereas the measured B in experiment has also a contribution from the lattice of ions. We see that the electronic contribution is clearly just as important as the ionic contribution

Free electron gas at finite temperature

Fermi occupation function - at finite temperature T

$$f_i = \frac{1}{e^{(\varepsilon_i - \mu)/k_B T} + 1}$$

is the average number of electrons in single electron state "i", where ε_i is the energy of this state. Note: for fermions, since there can only be 0 or 1 electron in any given state, f_i is also equal to the probability that state "i" is occupied.

Here "i" stands for the complete set of quantum numbers needed to specify the single electron state. For a free electron, "i" labels both the wavevector $\vec{k}$ and spin s.

For a derivation of the fermi occupation function see Ashcroft + Mermin pages 40-42, or Kittel Appendix D, or any book on statistical mechanics.

μ is the chemical potential, determined by the condition that

$$\sum_i f_i = N$$

sum over all single electron states

total number of fermions in the system

or, dividing by volume V,

$$\frac{N}{V} = n = \underbrace{\frac{1}{V}\sum_i f_i}$$ determines μ as function of density n and temperature T.

$\uparrow$ ~~there~~ is independent of V in the thermodynamic limit

In terms of the density of states $g(\varepsilon)$

$$n = \frac{1}{V}\sum_i f_i = \frac{1}{V}\sum_{\vec{k}}\sum_s f_{\vec{k},s} = \int d\varepsilon\, g(\varepsilon)\, f(\varepsilon)$$

$\uparrow$ since f depends on $\vec{k}$ and s only through $\varepsilon_{\vec{k},s}$

for metal, n is fixed constant at all temp T $\longrightarrow$

So

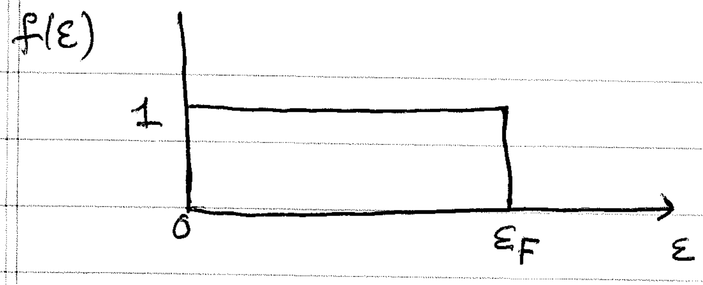
$$\boxed{n = \int d\varepsilon\, g(\varepsilon)\, \frac{1}{e^{(\varepsilon-\mu)/k_BT}+1}}$$ $\leftarrow$ determines $\mu(T,n)$

As $T\to 0$, $$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_BT}+1} = \begin{cases} 0, & \varepsilon > \mu \\ 1, & \varepsilon < \mu \end{cases}$$

So
$$n = \int_0^{\mu} d\varepsilon\, g(\varepsilon)$$

But earlier we had
$$n = \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)$$

So as $T\to 0$, $\mu \to \varepsilon_F$ the Fermi energy.

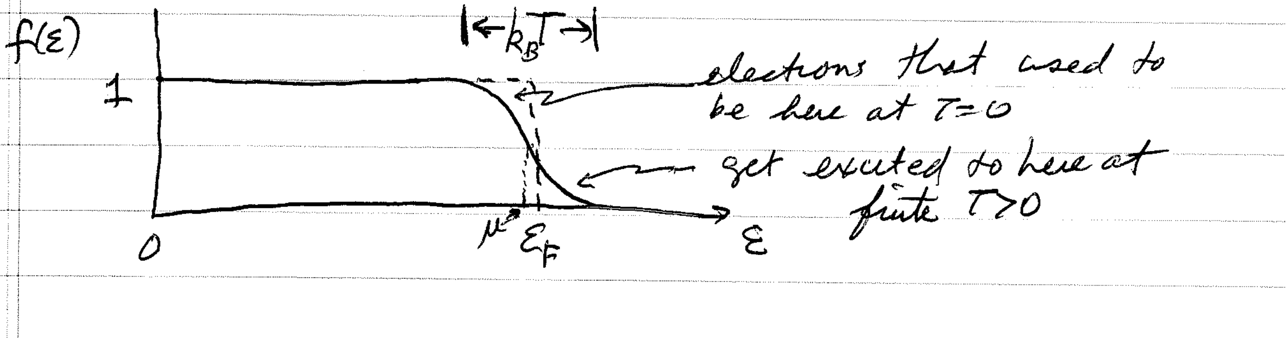


at $T=0$

At finite temperature, electrons can absorb thermal energy k_BT from the heat reservoir that keeps the system at temperature T (we are thinking of the canonical ensemble)

But for an electron with $\varepsilon \ll \varepsilon_F - k_BT$, absorbing k_BT energy would just take it to a state that is already filled. Pauli exclusion principle prevents this from happening.

$\Rightarrow$ The only electrons which can change their state when the system is at finite temperature are those within $\sim k_BT$ of ε_F. Only these states can go ~~to~~ from a filled to an empty state by absorbing k_BT energy from the heat bath



when $\varepsilon = \mu$, $f(\varepsilon) = 1/2$

Since $g(\varepsilon) \sim \sqrt{\varepsilon}$, there are more empty states within $k_B T$ above ε_F than there are within $k_B T$ below ε_F.

Since $f(\mu) = 1/2$ is the dividing point in energy between states which are more likely filled and those that are more likely empty (since $f(\varepsilon)$ is also the probability the state is occupied) we see that at finite temperature $\mu(T, n)$ must decrease somewhat from its value ε_F at $T=0$.

A more precise calculation (see the "Sommerfeld expansion" in Ashcroft + Mermin pgs 45-47) gives the result (Ashcroft + Mermin Eq (2.78))

$$\mu(T,n) = \varepsilon_F \left[1 - \frac{1}{3} \left(\frac{\pi k_B T}{2 \varepsilon_F} \right)^2 \right]$$

↑ gives dependence on T

dependence of μ on n is via ε_F

since $T_F \sim 10^4$ °K for most metals, the correction to the chemical potential at finite temperature are

$$|\mu(T) - \varepsilon_F| \sim \left(\frac{T}{T_F} \right)^2 \sim 10^{-4} \text{ at room temperature}$$

So for most purposes it will be OK to approx $\mu(T) \approx \varepsilon_F$ even at finite temperature.

Derivation of $\mu(T)$ for $T \ll T_F$

density of electrons is $n = \int_0^\infty d\varepsilon\, g(\varepsilon)\, f(\varepsilon)$

density of electrons remains fixed as temperature varies

$$\Rightarrow \frac{\partial n}{\partial T} = 0 = \int_0^\infty d\varepsilon\, g(\varepsilon)\, \frac{\partial f}{\partial T}$$

fermi function $f(\varepsilon) = \frac{1}{e^x + 1}$ where $x = \frac{\varepsilon - \mu(T)}{k_B T}$

so $$\frac{\partial f}{\partial T} = \frac{\partial f}{\partial x}\frac{\partial x}{\partial T} = \left(-\frac{\partial f}{\partial x}\right)\left[\frac{x}{T} + \frac{1}{k_B T}\frac{d\mu}{dT}\right]$$

$$d\varepsilon = k_B T\, dx$$

$$\Rightarrow 0 = \int_{-\frac{\mu}{k_B T}}^{\infty} dx\, g(\varepsilon)\left(-\frac{\partial f}{\partial x}\right)\left[\frac{x}{T} + \frac{1}{k_B T}\frac{d\mu}{dT}\right]$$

Since $\left(-\frac{\partial f}{\partial x}\right)$ is strongly peaked about $\varepsilon = \mu$ and vanishes for $\varepsilon \ll \mu$ or $\varepsilon \gg \mu$,

we can ① extend lower limit of integration to $-\infty$

② approximate $g(\varepsilon) \simeq g(\mu) + g'(\mu)(\varepsilon - \mu)$

$$= g(\mu) + g'(\mu)\, k_B T\, x$$

then

$$0 = \int_{-\infty}^{\infty} dx\, \left[g(\mu) + g'(\mu)\, k_B T x\right]\left[\frac{x}{T} + \frac{1}{k_B T}\frac{d\mu}{dT}\right]\left(-\frac{\partial f}{\partial x}\right)$$

Now $\left(-\frac{\partial f}{\partial x}\right) = \frac{e^x}{(e^x+1)^2}$

one can check that $\left(-\frac{\partial f}{\partial x}\right)$ is symmetric function of x

Therefore $\int_{-\infty}^{\infty} dx \left(-\frac{\partial f}{\partial x}\right) x = 0$

So we get

$$0 = \frac{g(\mu)}{k_B T}\frac{d\mu}{dT}\int_{-\infty}^{\infty} dx \left(-\frac{\partial f}{\partial x}\right) + g'(\mu) k_B \int_{-\infty}^{\infty} dx \left(-\frac{\partial f}{\partial x}\right) x^2$$

where $\int_{-\infty}^{\infty} dx \left(-\frac{\partial f}{\partial x}\right) = f(-\infty) - f(\infty) = 1 - 0 = 1$

$$\int_{-\infty}^{\infty} dx \left(-\frac{\partial f}{\partial x}\right) x^2 = \int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x+1)^2} = \frac{\pi^2}{3}$$

$$0 = \frac{g(\mu)}{k_B T}\frac{d\mu}{dT} + \frac{\pi^2}{3} g'(\mu) k_B$$

$$\Rightarrow \frac{d\mu}{dT} = -\frac{\pi^2}{3}\frac{g'(\mu)}{g(\mu)} k_B^2 T$$

expect $\frac{g'(\mu)}{g(\mu)} \sim \frac{1}{\mu} \sim \frac{1}{\varepsilon_F}$ at low T

so $\frac{d\mu}{dT} \sim \frac{k_B T}{\varepsilon_F} \sim \left(\frac{T}{T_F}\right) \sim 10^{-2}$ is small for all metals

Therefore can approximate

$$\frac{d\mu}{dT} \simeq -\frac{\pi^2}{3}\frac{g'(\varepsilon_F)}{g(\varepsilon_F)} k_B^2 T$$

↑ replaced μ by ε_F in argument of g ad g'. Corrections to this just give terms higher order in T/T_F

$$\mu(T) = \varepsilon_F - \frac{\pi^2}{6}\frac{g'(\varepsilon_F)}{g(\varepsilon_F)}(k_B T)^2$$

$$\boxed{\mu(T) = \varepsilon_F\left[1 - \frac{\pi^2}{6}\frac{g'(\varepsilon_F)}{g(\varepsilon_F)}\frac{(k_B T)^2}{\varepsilon_F}\right]}$$

For free electron gas, $g(\varepsilon) = \frac{3}{2}\frac{m}{\varepsilon_F}\sqrt{\frac{\varepsilon}{\varepsilon_F}}$, $g(\varepsilon_F) = \frac{3}{2}\frac{m}{\varepsilon_F}$

$g'(\varepsilon) = \frac{3}{4}\frac{m}{\varepsilon_F}\sqrt{\frac{\varepsilon}{\varepsilon_F}}\frac{1}{\varepsilon}$, $g'(\varepsilon_F) = \frac{3}{4}\frac{m}{\varepsilon_F^2}$

$$\mu(T) = \varepsilon_F\left[1 - \frac{\pi^2}{6}\frac{\left(\frac{3}{4}\frac{m}{\varepsilon_F^2}\right)}{\left(\frac{3}{2}\frac{m}{\varepsilon_F}\right)}\frac{(k_B T)^2}{\varepsilon_F}\right]$$

$$\boxed{\mu(T) = \varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]}$$

so $\frac{\mu(T) - \varepsilon_F}{\varepsilon_F} \sim O\left(\frac{k_B T}{\varepsilon_F}\right)^2 \sim 10^{-4}$

⇒ In most situations can ignore T dependence of μ ad take $\mu(T) = \varepsilon_F$