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 at \( k_B T \) 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 \( \Delta E = k_B T \) of the Fermi energy. This is \( g(E_F) \Delta E = g(E_F) k_B T \)

So

\[
\Delta U = (k_B T) g(E_F) k_B T = g(E_F)(k_B T)^2
\]

So \( c_v = \frac{d\Delta U}{dT} = 2 g(E_F) k_B T \sim T \)

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 $T < T_F$) and $g(E_F)$ gives the density of such electrons.

For the free electron gas we had

$$g(E) = \frac{1}{2} \frac{m}{E_F} \sqrt{\frac{E}{E_F}}$$

So

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

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

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 $\sim \left( T/T_F \right)^2 \sim 10^{-2}$ 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. \[ U = \int_0^\infty d\varepsilon \, g(\varepsilon) \, \varepsilon \, f(\varepsilon) \Rightarrow \frac{dU}{dT} = \int_0^\infty d\varepsilon \, g(\varepsilon) \, \varepsilon \, \frac{df}{dT} \]
2. \[ m = \int_0^\infty d\varepsilon \, g(\varepsilon) \, f(\varepsilon) \Rightarrow 0 = \frac{dM}{dT} = \int_0^\infty d\varepsilon \, g(\varepsilon) \, \frac{df}{dT} \]

Subtract \( \varepsilon_F \) times \( \circ 2 \) from \( \circ 1 \)

\[ C_v = \frac{dU}{dT} = \frac{dU}{dT} - 0 = \int_0^\infty d\varepsilon \, g(\varepsilon) \, (\varepsilon - \varepsilon_F) \, \frac{df}{dT} \]

\[ \frac{df}{dT} \approx 0 \text{ except for energies with } k_BT \gg \varepsilon_F \]

\[ \Rightarrow \text{approx } g(\varepsilon) \text{ in integral by constant } g(\varepsilon_F) \]
\[ \frac{\partial u}{\partial T} = g(E_F) \int_0^\infty d\varepsilon (\varepsilon - E_F) \left( \frac{2 f}{\partial \varepsilon} \right) \]

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

Where \( x = \frac{(\varepsilon - \mu)}{k_BT} \).

- Ignore \( \mu(T) \) dependence on \( T \).
- Since \( \mu \approx E_F \), corrections give higher order term.

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

\[ \frac{\partial u}{\partial T} = g(E_F) \int_{-\infty}^{\infty} d\varepsilon \frac{(\varepsilon - E_F)^2}{k_BT^2} \left( \frac{-2 f}{\partial x} \right) \]

\[ = g(E_F) k_B^2 T \int_{-\infty}^{\infty} dx \frac{1}{x^2} \left( -\frac{2 f}{\partial x} \right) \]

\[ = g(E_F) k_B^2 T \int_{-\infty}^{\infty} dx \frac{1}{x^2} \frac{e^x}{(e^x + 1)^2} \]

\[ = \frac{\pi^2}{3} \]

\[ \Rightarrow \quad C_v = \frac{\partial u}{\partial T} = \frac{\pi^2}{3} g(E_F) k_B^2 T \]
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. The conic contribution goes like $3 \mu_n n k_B$ at high temperatures ($\mu_n = n/2$ is ion density; $n$ = electron valence) but at low $T$, we will find that due to quantum effects, it goes like $T^2$. So at high $T$ = room temp, the conic 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

$$C_v = \gamma T + \alpha T^2$$

where our calculation predicts $\gamma = \frac{\pi^2}{3} \frac{n k_B}{T_F}$

one plots $\frac{C_v}{T} = \gamma + \alpha T^2$ and determines $\gamma$ by extrapolating to the $T \to 0$ intercept.
one finds (see A+M table 3.03)

<table>
<thead>
<tr>
<th>metal</th>
<th>$\gamma$ (theory)</th>
<th>$\gamma$ (expt)</th>
<th>$(10^{-4} \text{ gal/mole} \text{ cm}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.8</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>2.4</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>4.0</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>4.6</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>1.5</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1.5</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>4.3</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

The alkali metals (Li, Na) come out reasonable. The noble metals (Cu, Ag, Au) come out reasonable. Both alkali + noble metals have valence $\mathbf{Z} = 1$.

But there are much bigger discrepancies for $\frac{Fe, Mn, Bi, Sb}{T}$

~10 times too big  ~10 times too small

The difference between theory and 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 cons shifts the energy spectrum $E_k$ from the single free electron $\frac{m^*}{2}k^2/2m^*$.

We can often approximate the true $E_k$ as $\frac{m^*}{2}k^2/2m^*$ 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 of 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

$$\Delta x \sim \frac{k}{\Delta p} \gg \frac{1}{p_F}$$

So the electron cannot be localized to atomic length scales, but can be localized on the length scales of macroscopically varying electric, magnetic fields of temperature gradients $\sim 1000 \,^\circ F$, so OK for motion in EM waves in visible spectrum.
but not for X-rays \( (\Delta \lambda \sim A) \).

We also need \( \Delta x \ll l \) the mean free path.
Classical motion may fail when \( l \sim 10A \),

\[ l = \frac{v}{c} \quad \text{where} \quad \frac{c}{v} \sim 10^{-14} \text{sec} \quad \text{and} \]
\[ v \sim v_F \sim 10^8 \text{cm/sec} \]

so \( l \sim 10^8 \cdot 10^{-14} \text{cm} = 10^{-6} \text{cm} = 100A \)
so looks OK.

Using Drude & Equation motion + Fermi-Dirac
Statistics we then have

1. dc and ac electric conductivity same as
   for classical Drude model, since no
   thermo was involved

2. For thermal conductivity we had

\[ K = \frac{1}{3} v^2 \tau \sigma \]

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

\[ \Rightarrow K = \frac{1}{3} \frac{2eF}{m} \frac{\pi^2}{2} \left( \frac{k_B T}{eF} \right) n k_B \tau \]
\[ = \frac{\pi^2}{3m} \tau n k_B^2 T \]
and Wiedemann–Franz coefficient is

\[ \frac{K}{\sigma T} = \frac{\pi^2 \tau m k_B^2}{m e^2 c} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 = 2.94 \times 10^{-8} \text{ watt} \cdot \text{cm}^{-1} \text{K}^{-2} \]

excellent agreement with experiment

3. Thermopower

\[ \alpha = -\frac{C_0}{3me} = -\frac{\pi^2 k_B}{6 e} \left( \frac{k_B T}{eF} \right) \]

\[ = -1.42 \left( \frac{k_B T}{eF} \right) \times 10^{-4} \text{ volt} \cdot \text{K}^{-1} \]

more reasonable result than classical value