Electron Gas Heat Capacity

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Classical statistical mechanics predicts that a free particle will have a heat capacity of $\frac{3}{2}k_B$ per particle, which gives an electron gas formed by N atoms each contributing one valence electrons a heat capacity of $\frac{3}{2}Nk_B$. However, experimental values for the electron gas heat capacity at room temperatures are usually less than 0.01 of this value.

We now know that this discrepancy is because the Pauli exclusion principle and Fermi-Dirac distribution were not accounted for. Examining the Fermi-Dirac distribution as temperature changes, we see that at temperatures of order 10^3 or less, only the electrons near the Fermi energy (approximately within $\Delta E = k_B T$) have a chance of being thermally excited.

To calculate the heat capacity, we note the identities:

$$N = \int_0^\infty f(E)D(E)dE \tag{1}$$

$$N = \int_0^{E_F} D(E)dE \tag{2}$$

where the second identity comes from the definition of E_F - the energy of the highest occupied state at absolute zero, in which all states with energy beneath E_F are filled. Setting these two identities equal to each other, multiplying by E_F, and splitting the first integral into two parts:

$$\int_0^{E_F} E_F f(E)D(E)dE + \int_{E_F}^\infty E_F f(E)D(E)dE = \int_0^{E_F} E_F D(E)dE \tag{3}$$

Defining the increase in energy of a system heated from absolute zero:

$$\Delta U = U(T) - U(0) = \int_0^\infty Ef(E)D(E)dE - \int_0^{E_F} ED(E)dE \tag{4}$$

Note that we can rewrite (3) as:

$$\int_0^{E_F} E_F D(E)dE - \int_0^{E_F} E_F f(E)D(E)dE - \int_{E_F}^\infty E_F f(E)D(E)dE = 0$$

Since this relation is equal to zero, we can add it to the right side of (4) without changing the equality:

$$\begin{aligned}\Delta U &= \int_0^{E_F} D(E)\left[Ef(E) - E + E_F - E_F f(E)\right]dE + \int_{E_F}^\infty (E - E_F)f(E)D(E)dE \\ &= \int_0^{E_F} D(E)(1 - f(E))(E_F - E)dE + \int_{E_F}^\infty (E - E_F)f(E)D(E)dE \end{aligned} \tag{5}$$

The first integral represents the energy needed to bring electrons with energy $E < E_F$ up to the Fermi energy, and the second integral represents the energy needed to bring electrons with energy $E = E_F$ up to an energy $E > E_F$.

To find the electron heat capacity, we simply differentiate ΔU with respect to temperature T (noting that $f(E)$ is the only temperature dependent quantity):

$$C_{el} = \frac{\partial(\Delta U)}{\partial T} = \int_0^\infty (E - E_F)\frac{df}{dT}D(E)dE \tag{6}$$

At temperatures of interest for metals $\left(T < .01\frac{E_F}{k_B}\right)$, it is a good approximation to take $\mu = E_F$, which gives the derivative:

$$\frac{df}{dT} = \frac{E - E_F}{k_B T^2}\frac{e^{\frac{E-E_F}{k_B T}}}{\left(e^{\frac{E-E_F}{k_B T}} + 1\right)^2} \tag{7}$$

it is also a good approximation to evaluate $D(E)$ at E_F and bring it outside the integral. Doing so and defining $x = \frac{E-E_F}{k_B T}$:

$$C_{el} \approx k_B^2 T D(E_F)\int_{-\frac{E_F}{k_B T}}^\infty x^2 \frac{e^x}{(e^x + 1)^2}dx \tag{8}$$

Since at low temperatures the integrand is negligible at the lower bound $-\frac{E_F}{k_B T}$, we can replace the lower bound with $-\infty$ to give the integral a simple value:

$$\int_{-\infty}^\infty x^2 \frac{e^x}{(e^x + 1)^2} = \frac{\pi^2}{3} \tag{9}$$

The heat capacity thus becomes:

$$\begin{aligned} C_{el} &\approx \frac{\pi^2}{3}D(E_F)k_B^2 T \\ &= \frac{\pi^2}{2}N k_B \frac{T}{T_F} \end{aligned} \tag{10}$$

where we recall $T_F = \frac{E_F}{k_B}$ is the Fermi temperature.