

The Sackur-Tetrode Entropy and Experiment

In this section we'll be quoting some numbers found in K&K which are quoted from the literature.

You may recall that I've several times asked how one would measure absolute entropy? I suspect that I pretty much gave it away (if you hadn't figured it out already) in the last section. The answer is you have to measure heat transfers from a state of known absolute entropy to the desired state so that you can calculate $\int dQ/\tau$. What is a state of known entropy? Answer, at absolute 0, one expects the entropy to be very small and we can take it to be 0. Actually, there is the *third law of thermodynamics* (not as famous as the first two!) which says that the entropy should go to a constant as $\tau \rightarrow 0$.

At absolute 0, a reasonable system will be in its ground state. In fact the ground state might not be a single state. For example if we consider a "perfect crystal," its ground state is clearly unique. But real crystals have imperfections. Suppose a crystal is missing a single atom from its lattice. If there are N atoms in the crystal there are presumably N different sites from which the atom could be missing so the entropy is $\log N$. Also, there's presumably an energy cost for having a missing atom, so the crystal is not really in its ground state. But this might be as close as we can get with a real crystal. The point is that the energy and the entropy are both very small in this situation and very little error is made by assuming that $\sigma(0) = 0$. (Compare $\log N$ with $N \log(n_Q/n)$ when $N \sim 10^{23}$!)

In fact, a bigger problem is getting to very low temperatures. In practice, one gets as low as one can and then extrapolates to $\tau = 0$ using a Debye law (assuming an insulating solid). So to measure the entropy of a monatomic ideal gas such as neon, one makes heat capacity measurements and does the integral $\int C(\tau) d\tau/\tau$. The heat capacity measurements go to as low a τ as needed to get a reliable extrapolation to 0 with the Debye law. According to K&K, the calculation goes like this: solid neon melts at 24.55 K. At the melting point, its entropy (by extrapolation and numerical integration) is

$$S_{\text{melting}} - S_0 = 14.29 \frac{\text{J}}{\text{mol K}} .$$

To melt the solid (which occurs at a constant temperature) requires 335 J mol^{-1} so the entropy required to melt is

$$\Delta S_{\text{melt}} = 13.65 \frac{\text{J}}{\text{mol K}} .$$

Again, a numerical integration is required to find the entropy change as the liquid neon is taken from the freezing point to the boiling point at 27.2 K. This is

$$S_{\text{boiling}} - S_{\text{freezing}} = 3.85 \frac{\text{J}}{\text{mol K}} .$$

Finally, 1761 J mol^{-1} is required to boil the neon at the boiling point, and

$$\Delta S_{\text{boil}} = 64.74 \frac{\text{J}}{\text{mol K}} .$$

Now we have a gas to which we can apply the Sackur-Tetrode expression. Assuming $S_0 = 0$, the total is

$$S_{\text{vapor}} = \Delta S_{\text{boil}} + (S_{\text{boiling}} - S_{\text{freezing}}) + \Delta S_{\text{melt}} + (S_{\text{melting}} - S_0) = 96.40 \frac{\text{J}}{\text{mol K}},$$

$$\sigma = 6.98 \times 10^{24} / \text{mol},$$

where I have quoted the sum from K&K which differs slightly from the sum you get by adding up the four numbers presumably because there is some round-off in the input numbers. (For example, using a periodic table on the web, I find the melting and boiling points of neon are 24.56 K and 27.07 K.) According to K&K, the Sackur-Tetrode value for neon at the boiling point is

$$S_{\text{Sackur-Tetrode}} = 96.45 \frac{\text{J}}{\text{mol K}},$$

which is in very good agreement with the observed value.

When I plug into the Sackur-Tetrode expression I actually get,

$$S_{\text{Sackur-Tetrode}} = 96.47 \frac{\text{J}}{\text{mol K}},$$

still in very good agreement with the observed value. Why did I get a slightly different value than that quoted in K&K? I used

$$S = R \left[\log \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{p}{kT} \right] + \frac{5}{2} \right],$$

Everything can be looked up, but I'm using p/kT instead of N_0/V , which assumes the ideal gas law is valid. However, this expression is being applied right at the boiling point, so it's not clear that the ideal gas law should work all that well.

Some other things to note. (1) If we had left out the $N!$ over counting correction, We would have to add

$$R(\log N_0 - 1) = 447 \frac{\text{J}}{\text{mol K}},$$

to the above. This swamps any slight problems with deviations from the ideal gas law or inaccuracies in the numerical integrations! (2) The Sackur-Tetrode expression includes \hbar which means it depends on quantum mechanics. So this is an example where measurements of the entropy pointed towards quantum mechanics. Of course, \hbar occurs inside a logarithm, so it might not have been so easy to spot!

The Ideal Fermi Gas

Consider a metal like sodium or copper (or the other metals in the same columns in the periodic table). These metals have one valence electron—an electron which can be easily removed from the atom, so these atoms often form chemical bonds as positively charged ions. In the solid metal, the valence electrons aren't bound to the atoms. How do we know this? Because the metals are good conductors of electricity. If the electrons were bound to the atoms they would be insulators. Of course, there are interactions between the electrons and the ions and between the electrons and other electrons. But, as a first approximation we can treat all the valence electrons as forming a gas of free (non-interacting) particles confined to the metal.

Let's do a little numerology. First, let's calculate the quantum concentration for an electron at room temperature,

$$\begin{aligned} n_Q &= \left(\frac{m_e kT}{2\pi\hbar^2} \right)^{3/2}, \\ &= \left(\frac{(9.108 \times 10^{-28} \text{ g}) (1.380 \times 10^{-16} \text{ erg K}^{-1}) (300 \text{ K})}{2\pi (1.054 \times 10^{-27} \text{ erg s})^2} \right)^{3/2}, \\ &= 1.26 \times 10^{19} \text{ cm}^{-3}, \\ &= \left(\frac{1}{43 \text{ \AA}} \right)^3. \end{aligned}$$

In other words, the density of electrons is equal to the room temperature quantum concentration if there is one electron every 43 Å. Now consider copper. It has a density of 8.90 g cm⁻³ and an atomic mass of 63.54 amu. So the number density of copper atoms is

$$n_{\text{Cu}} = 8.44 \times 10^{22} \text{ cm}^{-3} = \left(\frac{1}{2.3 \text{ \AA}} \right)^3.$$

The number of electrons in the electron gas (assuming one per copper atom) exceeds the quantum concentration by a factor of 6700. For copper the actual concentration and the quantum concentration are equal at a temperature of about 100,000 K (assuming we could get solid copper that hot!).

The upshot of all this is that we are definitely not in the classical domain when dealing with an electron gas in metals under normal conditions. We will have to use the Fermi-Dirac distribution function. Low energy states are almost certain to be filled. When this is true, the system is said to be *degenerate*. Furthermore, the electron gas is “cold” in the sense that thermal energies are small compared to the energies required to confine them to high densities. (This is most easily seen from an uncertainty principle argument.)

So as a first approximation, we can use the Fermi-Dirac distribution at zero temperature. This means we will ignore thermal energies altogether. At zero temperature, the Fermi-Dirac distribution becomes,

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/\tau} + 1} \rightarrow \begin{cases} 1, & \epsilon < \mu; \\ 0, & \epsilon > \mu. \end{cases}$$

Imagine a chunk of copper in which all the valence electrons have been removed (it would have a rather large electric charge ...). Add back one valence electron remembering that the temperature is 0. This electron goes into the lowest available state. Add another electron, it goes into the state with the next lowest energy. Actually it's the same center of mass state and the same energy, but the second electron has its spin pointing in the opposite direction from the first. The third electron goes in the state with the next lowest energy. And so on. What we are doing is filling up states (with no gaps) until we run out of valence electrons. Since we have the lowest possible energy, this configuration must be the ground state (which is the state the system should be in at 0 temperature!).

We must choose the chemical potential so that our metal has the correct number of valence electrons. To do this, we need to know the number of states. Since we are considering free electrons, we are dealing with single particle states in a box. This is the same calculation we've done before. The number of states with position vector in the element d^3x and momentum vector in the element d^3p is

$$dn(\mathbf{x}, \mathbf{p}) = 2 \frac{d^3x d^3p}{8\pi^3 \hbar^3},$$

where the factor of 2 arises because there are two spin states for each center of mass state. When the number of states is used in an integral, the integral over d^3x just leads to the volume of the box, V . The element $d^3p = p^2 dp d\Omega$ and the solid angle may be integrated over to give $4\pi p^2 dp$. Finally, the independent variable may be converted from momentum to energy with $p^2/2m = \epsilon$, and we have

$$dn(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} d\epsilon.$$

It's customary to write this as the density of states per unit energy

$$\mathcal{D}(\epsilon) d\epsilon = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} d\epsilon.$$

Now we're ready to calculate μ . At zero temperature, the occupancy is 1 up to μ and 0 above μ , so the total number of electrons is

$$N = \int_0^\mu \mathcal{D}(\epsilon) d\epsilon.$$

Before we do this integral, a bit of jargon. The energy of the highest filled state at zero temperature is called the Fermi energy, ϵ_F . So $\mu(\tau = 0) = \epsilon_F$. Then

$$N = \int_0^{\epsilon_F} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} d\epsilon = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon_F^{3/2},$$

or

$$\epsilon_F = (3\pi^2 n)^{2/3} \frac{\hbar^2}{2m},$$

where $n = N/V$ is the concentration. One also speaks of the Fermi temperature defined by $\tau_F = kT_F = \epsilon_F$. This is not actually the temperature of anything, but is a measure of the energy that separates degenerate from non-degenerate behavior. The Fermi temperature is a few tens of thousands of Kelvins for most metals, so the electron gas in typical metals is cold. Having determined the Fermi energy, we can determine the total energy of the gas. We just add up the energies of all the occupied states

$$U_0 = \int_0^{\epsilon_F} \epsilon \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} d\epsilon = \frac{V}{5\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon_F^{5/2} = \frac{V}{5\pi^2} (3\pi^2 n)^{5/3} \frac{\hbar^2}{2m} = \frac{3}{5} N \epsilon_F,$$

where the subscript on U indicates the ground state energy.

In the ground state, the average energy of an electron is $3/5$ the Fermi energy. Also note that the concentration contains V^{-1} which means $U_0 \propto V^{-2/3}$ which means that as the system expands, the energy goes down which means it must be exerting a pressure on its container. This is called degeneracy pressure. In fact,

$$p = - \left(\frac{\partial U_0}{\partial V} \right)_{\sigma, N} = \frac{2}{3} \frac{U_0}{V},$$

so

$$pV = \frac{2}{3} U_0,$$

just as for an ideal gas. Note that the derivative is to be taken at constant entropy. We are dealing with the ground state, so the entropy is constant at 0.

As a point of interest, using the concentration for copper that we calculated earlier, we find

$$\epsilon_F = 7.02 \text{ eV} \quad \text{and} \quad T_F = 81,500 \text{ K},$$

and the electron gas in copper really is “cold” all the way up to the point where copper melts! (1358 K)

Heat Capacity of a Cold Fermi Gas

In the preceding section we considered the Fermi gas in its ground state. This does not allow us to consider adding heat to the gas because the gas would no longer be in the ground state. To calculate the heat capacity, we need to expand our treatment a bit.

What we need to do is calculate the energy of the gas as a function of temperature. We will calculate the difference between the ground state energy and the energy at temperature τ and we will make use of the fact that the gas is cold.

With a cold gas, all the action occurs within τ of μ . That is the occupancy goes from 1 to 0 over a range of a few τ centered at μ . Since we have a cold gas, this is a relatively narrow range.

The difference in energy between the gas at temperature τ and the gas in the ground state is

$$\begin{aligned}\Delta U(\tau) &= \int_0^\infty \mathcal{D}(\epsilon) f(\epsilon) \epsilon d\epsilon - U_0, \\ &= \int_0^\infty \mathcal{D}(\epsilon) f(\epsilon) (\epsilon - \epsilon_F) d\epsilon + \int_0^\infty \mathcal{D}(\epsilon) f(\epsilon) \epsilon_F d\epsilon - U_0, \\ &= \int_0^\infty \mathcal{D}(\epsilon) f(\epsilon) (\epsilon - \epsilon_F) d\epsilon + N\epsilon_F - U_0.\end{aligned}$$

Now, we differentiate with respect to τ to get the heat capacity.

$$\begin{aligned}C_V &= \frac{\partial \Delta U}{\partial \tau}, \\ &= \int_0^\infty \mathcal{D}(\epsilon) \frac{df(\epsilon)}{d\tau} (\epsilon - \epsilon_F) d\epsilon.\end{aligned}$$

So far, everything is “exact,” now we start making approximations. At $\tau = 0$, the distribution is a step function, so its derivative is a delta function (a very sharply peaked function in the neighborhood of the step). This means that the main contribution to the integral occurs (even if τ is not 0) when ϵ is very close to μ . So we will ignore the variation in the density of states, evaluate it at μ and take it out of the integral. What about μ ? At $\tau = 0$, $\mu = \epsilon_F$. As τ increases, μ decreases, but when $\tau \ll \epsilon_F$, the change in μ is negligibly small (plot some curves!), so we will take $\mu = \epsilon_F$. Then we have

$$C_V = \mathcal{D}(\epsilon_F) \int_0^\infty \frac{df(\epsilon)}{d\tau} (\epsilon - \epsilon_F) d\epsilon.$$

Now,

$$\frac{df}{d\tau} = \frac{d}{d\tau} \left(\frac{1}{e^{(\epsilon - \epsilon_F)/\tau} + 1} \right) = \frac{\epsilon - \epsilon_F}{\tau^2} \frac{e^{(\epsilon - \epsilon_F)/\tau}}{\left(e^{(\epsilon - \epsilon_F)/\tau} + 1 \right)^2}.$$

At this point, we change variables to $x = (\epsilon - \epsilon_F)/\tau$ and we have

$$C_V = \tau \mathcal{D}(\epsilon_F) \int_{-\infty}^{+\infty} \frac{x^2 e^x dx}{(e^x + 1)^2},$$

where the actual lower limit of integration, $-\epsilon_F/\tau$, has been replaced by $-\infty$ since all the contribution to the integral is in the neighborhood of $x = 0$. It turns out that the integral is $\pi^2/3$, so

$$C_V = \frac{\pi^2}{3} \mathcal{D}(\epsilon_F) \tau,$$

a surprisingly simple result! If we plug in the expression for the density of states, we have

$$\mathcal{D}(\epsilon_F) = \frac{3N}{2\epsilon_F},$$

and

$$C_V = \frac{\pi^2}{2} N \frac{\tau}{\epsilon_F} = \frac{\pi^2}{2} N \frac{\tau}{\tau_F}.$$

In conventional units,

$$C_V = \frac{\pi^2}{2} N k \frac{T}{T_F}.$$

Some comments. This is proportional to T which means that the energy of the electron gas is $U_0 + \text{constant} \cdot \tau^2$. Can we see how this happens? In going from 0 to τ , we are exciting electrons in the energy range from $\epsilon_F - \tau \rightarrow \epsilon_F$ by giving them a thermal energy of roughly τ . The number of such electrons is roughly $N\tau/\epsilon_F$, so the added energy is roughly $N\tau^2/\epsilon_F$. The Fermi gas heat capacity is quite a bit smaller than that of a classical ideal gas with the same energy and pressure. This is because only the fraction τ/τ_F of the electrons are excited out of the ground state. At low temperatures, heat capacities of metals have a linear term due to the electrons and a cubic term due to the lattice. Some experimental data may be found in K&K.