

Free electron gas at finite temperature

Fermi occupation function - at finite temperature T

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

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 ,

$$\frac{N}{V} = n = \frac{1}{V} \sum_i f_i \quad \text{determines } \mu \text{ as function of density } n \text{ and temperature}$$

↑
this is independent of V in the thermodynamic limit

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

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

↑ since f depends on \vec{k} and s only through $\epsilon_{\vec{k},s}$

So

$$n = \int d\epsilon g(\epsilon) \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$$

← determines $\mu(T, n)$

for metal,
 n is fixed
constant at
all temp T

$$\text{As } T \rightarrow 0, \quad f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1} = \begin{cases} 0, & \epsilon > \mu \\ 1, & \epsilon < \mu \end{cases}$$

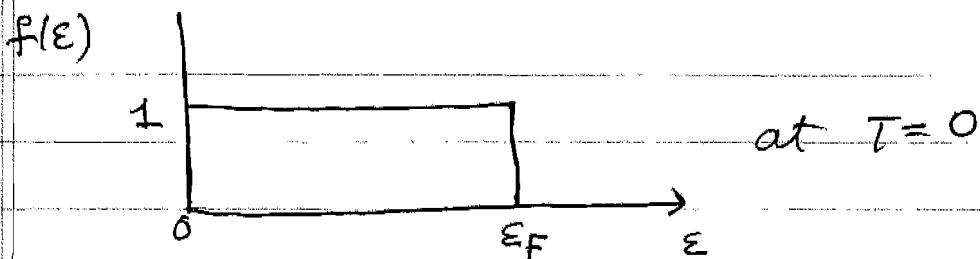
So

$$n = \int_0^{\mu} d\epsilon g(\epsilon)$$

But earlier we had

$$n = \int_0^{\epsilon_F} d\epsilon g(\epsilon)$$

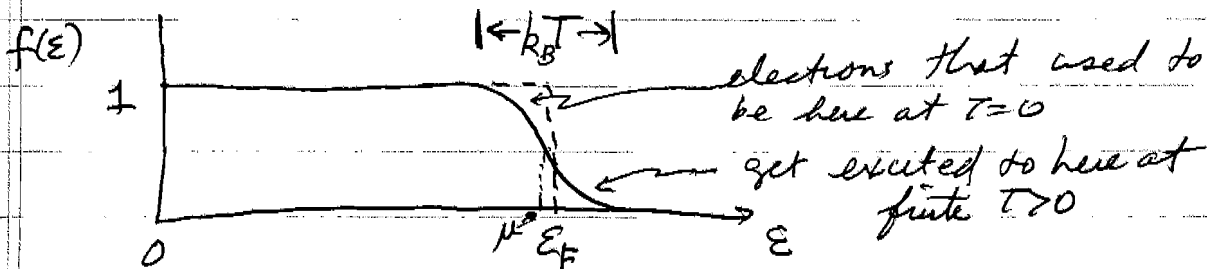
So as $T \rightarrow 0$, $\mu \rightarrow \epsilon_F$ the Fermi energy.



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

But for an electron with $E \ll E_F - k_B T$, absorbing $k_B T$ 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 $\sim k_B T$ of E_F . Only these states can go from a filled to an empty state by absorbing $k_B T$ energy from the heat bath



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

Since $g(E) \sim \sqrt{E}$, there are more empty states

within $k_B T$ above E_F than there are within $k_B T$ below E_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 $f(\epsilon)$ is also the probability the state is occupied) we see that at finite temperature $\mu(T, n)$ must decrease somewhat from its value E_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))

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

↑ gives dependence on T
dependence of μ on n is via E_F

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

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

So for most purposes it will be OK to approx $\mu(T) \approx E_F$ 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 $x = \frac{\varepsilon - \mu(T)}{k_B T}$

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

$$d\varepsilon = k_B T dx$$

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

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 $-\infty$

$$\text{② approximate } g(\varepsilon) = g(\mu) + g'(\mu)(\varepsilon - \mu)$$

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

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

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

therefore can approximate

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

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

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

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

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

$$g'(\epsilon) = \frac{3}{4} \frac{m}{\epsilon_F} \sqrt{\frac{\epsilon}{\epsilon_F}} \frac{1}{\epsilon}, \quad g'(\epsilon_F) = \frac{3}{4} \frac{m}{\epsilon_F^2}$$

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

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

so $\frac{\mu(T) - \epsilon_F}{\epsilon_F} \sim 0 \left(\frac{k_B T}{\epsilon_F}\right)^2 \sim 10^{-4}$

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

Specific Heat of Electron Gas

Hand waving argument

Specific heat per volume $c_v = \frac{dU}{dT}$
where $u = \frac{E}{V}$ is energy per volume

When start at $T=0$ and increase temperature to T , it is only the electrons within $k_B T$ of E_F that can absorb $\Delta E = k_B T$ of energy from the thermal bath. So the change in energy per volume is

$$u - u_0 = \Delta u = k_B T \times (\text{number of electrons that absorb energy from heat bath per volume})$$

The ~~most~~ number of electrons that absorb energy is just the number of electrons with $\Delta E = k_B T$ of the Fermi energy. This is $g(E_F) \Delta E = g(E_F) k_B T$
 \uparrow density of electrons per energy per volume

So

$$\Delta u = (k_B T) g(E_F) k_B T = g(E_F) (k_B T)^2$$

$$\text{So } c_v = \frac{d\Delta u}{dT} = 2 g(E_F) k_B^2 T \sim T$$

Specific heat of conduction electrons at $T \ll T_F$ is linear in temperature

and proportional to the density of states at the Fermi energy $g(E_F)$. We will see that many thermodynamic quantities are proportional to $g(E_F)$. This is because it is only the electrons close to E_F that are able to do anything different from the ground state at finite T , (when $T \ll T_F$) and $g(E_F)$ gives the density of such electrons.

For the free electron gas we had

$$g(\epsilon) = \frac{3}{2} \frac{m}{E_F} \sqrt{\frac{\epsilon}{E_F}}$$

$$\text{So } g(E_F) = \frac{3}{2} \frac{m}{E_F}$$

$$\Rightarrow C_V \sim 3m \frac{k_B^2 T}{E_F} = 3m k_B \left(\frac{T}{T_F} \right)$$

Compare this to a classical ideal gas where

$$C_V = \frac{3}{2} m k_B$$

We see that the specific heat of the quantum fermi gas is $\sim (T/T_F) \sim 10^{-2}$ times smaller at room temperature.

Also, whereas the classical C_V is independent of temperature, the quantum C_V is linear in temperature. This difference will help fix some of the problems with the classical Drude model.

A more precise calculation using the Sommerfeld expansion (see Ashcroft + Mermin pgs 45-47, Eq (2-81) or Kittel pgs 142-144) gives the result

$$C_V = \frac{\pi^2}{3} g(E_F) k_B^2 T$$

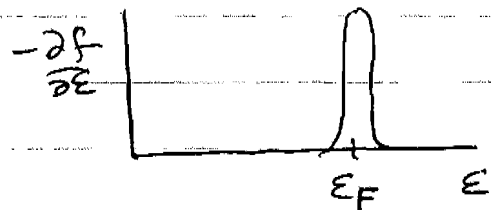
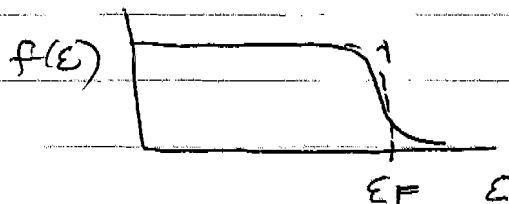
Quick derivation ∞ (from Kittel)

$$\textcircled{1} \quad u = \int_0^{\infty} d\varepsilon g(\varepsilon) \varepsilon f(\varepsilon) \Rightarrow \frac{du}{dT} = \int_0^{\infty} d\varepsilon g(\varepsilon) \varepsilon \frac{\partial f}{\partial T}$$

$$\textcircled{2} \quad n = \int_0^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon) \Rightarrow 0 = \frac{\partial n}{\partial T} = \int_0^{\infty} d\varepsilon g(\varepsilon) \frac{\partial f}{\partial T}$$

Subtract E_F times $\textcircled{2}$ from $\textcircled{1}$

$$C_V = \frac{du}{dT} = \frac{du}{dT} - 0 = \int_0^{\infty} d\varepsilon g(\varepsilon) (\varepsilon - E_F) \frac{\partial f}{\partial T}$$



$\frac{\partial f}{\partial T} \approx 0$ except for energies within $k_B T$ of E_F

\Rightarrow approx $g(\varepsilon)$ in integral by constant $g(E_F)$

$$\frac{\partial u}{\partial T} = g(E_F) \int_0^{\infty} d\varepsilon (\varepsilon - E_F) \left(\frac{\partial f}{\partial T} \right)$$

$$\frac{\partial f}{\partial T} = \frac{\partial}{\partial T} \left[\frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1} \right] \approx \left(\frac{\partial f}{\partial x} \right) \left(\frac{\varepsilon - \mu}{k_B T^2} \right)$$

where $x = \left(\frac{\varepsilon - \mu}{k_B T} \right)$. { ignore $\mu(T)$ dependence on T
 since $\mu \approx E_F$. correction
 give higher order terms

At low $T \ll T_F$, we can replace $\mu(T) \approx E_F$

$$\begin{aligned} \text{So } \frac{\partial u}{\partial T} &= g(E_F) \int_0^{\infty} d\varepsilon \frac{(\varepsilon - E_F)^2}{k_B T^2} \left(-\frac{\partial f}{\partial x} \right) \\ &= g(E_F) k_B^2 T \int_0^{\infty} dx x^2 \left(-\frac{\partial f}{\partial x} \right) \\ &= g(E_F) k_B^2 T \int_0^{\infty} dx x^2 \frac{e^x}{(e^x + 1)^2} \\ &= \frac{\pi^2}{3} \end{aligned}$$

$$\Rightarrow C_V = \frac{\partial u}{\partial T} = \frac{\pi^2}{3} g(E_F) k_B^2 T$$

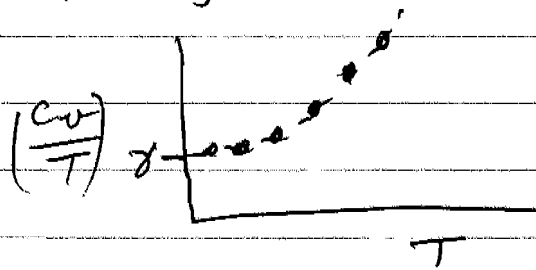
Above is just the contribution to the specific heat of a metal from the conduction electrons. The total specific heat of the metal also includes contributions from vibrations of the ions. This ionic contribution goes like $3n_{\text{ion}} k_B$ at high temperatures ($n_{\text{ion}} = n/z$ is ion density; $z =$ electron valence) but at low T , we will find that due to quantum effects it goes like T^3 . So at high $T \sim$ room temp, the ionic contribution to metallic specific heat dominates the electronic part, and we cannot measure the electronic part to test it against theory. But at low T , one can measure C_V and fit it to the form

$$C_V = \gamma T + AT^3$$

function of
density n

where our calculation predicts $\gamma = \frac{\pi^2}{2} \frac{nk_B}{T_F}$

one plots $\frac{C_V}{T} = \gamma + AT^2$ and determines γ by extrapolating to the $T \rightarrow 0$ intercept



one finds (see A+M table 3.3)

metal	γ (theory)	γ (expt)	$(10^{-4} \frac{\text{cal}}{\text{mole } ^\circ\text{K}^2})$
Li	1.8	4.2	
Na	2.6	3.5	
K	4.0	4.7	
Rb	4.6	5.8	
Mn	1.5	40.	
Fe	1.5	12	
Bi	4.3	0.2	

The alkali metals (Li, Na) come out reasonable
 The noble metals (Cu, Ag, Au) come out reasonable
 Both alkali & noble metals have valence $Z=1$

But there are much bigger discrepancies for

Fe, Mn, Bi, Sb

\uparrow ~ 10 times too big \uparrow ~ 10 times too small

The difference between γ_{theory} and γ_{expt} is usually due to the difference between the real $g(E_F)$ and the free electron approximation for $g(E_F)$. This is because the potential energy due to the ions shifts the energy spectrum E_k from the simple free electron $\frac{\hbar^2 k^2}{2m}$. We can often approx the true E_k as $\frac{\hbar^2 k^2}{2m^*}$ where m^* is the effective mass that can be either bigger or smaller than the free electron mass.