Section 10 – Quantum Effects Seen Macroscopically

"… het groote geschiedt niet bij impulsie alleen en is een aaneenschakeling van kleine dingen die tot elkaar gebragt zijn."

Vincent Van Gogh – letter to his brother Theo, 22 Oct 1882

We often tend to think of these quantum effects as being seen only in small systems, such as atoms. There are a number of macroscopic effects whose behaviors are controlled by underlying quantum effects. In this section, we'll discuss several of these.

Molar Heat Capacity

Previously, we discussed the molar heat capacities of an ideal gas and of a crystalline solid. Solids follow the Dulong-Petit law:

$$c_M = 3RT \ .$$

Gases are a bit more complicated. For monatomic gases, which can translate only, we showed that

$$c_{MV} = \frac{3}{2}RT \ ,$$

but that diatomic gases, which we model as a spring with a mass at each end, are either

$$c_{MV} = \frac{5}{2}RT \text{ or } c_{MV} = \frac{7}{2}RT \ ,$$

depending on whether the molecules rotate only, or rotate and vibrate. However, one might well wonder why a diatomic molecule wouldn't vibrate.

Let's consider some data for diatomic hydrogen gas.[1]

We can see that at low temperatures, the molecule acts as if it translates only and doesn't rotate or vibrate. At intermediate temperatures, it translates and rotates, but doesn't vibrate. It appears that at quite high temperatures, H_2 would also vibrate; unfortunately for us, the molecule dissociates at these temperatures. This effect of excluding certain motions because of quantum behaviors is called 'freezing out' the motion. Section 8 showed us that there are restrictions on several on these motions; angular momentum and energy are required to have minimum values larger than zero. When the energy available to our particle is less than the minimum allowed energy, that motion

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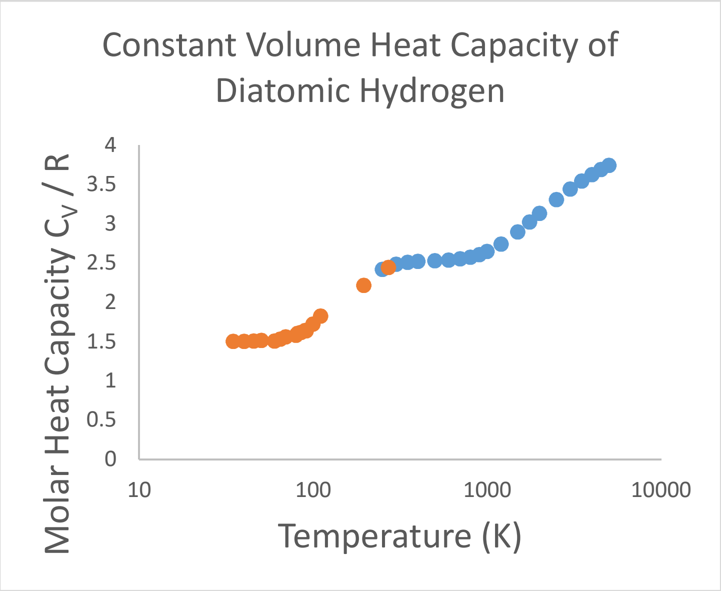
[1] Insert TWO references.

should cease. Let's run the numbers for some rough estimates. Keep in mind of course that some particles have more, and others less, energy than the average value.

We have shown previously that the average energy of translation of a gas molecule is given by

$$K_{\text{Translation}} = \frac{3}{2} k_B T \ ,$$

where T is the absolute temperature of the gas. The lowest allowed translational energy allowed for a particle trapped in a cubic container is, from Section 8,



$$E_1 = 3 \frac{h^2}{8ma^2} .$$

where we've set n = 1 and multiplied by three to account for motion in all three directions. Setting these equal, we see that the temperature below which there is not enough energy to support translational motion is approximately

$$T = \frac{2h^2}{8ma^2 k_B} .$$

EXAMPLE 10-1

> Estimate the temperature below which we would expect 'no motion' for H_2 in a 1 cm cubic container.
>
> $$T = \frac{2h^2}{8ma^2 k_B} = \frac{2(6.63\times10^{-34})^2}{8(2\times1.67\times10^{-27})(0.01^2)(1.38\times10^{-23})} \approx 10^{-14}\ \text{Kelvins} \ .$$
>
> Well, since the lowest temperature achieved by humans is about 10^{-7} Kelvins, the translational movement will not, under normal circumstances, be frozen out.

Next, let's consider rotational motion. We've shown that for a rotating object, the lowest non-zero angular momentum value is given by

$$L_{z\,1} = \hbar \ .$$

The corresponding energy of rotation about a specific axis for a diatomic hydrogen molecule, assuming a simple dumbbell shape of two point masses separated by distance d, is

$$K_r = \frac{L^2}{2I} = \frac{\hbar^2}{2\left(2m\left(\frac{d}{2}\right)^2\right)} \quad .$$

The kinetic energy of rotation around one axis should on average equal

$$\mathrm{K_r} = \frac{1}{2}\mathrm{k_B T}.$$

Setting these equal, we find the freeze out temperature to be approximately

$$\mathrm{T} = \frac{2\hbar^2}{\mathrm{k_B m d^2}} \; .$$

EXAMPLE 10-2

Estimate the transition temperature to freeze out rotation for H_2.

$$\mathrm{T} = \frac{2\hbar^2}{\mathrm{k_B m d^2}} = \frac{2\times(1.05\times10^{-3}\ )^2}{(1.38\times10^{-23})(1.67\times10^{-27})(74\times10^{-12})^2} = \text{175 Kelvins}.$$

You may notice in the graph above that about half of the hydrogen's rotational energy contribution disappears when the temperature is about 160K or so.

Next, let's estimate the freeze out temperature for vibration. The lowest energy of vibration of a one dimensional harmonic oscillator is[2]

$$\mathrm{E_1} = \frac{\hbar}{2}\sqrt{\frac{\mathrm{C}}{\mathrm{m}}} \quad ,$$

where C is the 'spring constant.' Since we have two masses vibrating, we'll cut the spring in two, and therefor double the spring constant, and consider just one mass. The spring constant of an H-H bond is estimated to be 570 N/m. So, we'll set E_1 equal to the average energy expected from vibration:

$$\frac{\hbar}{2}\sqrt{\frac{C}{m}} = \frac{2}{2}k_B T \; .$$

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[2] The Wilson-Sommerfeld calculation gave us twice this amount, but I'm using the more accurate result we will get later in Section 11.

We took two halves here because the energy includes both kinetic and potential energy.

$$T = \frac{\hbar}{2\,k_B}\sqrt{\frac{C}{m}}\ .$$

EXAMPLE 10-3

Estimate the freeze out temperature for H_2 in terms of vibration. We'll consider one mass only, but then need to double C.

$$\mathrm{T} = \frac{\hbar}{2\,\mathrm{k_B}}\sqrt{\frac{\mathrm{C}}{\mathrm{m}}} = \frac{1.06\times10^{-34}}{2\times1.38\times10^{-23}}\sqrt{\frac{2\times570}{1.67\times10^{-27}}} = \boxed{3200\text{ Kelvins}}\ .$$

So, for hydrogen, as the temperature cools to several thousand Kelvins, we would expect that the vibrational motion contribution to the heat capacity will become negligible, which is roughly compatible with the experimental data. Remember, at these temperatures, the hydrogen molecules begin to break up. In any case, we can clearly see the three regions of different behaviors.

Let's take a quick look at vibration in some other diatomic molecules:

Compound	Estimated Temperature	Observed Temperature at which $C_V = {}^6\!/_2\, k_B$[3]
H_2	3200 K	1700 K
HCl	2070 K	1300 K
F_2		400 K
Cl_2	400 K	250K

HOMEWORK 10-1

Estimate the transition temperature to freeze out vibrational motion in F_2. How does your result compare to the value taken from actual data?

Finally, let's examine the behavior of a solid. In Physics Two, we worked out that the average energy of an atom in a crystal should be $3k_BT$, that is, ${}^1\!/_2 k_BT$ for each of the kinetic and potential energies in each of the three axis directions (the DuLong-Petit law). Should we not again expect that this motion will be affected at low temperatures?

In three dimensions, the lowest energy of an oscillator is[4]

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[3] That is, halfway between $5/2k_B$ and $7/2k_B$.

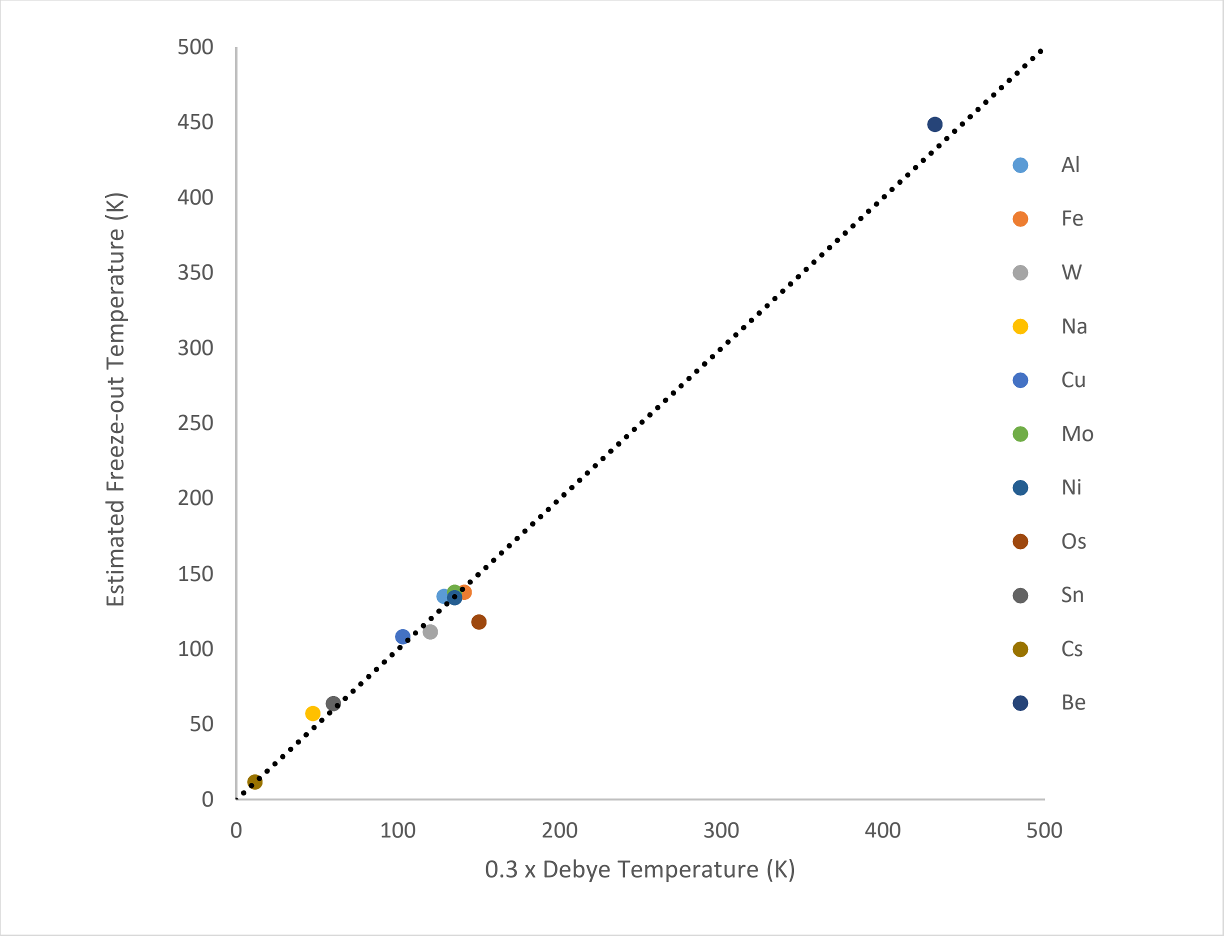
[4] Using the 'correct' relationship and multiplying by three to account for each direction of motion, x, y, and z.

$$E = \tfrac{3}{2}\hbar\sqrt{\frac{C}{m}}\ ,$$

which we'll set equal to $3k_BT$ to obtain

$$T = \frac{\hbar}{2k_B}\sqrt{\frac{C}{m}}\ .$$

Let's calculate this temperature for a number of metallic crystals. We'll need an estimate for the 'spring constants' for each metal. We can obtain that from the Young's modulus (see Note One). The graph refers to a quantity called the *Debye temperature*, Θ_D. Its meaning is beyond the scope of this course, but we might think of it as a quantity that characterizes the temperature at which the molar heat capacity deviates from classical theory. From theory, the molar heat capacity falls to one half of its classical value at about 0.3 Θ_D. The graph compares our roughly calculated freeze-out temperatures for a number of metallic elements with the corresponding Debye temperatures, and shows fairly good agreement. The dotted line has slope one and indicates where the two values would be equal.



HOMEWORK 10-2

The Quantum Hall Effect

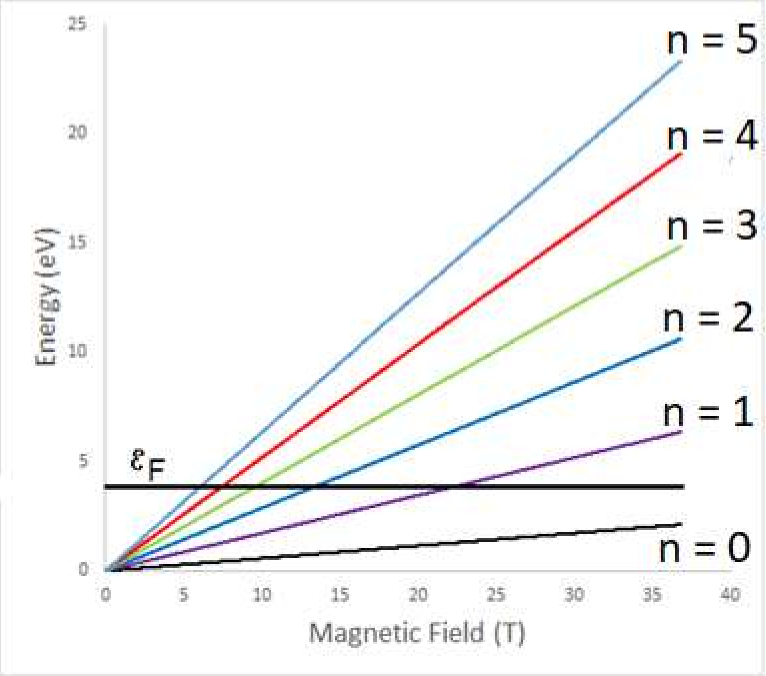
The *quantum Hall effect* is seen at very low temperatures and very high magnetic fields. We saw in Physics Two that charged particles in a transverse magnetic fields will move in circular orbits with a frequency (the *cyclotron frequency*) of

$$\omega_C = \frac{qB}{m}.$$

This circular motion can be thought of as comprising two harmonic oscillators moving at right angles to one another with the same frequency. As such, the particle possesses quantized energy levels given by

$$E_j = \left(n + \tfrac{1}{2}\right)\hbar\omega_C = \left(n + \tfrac{1}{2}\right)\hbar\frac{qB}{m} \quad , \quad n = 0, 1, 2, 3, \ldots \; .$$

Note, however, that there is no potential energy involved; that is why the energy levels are half what we might expect for the sum of two oscillators. The allowed energy levels are proportional to the applied B-field and are sketched on the graph below.



If the temperature is very low, we expect the vast majority of conduction electrons to be in their lowest possible energy states. The maximum energy in this situation is called the *fermi energy*, E_F; no electrons are available for conduction above this energy.[5] As the magnetic field is increased, we expect the allowed energy levels to become farther and farther apart. For sufficiently high B, only the lowest energy state is accessible to the carriers, and this corresponds to a particular conductivity in the sample. In the figure, the six lowest allowed energy levels are plotted as a function of applied magnetic field, B; there are obviously many more levels represented by lines of increasing slope, passing

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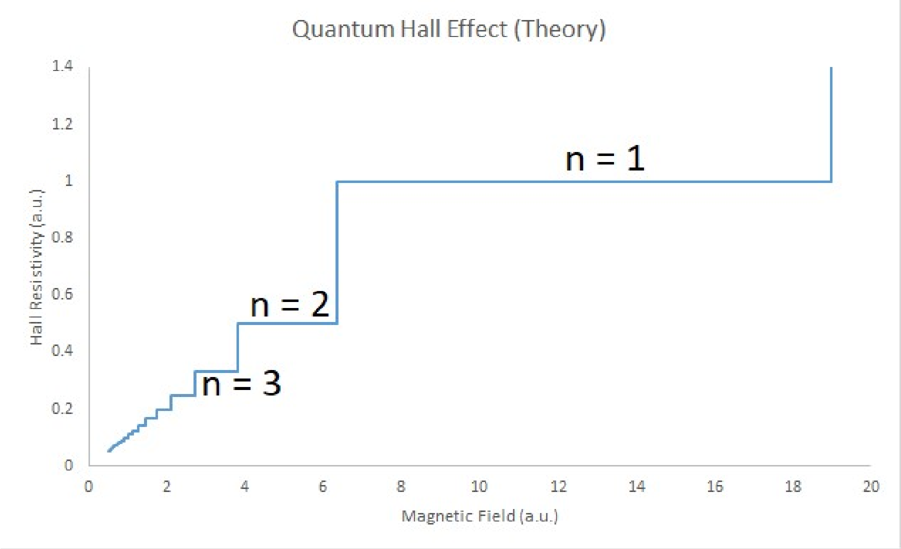
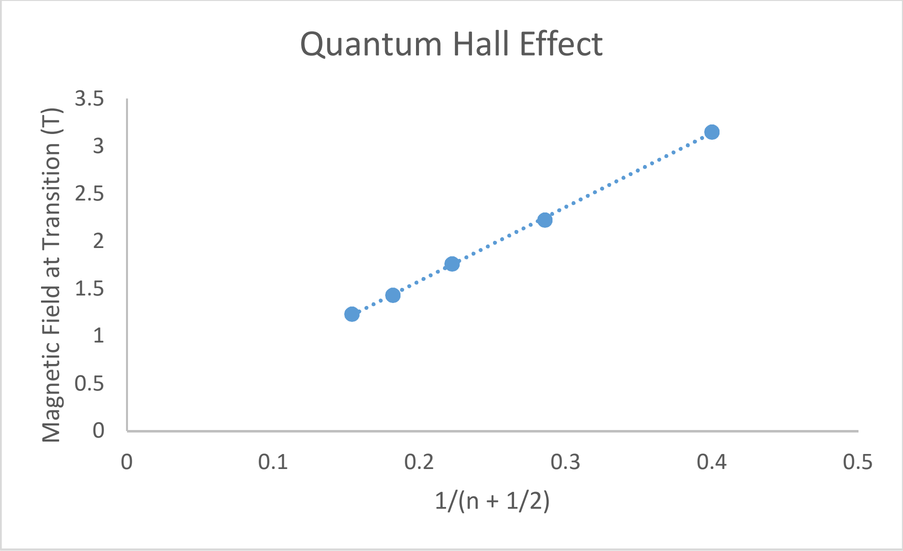
[5] At zero temperature, all of the electrons have energies equal to or below the Fermi energy, and no electrons have energy above the Fermi energy.

through the origin. The position of the line representing the fermi energy was chosen as a typical value for metals at low temperatures (~4eV).

As we look at, for example, B = 30T, we see that only the n = 0 state is available to the conduction electrons and conductivity is therefor low. As the magnetic field is decreased to 20T, however, the n = 1 state also becomes available, and more electrons are able to move. As the field continues to decrease, more and more levels become available and the resistivity of the material will decrease in steps. The magnetic field strengths at which transitions from one conductivity value to another occur are then

$$B_n = \frac{E_F m}{\hbar q} \frac{1}{n + \frac{1}{2}} .$$





The graph illustrates the theoretical behavior of a two-dimensional system of electrons.[6] As the magnetic field is reduced, the steps become smaller and closer together, so that as B goes to zero, the expected classical behavior of the Hall resistivity being proportional to the applied magnetic field is observed. That is, the steps come to resemble a line.

We haven't worked on the theory for the values of the resistivities, only where the transitions between them appear, so let's concentrate on that. The graph shows experimentally determined transitional B-field values plotted against $(n + {}^{1}/_{2})^{-1}$. The

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[6] Tong, David, 'The Quantum Hall Effect: TFIR Infosys Lectures,' preprint (2016).

data are for a GaAs/$Al_xGa_{1-x}As$ heterostructure at a temperature of 0.008 K.[7] The linear relationship helps to verify the equation above.

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[7] Von Klitzing, Klaus, Nobel Lecture: 'The Quantized Hall Effect' (1985).

Summary

We’ve looked at two examples of quantum effects that manifest macroscopically.