Lecture 29 - Heat capacities in metals

What's Important:
- electrons in metals
- heat capacities

Text: Reif Sec. 19.7; Kittel Chap. 7

Heat capacities in metals are covered in two lectures. Here, the experimental situation is described and compared against expectations for a Fermi gas at low temperature. The proof for the result is given in the following lecture.

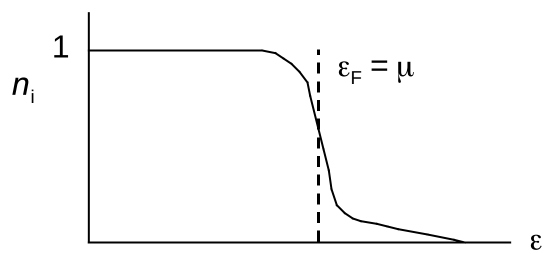
Electrons in metals

Some time back we established that the molar heat capacity of an ideal gas is

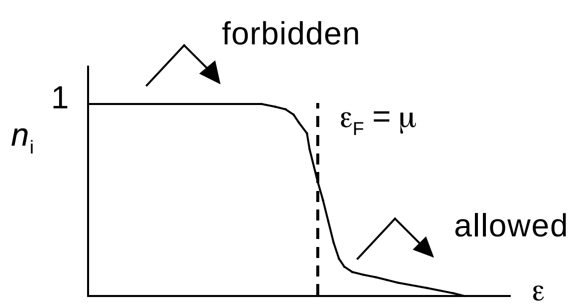
$$C_v = (3/2)R, \tag{29.1}$$

where the subscript V indicates the system is held at constant volume. In Eq. (29.1), the heat capacity is independent of temperature.

In an ideal gas, all atoms or molecules are able to take part in the emission or absorption of energy - there is no restriction on which states the particles can occupy. In metals, the carriers of energy are electrons which, as fermions, may not have the same freedom as MB particles. Consider the distribution of electron energies at low temperatures. Schematically:



If we try to add a small amount of energy to an electron whose energy is much less than the Fermi energy ε_F, the resulting kinetic energy will also be much less than ε_F. In all likelihood, this new state is already occupied, and the addition of energy is forbidden. In other words:



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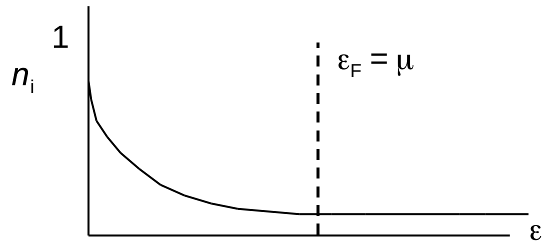
Hence, at $k_B T << \varepsilon_F$ few electrons are available to absorb extra energy. However, at high temperatures, the situation is more similar to the classical gas:



So, we expect C_v to increase with temperature when $k_B T << \varepsilon_F$. To find the actual Fermi energy of a metal, we can

- do scattering experiments to determine v_F
- measure conduction electron density, then obtain ε_F from N/V.

Some examples are:

Metal (monovalent)	Electron concentration (m^{-3})	ε_F (eV)	$T_F = \varepsilon_F / k_B$
Li	4.6×10^{28}	4.7	5.5×10^4
Na	2.5×10^{28}	3.1	3.7×10^4
K	1.3×10^{28}	2.1	2.4×10^4
Cu	8.5×10^{28}	7.0	8.2×10^4
Ag	5.8×10^{28}	5.5	6.4×10^4
Au	5.9×10^{28}	5.5	6.4×10^4

Note that the conduction electron densities are remarkably constant.

Clearly for the monovalent metals listed above, we observe $k_B T << \varepsilon_F$ and C_v should be nowhere near the ideal (electron) gas value.

Comparison with theory

In the following lecture, we establish that the heat capacity of a low temperature Fermi gas is given by

$$\frac{C_v}{V} = \left(\frac{\pi^2}{2} \cdot \frac{N}{V} \cdot \frac{k_B}{T_F} \right) T \qquad (29.2)$$

where all the quantities in brackets can be obtained experimentally. In contrast to Eq. (29.1), the specific heat of a Fermi gas vaniushes at $T = 0$. Let's evaluate Eq. (29.2) for potassium, for which our table gives

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$N/V = 1.34 \times 10^{28}$ conduction electrons per m^3
$T_F = 2.4 \times 10^4$ K,

so that

$$\frac{C_v}{V} = \left(\frac{\pi^2}{2} \cdot 1.34 \times 10^{28} \cdot \frac{1.38 \times 10^{-23}}{2.4 \times 10^4}\right) T$$

$$= 38.0T \quad \text{J/(K} \cdot \text{m}^3\text{)}$$

$$= 38.0 \times 10^{-6} T \quad \text{J/(K} \cdot \text{cm}^3\text{)}$$

To convert this to a molar specific heat, divide by the density of potassium (0.862 g/cc) and multiply by the atomic weight (39.1). One finds

$$\frac{C_v}{T} = 38.0 \times 10^{-6} \cdot \frac{39.1}{0.862}$$

$$= 1.72 \times 10^{-3} \quad \text{J/(K}^2 \cdot \text{mole)}$$

This prediction is surprisingly close to the experimental measurement (Kittel, p. 212): 2.08×10^{-3} J / K^2•mole.

Typical disagreement between the ideal Fermi gas prediction and experiment is of the order 20-40%. The disagreement is usually resolved by assigning the electrons an effective mass owing to their interactions with other electrons or the metal lattice.

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