**Thermal Equilibrium Properties**

We’ll take a look at a variety of thermal properties…

**Magnetic Susceptibility**

So now we want to calculate the response of free electrons in a metal to a magnetic field. In the B field excitations file, I confined myself to 2D, but now I’m going to go back to 3D, as I had in the QM folder/Particle in B field. In the previous file, we calculated L in terms of **A**, out to 2nd order. And this is in principle enough to calculate the magnetic susceptibility. But that way looked difficult. So I’m going to do it this way. So in the QM Landau gauge file, we said: **A** = (0,Bx,0), and we had for H:



[e can be positive or negative, and B is total magnetic field, external + induced], and wavefunctions/energies,



Well, we’re just going to presume electrons now, so γ is negative.

**Paramagnetic response of free electrons (3D, T ~ Room Temperature)**

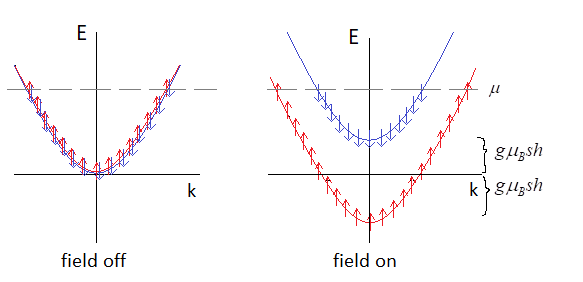
Despite our preamble, we’ll consider first the case where the electrons are not interacting with field kinetically, but only through their spin d.o.f. Basically, just not bothering to write py → py – eA = py – eBx, and instead just keeping py → py. Not sure what the point of this calculation would be, except that it’s easier to do, and I guess could say it captures the paramagnetic response. Well, it might be that when we add impurities to a metal (next folder), the full diamagnetic response we’ll consider below is interupted, leaving only the paramagnetic response we’re considering now. I’m going to call the magnetic field, **h**. And this field would be the bulk internal field generated by some external field plus the sum of the internal fields generated by all the other electrons. So now we have (γ = e/2m):



and so energy levels,



At T = 0, and **h** = 0, the electrons will be filled equally up to the chemical potential, where μ = EF, and let ρ(ε) be the density of states (including spin, say). When we turn on the field, the spin-up (well, actually, magnetic moment up – spin down) column will decrease in energy by gμBsh (s = ½); the spin-down (magnetic moment down – spin up) column will increase in energy by the same amount. The diagram will look like this, illustrated for k in 1D, but really k is a 3D vector:



(assuming field isn’t ridiculously large, they should line up at same top energy as before the field was introduced, or well, if there is a chemical potential then they will for sure). The number of up (mag moment) spins (per unit volume) is (red guy):



(where 0 is what we’re calling the energy at the bottom of the parabola, and energy at top is, relatively, μ + gμBsh). And the number of down (mag moment) spins is (blue guy):



(noting that the bottom of the parabola is what we’re calling energy 0, and the top energy of the parabola, formerly μ, is μ – gμBsh now). So the total energy (per unit volume) is (where ε = k2/2m):



And this is:



We can approximate for small deviations about μ, i.e., small fields.



Now the first guy is just the energy of the particles in absence of the field, it’s just the (3/5)NEF I think (presuming we’re at T = 0 so μ = EF). The middle guy seems to suggest that we’d have a net magnetic moment, even at zero field (‘cause M = -∂U/∂h is non-zero even when h = 0), i.e., ferromagnetism. We can’t really trust/use the first two guys because they involve the kinetic energy, ε = k2/2m, which isn’t really the physical kinetic energy, because we ignored the fact that p → p – eA. So really, all we have is:



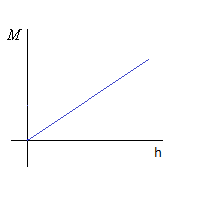
Okay, now the magnetic moment operator is defined as (see discussion in QM folder/Magnetic Field files, or the Thermodynamics/Equilibrium Systems file, or Statistical Mechanics / Paramagnetic files):



So, since g = 2 basically, and s = ½, we have:



Graphically this would look like:



Maybe a more direct way to do this would just be (σ = ±1/2):



(and γ = e/2m, sign of e included) To first order in T, we can treat μ as a constant εF, as can see graphically above. And to first order in h, we can write this as:



In the low T limit (really, just kT << εF ~ 104K), we have:



and this is of course,



And then the susceptibility is:



Since s = ½, this is basically μB2ρF. I’m kind of calling this the susceptibility, but really, the susceptibility is defined via M = χPH, where H = Bfree/μ0. So let’s figure this out.



So the susceptibility would really be:



What is that number χμ0? Well, we have to put it in MKS units, ‘cause right now I don’t see any ℏ’s, which means we set it to 1. Well actually, we don’t because this is a unitless quantity. So the ℏ’s will just cancel out. So, filling everything in, note kF ~ 1/0.7nm for Copper:



And therefore,



Preeetty small. No wonder people don’t usually make a distinction between B and Bfree (~μ0H).

**Diamagnetic response of free electrons (3D, T ~ Room Temperature)**

Now let’s let our electrons move. We’re going to do just the diamagnetic response though – basically ignore the spin contribution to the energy – because adding spin makes it more complicated because the energy levels are not evenly spaced – see the crystal excitations file in B field in the Free Day folder. However, all the spin up levels are themselves evenly spaced, and the spin down levels are themselves evenly spaced. So we could do this calculation below for the two evenly spaced sets of levels. But then our L will be a sum of two functions and it’ll still be kind of complicated – maybe pursue that sometime. So just going to do the easy thing and forget spin, and get the purely orbital diamagnetic response. So energy levels are:



Okay now then, calculating L, and renaming B as h, because that’s what I do apparently,



where Φ = BA, and Φ0 = 2π/|e|, and these terms come about due to the degeneracy of the energy levels w/r to ky. Also, extra factor of 2 is to account for both spins, and so all particles, even though we’re neglecting the spin contribution to the energy levels. Now we need to go out to order h2, if we want the magnetization. Going to absorb the exp(-βkz2/2m) term into z and call it z´ for a bit.



So now,



Now we have to work out that sum:



What limit are we looking for? I’d say, εF >> kT >> ωc = |e|h/m. That way we’re in small h territory, but T is high enough to occupy different Landau levels, but not so high as to melt our material. So βμ will be large, as will z´´. But βωc will small. In our limit kT >> ωc, the exponent ought to be very slowly varying with index n, and so the sum ought to be amenable to approximation with an integral. Here’s a quick and dirty ‘derivation’ of a sum rule. So take an integral from 0 to ∞ and break it up into a bunch of unit intervals. Then Taylor expand f about the midpoint of each interval, out to 2nd order, and do the integrals.



Now then we have:



If this formula is converging, and it seems like it would, then to ‘first’ order accuracy it would stand to reason that we could use this formula on the f´´ term itself,



and just keep the first order term,



and so then



Applying this to our expression, we’d have:



Now we’ll do a couple changes of variables in the integral term,



We’ll note that that the first term is O(h-1) and the second term is O(h), so it does seem that our sum formula approximation is converging, in a sense, for small h. Back to L then,



We only need L to second order in h, which is enough to get the magnetization and susceptibility. Since Φ = hA, ωc = |e|h/m, the last term is already of that order and so we can set ωc = 0 in the exp(-βωc/2) terms. I think I’ll convert kz sum to integral. So Σkz → ∫dkz/(2π/Lz),



So it suffices to say:



and finally,



Then the magnetization (magnetic moment per volume) is:



Filling in z´,



Noting definition:



we can can write this as:



We’ll recall from the Stat Mech/Fermion gas file that fν(z) has the following asymptotic properties:



and that,



so we can write, in the large z limit (which is appropriate for kT << εF – see Stat Mech/Independent particles),



But…we need to solve for z now, in terms of n. So let’s consider:



In the small h limit, we should be able to just keep the first term:



Guess I’ll change variables again,



Hmmm….maybe I’ll take a derivative w/r to z and then try to integrate the result w/r to z.



Then,



which in the large z limit can be taken to be:



So then,



Reassuringly, this is the Fermi energy at T = 0 (and h = 0), which is what we should get in the smallish T (really kT << εF, which still encompasses room temperature), small h limit. Okay so now plug μ back into M:



Now going to massage it into standard form. So note [3π2n]1/3 = kF. So we can write:



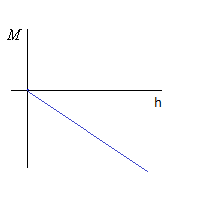
And the 3D density of states at the Fermi surface is ρF = mkF/π2. So,



which is the correct result. If we were to say |e|/2m is the Bohr magneton (can’t necessarily because m here is the band mass, not rest mass), then we’d have:



(note χ is not technically the dimagnetic susceptibility since it’s the proportionality constant between M and the local interstial magnetic field h = B, and not the proportionality constant between M and **H**. See above for getting χm. It’s easy, and basically the same as χ). So we have an orbital diamagnetic response.



**Total response of free electrons (3D, T ~ Room Temperature)**

We could naively add the two responses together, suggesting metals are slightly paramagnetic. I’d think that if we introduce disorder, perhaps through impurities, this will inhibit the formation of the currents that would constitute the diamagnetic response. And so the metal would be definitely paramagnetic. If we were to see what Hund’s rules say about inidividual metal atoms’ net magnetic moment, we’d see it is often not zero because there is a net JT value, and also a net gT value (See Quantum Mechanics/Many Identical Particles/Hund’s Rules, Stark+Zeeman Effect). And this gives it a net magnetic moment, and a consequent paramagnetic response. So that is a convergent line of thought. I suppose the two are consistent in that if even a *free* electron cannot establish a large enough current (and hence, diamagnetic response) to overwhelm its intrinsic (through spin) paramagnetic response, then certainly an electron stuck on an atom will not be able to. Of course, it’s not a good approximation to think of metals’ valence electrons as being in states at all similar to eigenstates of their host atom, since metal valence electrons can freely roam and aren’t stuck on their host atom.