Heat capacity of electron gas

4/7/21

The heat capacity of an ideal monoatomic gas is $C_V = \frac{3}{2}N$, but the heat capacity for electrons in metals is much lower because most of them are "trapped" in their quantum states and only those electrons close to the Fermi energy can actually change their energy.

Remember that $C_V = \frac{dU}{d\tau}$, so let's get $\Delta U \equiv U(\tau) - U(0)$.

Using Eq. 7.23,

$$\Delta U = \int_0^\infty d\varepsilon\, \varepsilon\, \mathcal{D}(\varepsilon) f(\varepsilon, \tau, \mu) - \int_0^\infty d\varepsilon\, \varepsilon\, \mathcal{D}(\varepsilon) f(\varepsilon, 0, \varepsilon_F)$$

$$\Delta U = \int_0^\infty d\varepsilon\, \varepsilon\, \mathcal{D}(\varepsilon) f(\varepsilon) - \underbrace{\int_0^{\varepsilon_F} d\varepsilon\, \varepsilon\, \mathcal{D}(\varepsilon)}_{U_0} \qquad \text{KK Eq. 7.24}$$

Consider Eq. 7.27

$$\Delta U = \int_{\varepsilon_F}^\infty d\varepsilon\, (\varepsilon - \varepsilon_F) f(\varepsilon) \mathcal{D}(\varepsilon) + \int_0^{\varepsilon_F} d\varepsilon\, (\varepsilon_F - \varepsilon)[1 - f(\varepsilon)]\, \mathcal{D}(\varepsilon) \qquad \text{KK Eq. 7.27}$$

$$\Delta U = \overset{\mathrm{I}}{\int_{\varepsilon_F}^\infty d\varepsilon\, \varepsilon\, f(\varepsilon) \mathcal{D}(\varepsilon)} - \overset{\mathrm{II}}{\int_{\varepsilon_F}^\infty d\varepsilon\, \varepsilon_F\, f(\varepsilon) \mathcal{D}(\varepsilon)}$$

$$+ \overset{\mathrm{III}}{\int_0^{\varepsilon_F} d\varepsilon\, \varepsilon_F\, \mathcal{D}(\varepsilon)} - \overset{\mathrm{II}}{\int_0^{\varepsilon_F} d\varepsilon\, \varepsilon_F\, f(\varepsilon) \mathcal{D}(\varepsilon)} - \underbrace{\int_0^{\varepsilon_F} d\varepsilon\, \varepsilon\, \mathcal{D}(\varepsilon)}_{U_0} + \overset{\mathrm{I}}{\int_0^{\varepsilon_F} d\varepsilon\, \varepsilon f(\varepsilon) \mathcal{D}(\varepsilon)}$$

I $\quad \int_0^\infty d\varepsilon\, \varepsilon\, \mathcal{D}(\varepsilon) f(\varepsilon)$

II $\quad - \int_0^\infty d\varepsilon\, \varepsilon_F\, \mathcal{D}(\varepsilon) f(\varepsilon)$

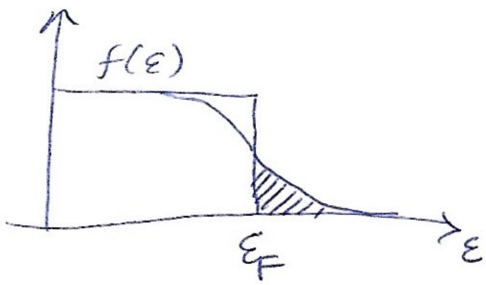
The number of electrons is conserved, so

$$N = \int_0^\infty d\mathcal{E}\, \mathcal{D}(\mathcal{E}) f(\mathcal{E}) = \int_0^{\mathcal{E}_F} d\mathcal{E}\, \mathcal{D}(\mathcal{E}) \quad \text{at } \tau = 0 \qquad \text{Eq. KK 7.25}$$

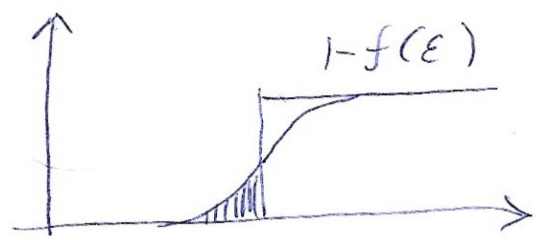
$$N\mathcal{E}_F = \int_0^\infty d\mathcal{E}\, \mathcal{E}_F\, \mathcal{D}(\mathcal{E}) f(\mathcal{E}) = \int_0^{\mathcal{E}_F} d\mathcal{E}\, \mathcal{E}_F\, \mathcal{D}(\mathcal{E}) \qquad \text{c.f. II, III}$$

So KK Eq. 7.27 is a statement of the conservation of particles, but also provides some more insight.

$$\Delta U = \int_{\mathcal{E}_F}^\infty d\mathcal{E}\,(\mathcal{E}-\mathcal{E}_F) f(\mathcal{E})\, \mathcal{D}(\mathcal{E}) + \int_0^{\mathcal{E}_F} d\mathcal{E}\,(\mathcal{E}_F-\mathcal{E})[1-f(\mathcal{E})]\, \mathcal{D}(\mathcal{E})$$



energy needed to move electrons from the Fermi energy to higher energies.



energy needed to move electrons from their original energy to the Fermi energy.

Consider a simple metal like potassium (K) which consist roughly of a lattice of ions (positively charged) and a sea of "free electrons" (each atom contributes 1 electron). It's density is 856 kg/m³ and molar volume of 45.94 cm³

so $\mathcal{E}_F = \dfrac{\hbar^2}{2m_e}\left(\dfrac{3\pi^2 N}{V}\right)^{2/3} = \dfrac{(1.05\times10^{-34}\ \mathrm{J\cdot s})^2}{2(9.11\times10^{-31}\ \mathrm{kg})}\left(\dfrac{3\pi^2\cdot 6.022\times10^{23}}{45.94\times10^{-6}\ \mathrm{m^3}}\right)^{2/3}$ $\quad 1\ \mathrm{cm^3} = 1\times10^{-6}\ \mathrm{m^3}$

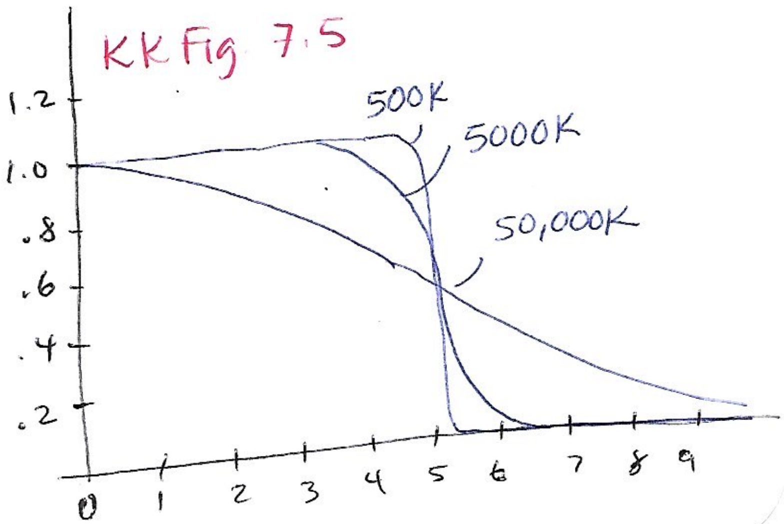
$$\mathcal{E}_F = \frac{1.1\times10^{-68}\ \frac{\mathrm{kg^2 m^4}}{\mathrm{s^2}}}{1.8\times10^{-30}\ \mathrm{kg}}\left(\frac{1.78\times10^{25}}{4.59\times10^{-5}\ \mathrm{m^3}}\right)^{2/3} = 6.05\times10^{-39}\ \frac{\mathrm{kg\,m^4}}{\mathrm{s^2}}\left(5.32\times10^{19}\ /\mathrm{m^2}\right)$$

$$\varepsilon_F = 3.22 \underset{\times 10^{-19}}{} \text{kg m}^2/\text{s}^2 = 3.22 \times 10^{-19}\ \text{J} = \tau_F$$

Since $\tau = k_B T$, in conventional units, $T = \tau / k_B$

$$T_F = \frac{3.22 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J/K}} = 23331\ \text{K}$$

This is typical of metals, but it is NOT the temperature of the electrons.



At room temperature, electrons in metals are very close to their ground state, so electrons behave like a degenerate ideal Fermi gas

In the ΔU equation, the only term that depends on the temperature is $f(\varepsilon, \tau, \mu)$, so only terms I and II

$$\frac{dU}{d\tau} = \frac{1}{d\tau}\left[\int_0^\infty d\varepsilon\ \varepsilon\ \mathcal{D}(\varepsilon) f(\varepsilon) - \int_0^\infty d\varepsilon\ \varepsilon_F\ \mathcal{D}(\varepsilon) f(\varepsilon)\right]$$

$$C_{el} = \frac{dU}{d\tau} = \int_0^\infty d\varepsilon\,(\varepsilon - \varepsilon_F)\frac{df}{d\tau}\mathcal{D}(\varepsilon)$$ KK Eq. 7.28

At the temperatures of interest $\tau \ll \tau_F$, $\frac{df}{d\tau}$ is zero almost everywhere, except close to ε_F, so

$$C_{el} \approx \mathcal{D}(\varepsilon_F)\int_0^\infty d\varepsilon\,(\varepsilon - \varepsilon_F)\frac{df}{d\tau}$$ KK Eq. 7.29

The integral is not pretty no matter what, but we can make it look not as awful by using

$$f(\varepsilon, \tau, \varepsilon_F) = \frac{1}{2}\left[1 - \tanh\left(\frac{\varepsilon - \varepsilon_F}{2\tau}\right)\right]$$

that we derived before

$$\frac{df}{d\tau} = \frac{d}{d\tau}\left[-\frac{1}{2}\tanh\left(\frac{\varepsilon-\varepsilon_F}{2\tau}\right)\right] = -\frac{1}{2}\operatorname{sech}^2\left(\frac{\varepsilon-\varepsilon_F}{2\tau}\right)\left[-\frac{(\varepsilon-\varepsilon_F)}{2\tau^2}\right]$$

$$\frac{df}{d\tau} = +\frac{(\varepsilon-\varepsilon_F)}{4\tau^2}\operatorname{sech}^2\left(\frac{\varepsilon-\varepsilon_F}{2\tau}\right)$$

so

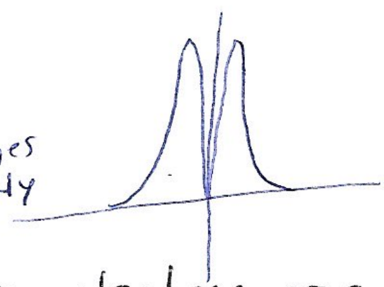
since tanh is centered at ε_F

$$C_{el} \approx \mathcal{D}(\varepsilon_F)\int_{-\infty}^{\infty} d\varepsilon \frac{(\varepsilon-\varepsilon_F)(\varepsilon-\varepsilon_F)}{4\tau^2}\operatorname{sech}^2\left(\frac{\varepsilon-\varepsilon_F}{2\tau}\right)$$

Let $x = \dfrac{\varepsilon-\varepsilon_F}{2\tau}$; $dx = \dfrac{d\varepsilon}{2\tau}$; $x^2 = \dfrac{(\varepsilon-\varepsilon_F)^2}{4\tau^2}$, then

$$C_{el} \approx \mathcal{D}(\varepsilon_F)\, 2\tau \underbrace{\int_{-\infty}^{\infty} dx\, x^2 \operatorname{sech}^2(x)}_{\pi^2/6}$$

converges quickly



$$\boxed{C_{el} = \frac{1}{3}\pi^2 \mathcal{D}(\varepsilon_F)\,\tau}$$

Heat capacity of an electron gas when $\tau \ll \tau_F$

KK Eq. 7.34

Remember that $\mathcal{D}(\varepsilon) = \dfrac{3N}{2\varepsilon}$ for the free electron gas, so

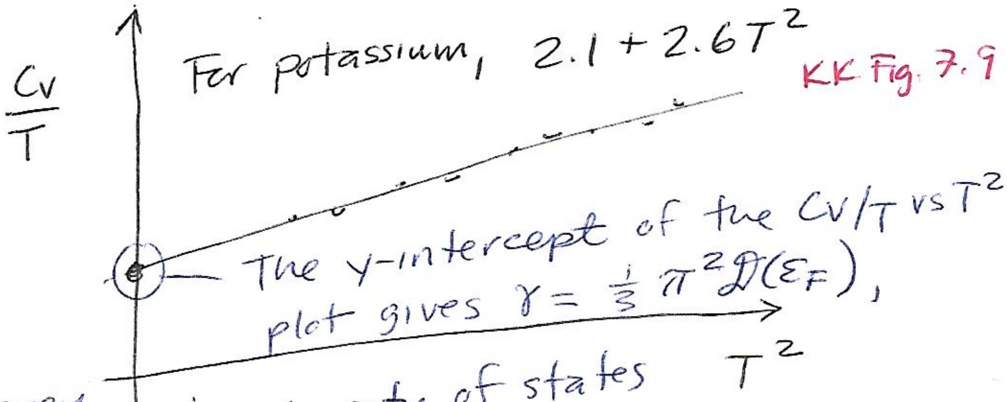
$$\mathcal{D}(\varepsilon_F) = \frac{3N}{2\varepsilon_F} = \frac{3N}{2\tau_F} \Rightarrow C_{el} = \frac{1}{\cancel{3}}\pi^2\frac{\cancel{3}N}{2\tau_F}\tau \Rightarrow \boxed{C_{el} = \frac{1}{2}\pi^2 N\, \tau/\tau_F}$$

KK Eq. 7.37

$$C_V = C_{el} + C_{ph} = \gamma\tau + A\tau^3$$ KK Eq. 7.42

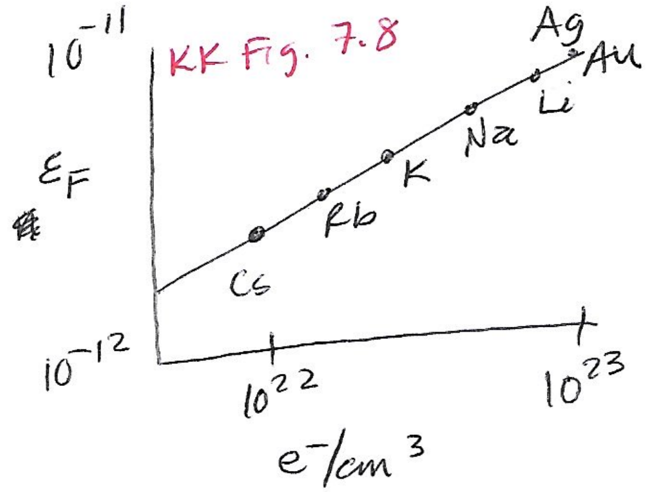
At low temperatures, the linear term (electrons) dominates

$$\frac{C_V}{\tau} = \gamma + A\tau^2$$



The y-intercept of the C_V/T vs T^2 plot gives $\gamma = \frac{1}{3}\pi^2 \mathcal{D}(\varepsilon_F)$, the density of states at the Fermi energy

Assume free electron gas, then $\gamma = \frac{1}{2}\pi^2 N/\tau_F$, so intercept provides Fermi energy.



$$\varepsilon_F = 5.83 \times 10^{-27}\, n^{2/3} \text{ ergs.}$$

Proportionality between $\varepsilon_F \propto n^{2/3}$ shows that studied metals have electrons living in a "free-electron gas"

A white dwarf is a stellar core remnant with a mass similar to the sun and a size similar to Earth. The sun has about 1.2×10^{57} proton/electron pairs and the Earth has a volume of $\frac{4}{3}\pi R_E^3 = \frac{4}{3}\pi(6.38 \times 10^6\,m)^3$

$V = 1.1 \times 10^{21}\,m^3$, so the concentration of electrons in the white dwarf is about $n = \frac{N}{V} = \frac{1.2 \times 10^{57}}{1.1 \times 10^{21}\,m^3} = 1.1 \times 10^{36}/m^3$.

The atoms are ionized in the whithe dwarf and the electrons behave similarly to a free electron gas

The Fermi energy of a typical white dwarf is then

$$\mathcal{E}_F = \frac{\hbar^2}{2m_e}\left(\frac{3\pi^2 N}{V}\right)^{2/3} = \frac{\hbar^2}{2m_e}\left(3\pi^2 n\right)^{2/3}$$

$$\mathcal{E}_F = \left(6.05\times10^{-39}\,\frac{\text{kg m}^4}{s^2}\right)\left(3.23\times10^{37}/m^3\right)^{2/3}$$

$$\mathcal{E}_F = \left(6.05\times10^{-39}\,\text{kg m}^4/s^2\right)\left(1\times10^{25}/m^2\right) = 6.1\times10^{-14}\,J = \tau_F$$

since $\tau = k_B T$, in conventional units, $T = \tau/k_B$

$$T_F = \frac{6.1\times10^{-14}\,J}{1.4\times10^{-23}\,J/K} = 4.5\times10^{9}\,K$$

Since the temperature of white dwarfs is "only" about $1\times10^{7}\,K$, only about 1 percent of T_F (the same as in metals), the electrons are degenerate, very close to the ground state. The Pauli Exclusion Principle keeps the white dwarf from collapsing.

Nevertheless, since $E = m_e c^2 = (9.11\times10^{-31}\,kg)(3\times10^{8}\,\frac{m}{s})^2 = 8.2\times10^{-14}\,J$, the electrons close to the Fermi energy are relativistic