

HEAT CAPACITY (due to "free" electrons)

1. Recall from the section on the heat capacity due to the lattice, that

$$C = \partial U / \partial T \quad \text{where} \quad \Delta U = U - U_{T=0} \quad (\text{since } U_{T=0} \neq 0)$$

where U is the internal energy (heat) of the system and can be calculated by adding up all of the energies of all of the available modes: $U =$ adding up each possible energy times the probability of having that energy, or integrating the density of states times the energy of each state times the probability of that state having that energy: $U = \int_0^\infty \epsilon f(\epsilon, T) D(\epsilon) d\epsilon$, so we have for the change in energy:

$$\Delta U = \int_0^\infty \epsilon f(\epsilon, T) D(\epsilon) d\epsilon - \int_0^\infty \epsilon f(\epsilon, 0) D(\epsilon) d\epsilon$$

but recall

$$f(\epsilon, 0) = 1 \quad \text{for } \epsilon < \epsilon_F \quad \text{and} \quad f(\epsilon, 0) = 0 \quad \text{for } \epsilon > \epsilon_F.$$

Note in particular that there is no T dependence in the $U_{T=0}$ term, so we can ignore it in finding C . Also note that both ϵ and $D(\epsilon)$ do not depend on temperature, but $f(\epsilon, T)$ does. Therefore,

$$C_{el} = \partial U / \partial T = \int_0^\infty \epsilon [\partial f(\epsilon, T) / \partial T] D(\epsilon) d\epsilon$$

And with $D(\epsilon) d\epsilon = (V/\pi^2) (2m/\hbar^2)^{3/2} \frac{1}{2} \epsilon^{1/2} d\epsilon$ (from part 5 of the previous section) and the Fermi-Dirac distribution: $f_{\text{Fermi-Dirac}}(\epsilon) = 1 / [e^{(\epsilon-\mu)/kT} + 1]$ we get

$$C_{el} = \partial U / \partial T = \int_0^\infty \epsilon [\partial \{1 / [e^{(\epsilon-\mu)/kT} + 1]\} / \partial T] [(V/2\pi^2) (2m/\hbar^2)^{3/2} \epsilon^{1/2}] d\epsilon;$$

We now evaluate the derivative: $\partial \{1 / [e^{(\epsilon-\mu)/kT} + 1]\} / \partial T = \{-1 / [e^{(\epsilon-\mu)/kT} + 1]^2\} \{e^{(\epsilon-\mu)/kT}\} \{-(\epsilon-\mu)/k_B T^2 - [\partial \mu / \partial T] / k_B T\}$.

The term $\partial \mu / \partial T$ is small since μ changes very slowly with T . To make things easier, we will **neglect this term and simply let $\mu = \epsilon_F$** . This still leads to a rather "ugly" expression for the heat capacity:

$$C_{el} \approx (V/2\pi^2) (2m/\hbar^2)^{3/2} (1/k_B T^2) \int_0^\infty \epsilon^{3/2} (\epsilon - \epsilon_F) e^{(\epsilon - \epsilon_F)/kT} [1 / \{e^{(\epsilon - \epsilon_F)/kT} + 1\}^2] d\epsilon.$$

2. Getting a nicer expression

To get some kind of "nice" expression for this, we need to be a little "tricky": consider the following:

$$\epsilon_F N = \text{constant} = \epsilon_F \int_0^\infty f(\epsilon, T) D(\epsilon) d\epsilon = \int_0^\infty \epsilon_F f(\epsilon, T) D(\epsilon) d\epsilon$$

and $\partial(\epsilon_F N) / \partial T = 0 = \int_0^\infty \epsilon_F [\partial f(\epsilon, T) / \partial T] D(\epsilon) d\epsilon$.

Therefore: $C_{el} = \partial U / \partial T - 0 = \int_0^\infty \epsilon [\partial f(\epsilon, T) / \partial T] D(\epsilon) d\epsilon - \int_0^\infty \epsilon_F [\partial f(\epsilon, T) / \partial T] D(\epsilon) d\epsilon$

or $C_{el} = \int_0^\infty (\epsilon - \epsilon_F) [\partial f(\epsilon, T) / \partial T] D(\epsilon) d\epsilon$

and writing out the derivative as we (approximately) calculated above:

$$C_{el} \approx \int_0^\infty (\epsilon - \epsilon_F) D(\epsilon) \{(\epsilon - \epsilon_F) / k_B T^2\} \{e^{(\epsilon - \epsilon_F)/kT}\} \{1 / [e^{(\epsilon - \epsilon_F)/kT} + 1]^2\} d\epsilon.$$

Now all the ϵ 's are in terms of the quantity $(\epsilon - \epsilon_F)$ except the $D(\epsilon)$ term. If we consider **low temperatures**, then the squared exponential term in the denominator will dominate and cause very little contributions for all ϵ that are significantly different than ϵ_F . Thus we can **approximate** again by assuming that $D(\epsilon) \approx D(\epsilon_F)$ and removing it from the integral. This assumption will allow us to express the integral in the following form:

$$C_{el} \approx D(\epsilon_F) \int_0^\infty \{(\epsilon - \epsilon_F)^2 / k_B T^2\} \{e^{(\epsilon - \epsilon_F)/kT}\} \{1 / [e^{(\epsilon - \epsilon_F)/kT} + 1]^2\} d\epsilon$$

and now we can make the substitution: $x = (\epsilon - \epsilon_F)/k_B T$ and $dx = d\epsilon/k_B T$ (or $d\epsilon = k_B T dx$) so that we get [including adjusting the limits]:

$$C_{el} \approx D(\epsilon_F) k_B^2 T \int_{-\epsilon_F/k_B T}^{\infty} \{x^2 e^x / [e^x + 1]^2\} dx ;$$

and if we again make an **approximation that the lower limit can be extended to $-\infty$** , then we have an integral that can be looked up:

$$\int_{-\infty}^{+\infty} \{x^2 e^x / [e^x + 1]^2\} dx = \frac{1}{3}\pi^2 ,$$

so that we finally have (at least to an approximation): $C_{el} \approx \frac{1}{3}\pi^2 D(\epsilon_F) k_B^2 T$.

If we now evaluate $D(\epsilon_F)$ we get: $D(\epsilon_F) = (V/2\pi^2) (2m/\hbar^2)^{3/2} \epsilon_F^{1/2}$;

but recall from previous considerations (i.e., when $T=0K$)

$$N = 2 (L_x/2\pi) (L_y/2\pi) (L_z/2\pi) \int_0^{k_F} 4\pi k^2 dk = 2 (V/8\pi^3) (4\pi k_F^3/3),$$

and $\epsilon_F = \hbar^2 k_F^2 / 2m$, (or $k_F = [2m\epsilon_F/\hbar^2]^{1/2}$,

so that $N = (V/3\pi^2) k_F^3 = (V/3\pi^2) [2m\epsilon_F/\hbar^2]^{3/2}$.

Putting this expression for N into the expression for $D(\epsilon_F)$ gives: $D(\epsilon_F) = 3N/2\epsilon_F$.

Finally then, we can give an approximate expression for the heat capacity due to the "free" electrons as:

$$C_{el} \approx \frac{1}{3}\pi^2 (3N/2\epsilon_F) k_B^2 T = \frac{1}{2}\pi^2 N k_B (k_B T/\epsilon_F) = \frac{1}{2}\pi^2 N k_B (T/T_F) = \gamma T .$$

Thus (for low temperatures, at least),

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

where the first term is due to the "free" electrons (good only for metals) and the second term is due to the lattice.

3. Thermal effective mass

Note that γ above is proportional to $(1/\epsilon_F)$, and ϵ_F is proportional to $[1/m_{el}]$ (since $\epsilon = \hbar^2 k^2 / 2m$). Thus γ is proportional to the value for m_{el} . By curve fitting, we can determine a value for γ and then compare this to the predicted value for γ from above. The difference in the values can then be attributed to a difference between the **thermal effective mass** and the actual mass of the electron. This "difference" is due to three main effects:

- (1) The electrons are not really free but are in a periodic potential due to the ion cores.
- (2) The electrons also interact with the phonons which makes them act like they are "dragging" the ions along with them.
- (3) The electrons also interact with other electrons which again makes them act like they are "dragging" other electrons along.

All in all, this theory can give a "nice" picture of "thermal" electrons carrying the heat capacity, with the **electrons acting as if they were "free" but with not quite the same mass as the real electrons**.

4. Comparison with classical theory

Classical theory says simply that all degrees of freedom should have an energy that is on average $\frac{1}{2}k_B T$ [recall that vibrational modes have both KE and PE so their average energy is $k_B T$ rather than $\frac{1}{2}k_B T$], and so the heat capacity should simply be (since we have 3-D and N electrons) $C = (3/2)Nk_B$. Note that **the "free" Fermi electron theory gives $C = (\frac{1}{2}\pi^2 N k_B T/T_F)$** . Thus the classical theory differs from this quantum theory by a factor of: $\frac{1}{3}\pi^2 (T/T_F)$.

5. Numerical example

For Copper, atomic mass of 63 grams/mole, $T_F = 86,600$ K, at room temperature, $C_{\text{electron}} = (\frac{1}{2}\pi^2 N k_B T / T_F) = (\frac{1}{2}\pi^2)(8.3 \text{ J/mole-K})(1 \text{ mole}/63 \text{ grams})(300\text{K}/86,600\text{K}) = .003 \text{ J/gram-K}$. This is about 1% of the lattice heat capacity of .386 J/gm-K for copper at room temperature.

Because the electrons are not all allowed to be in the same state, most of the electrons cannot accept a little thermal energy because the states above them are already filled. Note how the Fermi Distribution looks at small temperatures: [Distributions](#). This means that only a few of the electrons, the ones near the Fermi energy, can accept thermal energy; and so the heat capacity of the electrons is going to be small compared to the lattice vibrations which consist of phonons that can have the same energy since the phonons are not Fermions, but rather Bosons.