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,

$$\frac{N}{V} = m = \underbrace{\frac{1}{V} \sum_i f_i}_{} \qquad \text{determines } \mu \text{ as function of density } m \text{ and temperature } T.$$

This is independent of V in the thermodynamic limit

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

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

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

So

for metal, m is fixed constant at all temp T

$$\boxed{m = \int d\varepsilon \, g(\varepsilon) \, \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}} \quad \leftarrow \text{determines } \mu(T, m)$$
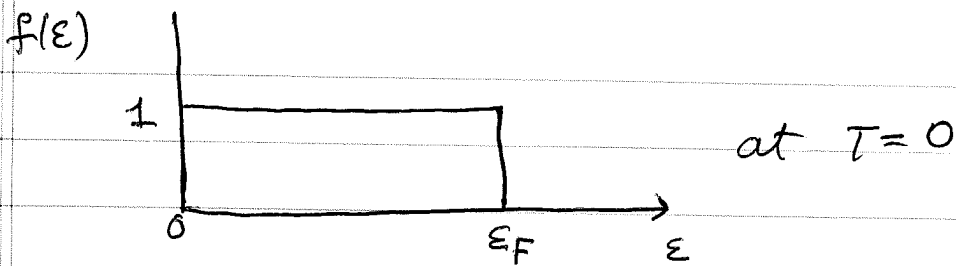
As $T \to 0$, $f(\varepsilon) = \dfrac{1}{e^{(\varepsilon - \mu)/k_B T} + 1} = \begin{cases} 0, & \varepsilon > \mu \\ 1, & \varepsilon < \mu \end{cases}$

So

$$m = \int_0^\mu d\varepsilon \, g(\varepsilon)$$

But earlier we had

$$m = \int_0^{\varepsilon_F} d\varepsilon \, g(\varepsilon)$$

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

$f(\varepsilon)$

1

0

ε_F

ε

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 from a filled to an empty state by absorbing k_BT energy from the heat bath

$f(\varepsilon)$

$|\leftarrow k_BT \rightarrow|$

1

μ ε_F

ε

0

electrons that used to be here at $T=0$

get excited to here at finite $T > 0$

when $\varepsilon = \mu$, $f(\varepsilon) = \frac{1}{2}$

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 $f(\mu) = \frac{1}{2}$ is the dividing point ~~between~~ in energy
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   (Ashroft + 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 $T_F \sim 10^4 \, {}^\circ K$ 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
$$n = \int_0^\infty d\varepsilon \, g(\varepsilon) \cdot f(\varepsilon)$$

density of electrons remains fixed as temperature varies

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

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

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

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

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

Since $\left(-\dfrac{\partial f}{\partial x} \right)$ 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 $g(\varepsilon) \doteq g(\mu) + g'(\mu)(\varepsilon - \mu)$

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

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

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

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

So we get

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

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

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

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

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

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

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

therefore can approximate

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

↳ replaced μ by ε_F in arguement of g and 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, $g(\varepsilon) = \frac{3}{2} \frac{m}{\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}}$, $g(\varepsilon_F) = \frac{3}{2} \frac{m}{\varepsilon_F}$

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

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

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

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

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

Specific Heat of Electron Gas

Hand waving argument

Specific heat per volume $\quad c_V = \dfrac{dU}{dT}$
where $U = \dfrac{E}{V}$ is energy per volume

When start at $T=0$ and increase temperature to T, it is only the electrons within $k_B T$ of ε_F that can absorb $\Delta \varepsilon = k_B T$ 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 number of electrons that absorb energy is just the number of electrons with $\Delta \varepsilon = k_B T$ of the Fermi energy. This is $g(\varepsilon_F)\Delta \varepsilon = g(\varepsilon_F) k_B T$

$\hookleftarrow$ density of electrons per energy per volume

So

$$\Delta U = (k_B T)\, g(\varepsilon_F)\, k_B T = g(\varepsilon_F)(k_B T)^2$$

So $\quad c_V = \dfrac{d\,\Delta U}{dT} = 2 g(\varepsilon_F) k_B^2 T \sim T$

Specific heat of conduction electrons at $T \ll T_F$ is <u>linear</u> in temperature

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

For the free electron gas we had

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

So $\quad g(\varepsilon_F) = \frac{3}{2} \frac{n}{\varepsilon_F}$

$$\Rightarrow \quad c_v \sim 3n \frac{k_B^2 T}{\varepsilon_F} = 3n k_B \left(\frac{T}{T_F}\right)$$

Compare this to a classical ideal gas where

$$c_v = \frac{3}{2} n k_B$$

We see that the specific heat of the
quantum fermi gas is $\sim \left(T/T_F\right) \sim 10^{-2}$ 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)
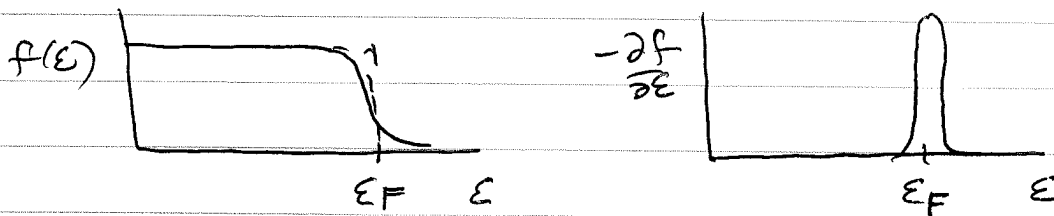gives the result

$$c_V = \frac{\pi^2}{3} g(\varepsilon_F) k_B^2 T$$

Quick derivation   (from Kittel)

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

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

Subtract ε_F Times ② from ①

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

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

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

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

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

where $x = \left(\frac{\varepsilon-\mu}{k_B T}\right)$. $\left[\begin{array}{l}\text{ignore } \mu(T) \text{ dependence on } T \\ \text{since } \mu \approx \varepsilon_F. \text{ Corrections} \\ \text{give higher order terms}\end{array}\right]$

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

So $\frac{\partial u}{\partial T} = g(\varepsilon_F) \int_{-\infty}^\infty d\varepsilon \, \frac{(\varepsilon-\varepsilon_F)^2}{k_B T^2}\left(-\frac{\partial f}{\partial x}\right)$

$$= g(\varepsilon_F) k_B^2 T \int_{-\infty}^\infty dx \, x^2 \left(-\frac{\partial f}{\partial x}\right)$$

$$= g(\varepsilon_F) k_B^2 T \underbrace{\int_{-\infty}^\infty dx \, x^2 \frac{e^x}{(e^x+1)^2}}_{= \frac{\pi^2}{3}}$$

$$\Rightarrow \quad C_v = \frac{\partial u}{\partial T} = \frac{\pi^2}{3} g(\varepsilon_F) k_B^2 T$$
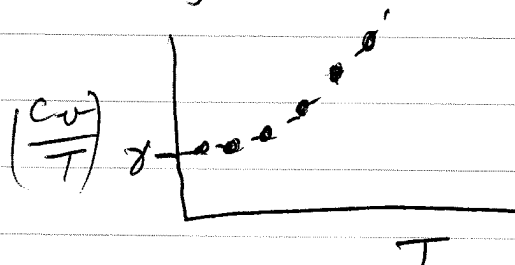
Above is just the contribution to the specific heat of a metal from the conduction electrons. The total specific heat of the metal also includes contributions from vibrations of the ions. This ionic contribution goes like $3 n_{ion} k_B$ at high temperatures ($n_{ion} = n/z$ is ion density ; z = electron valence) but at low T, we will find that due to quantum effects it goes like T^3. So at high $T \approx$ 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

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

function of density n

where our calculation predicts $\gamma = \dfrac{\pi^2}{2} \dfrac{n k_B}{T_F}$

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

one finds   (see A&M table 2.3)

metal	γ (theory)	γ (expt)	$\left(10^{-4} \dfrac{cal}{mole \, {}^{\circ}K^2}\right)$
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 discrepencies for
$\underline{Fe, \ Mn}, \ \underline{Bi, \ Sb}$
     ↑   ↑
~ 10 times too big   ~ 10 times too small

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

Transport Properties of the Sommerfeld Model

We have seen that we must use quantum Fermi-Dirac statistics to describe the thermodynamic behavior of conduction electrons.

What about the equation motion? Semiclassical arguments can be made to show that in many cases it remains OK to use the classical Drude equation of motion. We need to be able to construct electron wave packets which are localized on the desired spatial length scales.

We saw that the typical electron energy is set by the Fermi energy E_F. Hence the typical momentum is $p \sim p_F$. If we make a wave packet with $\Delta p \ll p_F$ then spread in spatial position is

$$\Delta x \sim \frac{\hbar}{\Delta p} \gg \frac{1}{k_F} \sim r_s$$

So the electron cannot be localized to atomic length scales, but can be localized on the length scales of macroscopically varying electric, magnetic fields or temperature gradients $\sim 1000 \, Å$. So OK for motion in EM waves in visible spectrum

but <u>not</u> for X-rays $(\lambda_{xray} \sim \mathring{A})$.

We also need $\Delta x \ll \ell$ the mean free path.
Classical motion may fail when $\ell \sim 10 \mathring{A}$.

$\ell \simeq v\tau$ where $\tau \sim 10^{-14}$ sec   and
$$v \sim v_F \sim 10^8 \ cm/sec$$
so $\ell \sim 10^8 \cdot 10^{-14} \ cm = 10^{-6} \ cm = 100 \mathring{A}$
so looks OK.

<u>Using Drude Equation motion + Fermi Dirac
Statistics we then have</u>

① <u>dc and ac electric conductivity</u> same as
   for classical Drude model, since no
   thermo was involved

② For <u>thermal conductivity</u> we had

$$\kappa = \frac{1}{3} v^2 \tau \ c_v$$

Now we should use $v \sim v_F$, $v_F^2 = \frac{2\varepsilon_F}{m}$
and $c_v = \frac{\pi^2}{3} \left(\frac{k_B T}{\varepsilon_F} \right) n k_B$

$\Rightarrow \kappa = \frac{1}{3} \frac{2\varepsilon_F}{m} \frac{\pi^2}{2} \left(\frac{k_B T}{\varepsilon_F} \right) n k_B \ \tau$

$\qquad = \frac{\pi^2}{3m} \tau \, n k_B^2 \, T$

and Wiedemann – Franz coefficient is

$$\frac{k}{\sigma T} = \frac{\frac{\pi^2}{3m} \tau m k_B^2}{\frac{n e^2 \tau}{m}} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.44 \times 10^{-8} \text{ watt} - \text{ohm} / {}^0 K^2$$

excellent agreement
with experiment

③ Thermopower

$$Q = -\frac{c_v}{3ne} = -\frac{\pi^2}{6}\frac{k_B}{e}\left(\frac{k_B T}{\varepsilon_F}\right)$$

$$= -1.42\left(\frac{k_B T}{\varepsilon_F}\right) \times 10^{-4} \text{ volt} / {}^0 K$$

more reasonable result than
classical value