**Nonequilibrium Properties**

Yeah. Note unlike in the Absorption file, we’ll be assuming weak enough E and B fields that no electrons will be excited into different bands.

**Conductivity**

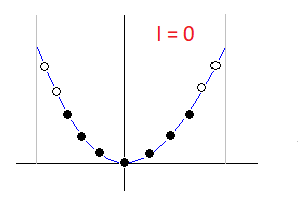
So let’s examine the equation for the current. In the semi-classical picture, we’ll recall the general formula for the time evolution of some statistical quantity from the stat mech file (see e.g. Stat Mech/Distribution Function, and Classical NESM RTA):



where nkσ(r) is the single particle distribution function (per a given band). As we expect no r-dependence, the expectation of the current would be:



If a band is full, so that nkσ(t) = 1, then we’ll just get zero. This is because εn(k) is a periodic function, and so if we integrate by parts, then can see we get zero due to evaluating εn(k) at the edges of the BZ. So full bands contribute no current. And in the GS, we can see that the bands would be full if there were an even number of electrons per unit cell, *and* there were no band overlap (see Nearly Free Electron model for more on this point). This is because in k-space, in each band, there are 2N slots (spin up/down × number of k-points in BZ) for electrons to go. And if there are an even number of electrons per unit cell, then there will be a whole number of bands occupied – if the bands don’t overlap. But if there is an odd number of electrons, and the bands don’t overlap, then one of the bands will necessarily be half full, like this:



But still there would be zero current, at present, since an equal number of electrons will be going left vs. right. But when we apply an electric field, we’ll get current. Since there are no impurities yet, would the current just continually accelerate? Well no not quite. The band structure is responsible for strange characteristics of the metal. If the mean free path is long enough (and its ∞ for now because no impurities), then we can actually obtain an AC current if the DC **E** is parallel to a Brillouin vector.

Let us consider nσ(**r**,**k**,t) to be the single particle occupation number function for the e-, where **r** is their position and **k** their crystal momentum (we’re presuming a semi-classical model where we can simultaneously specify these things). In the relaxation-time approximation, we have (see Stat Mech folder):



where nleq is the local equilibrium distribution function. We’ll presume no impurities at this point, and no other scattering mechanisms either. So τ → ∞. That brings us to:



We’ll also assume that ambient EM fields will drive the electrons through their Bloch states (within the band). We assume that the EM field isn’t so strong, or of such a frequency to pump an e- from one band to another. So we assume band index number to be a constant. Now we know that **v** = ∂εnk(t)/∂k, but what is ∂**k**/∂t? So we need to find out what the equation of motion is for the crystal momentum is. We assume that the introduction of the electric potential will modify the motion of the e-‘s in such a way as to keep the total energy constant – just as would be the case for a conservative potential. Then,



and so we have,



We assume the introduction of a magnetic field will look similarly. So altogether,



(remember *e* is negative) and then the d**r**/dt term would just be:



(and of course, as implicitly stated above, **v** = ∂εnk/∂**k**, as we confirmed, at least in the expectation sense, in previous file). So altogether,



or, filling in what **v** is,



From our knowledge of PDE’s, the solution to our Boltzman equation would just basically be (see Stat Mech, RTA file):



where **R**(t) and **K**(t) are the wavevector and position that would evolve (according to the dynamical equations above) into **r**, and **k** after elapsed time t, and n0 is the initial distribution function. Or in other words, **R**(t) and **K**(t) are where **r** and **k** were t seconds ago (if we treat those points as coordinates that evolve according to those equations of motion).

**Motion in Constant E field**

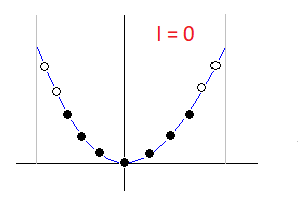
Then consider. If we apply an E-field along a lattice vector, then the electrons will move to the left in k-space as the equation above instructs them to (e negative).



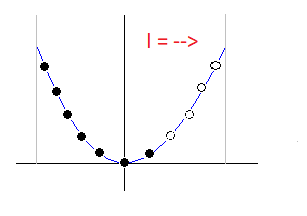
But the actual velocity of the electrons depends upon the derivative of the energy spectrum at that k point, and this oscillates along the band, and so the velocity of the particles will oscillate too. Let’s illustrate.

**rightward E, and rightward I**

First consider a bunch of particles occupying the mininum of a band.

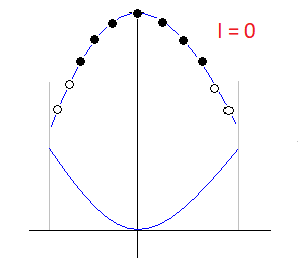


Then application of an E-field to the right, makes the electrons go to the left in k space, just like before. But then there is a net majority of electrons on the left. Therefore we have a net flow of negative charge to the left (because electrons in this region have a negative slope, and therefore negative velocity), which equates to a net flow of positive charge to the right. So current goes rightward. This is as we would expect.

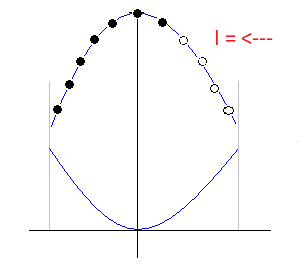


**Rightward E and leftward I**

But now consider a bunch of electrons symmetrically situated about a band maximum. The net velocity of the electrons is 0 because each electron going one way can be paired with another electron going another way.



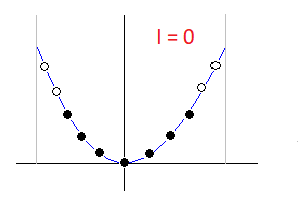
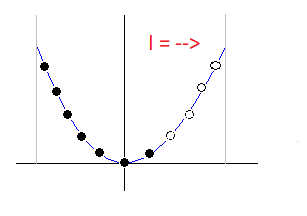
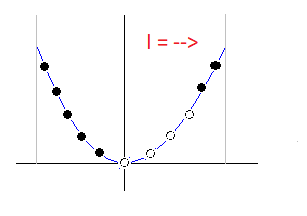
When we apply an E field to the right, the electrons will go to the left (in k-space) according to the equation of motion above.

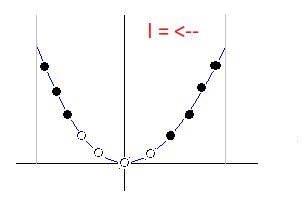
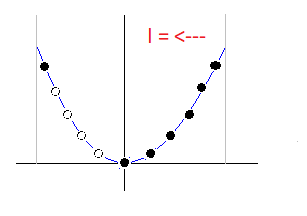
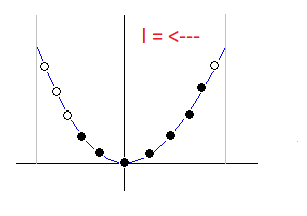


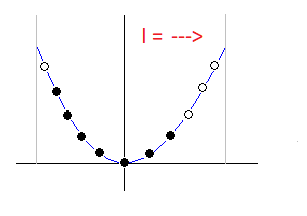
But then there will be a net # of electrons on the LHS of band maxima. Therefore more of them will be going to the right (b/c **v** is the derivative of ε(k) which would be positive on the LHS) than to the right. Therefore we’d have a net flow of positive charge to the left when apply E field to the right!

**E rightward, I alternating**

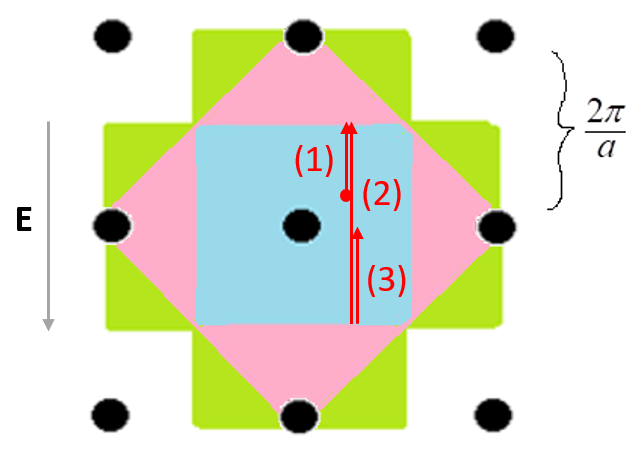
More generally, we can get an AC current. Consider our electrons centered about the band minimum. Putting an electric field to the right will cause them to go left, and when they hit the left end of the BZ, they will just start over at the right end (this is called Umklapp scattering I think). Looks something like this (time lapse in reading order):



So this was a 1D example. What about a 2D BZ? I’ve drawn the path a red electron would take in an ambient E field pointing downward. Every time it is about to hit a zone boundary it is kicked back in by a reciprocal lattice vector (you *could* consider it to simply be traveling undisturbed through the extended BZ scheme I think). Note the black spots are points in reciprocal lattice vector space, not atoms or anything.

 Shape

Description automatically generated with low confidence

So that was fun. Consider the special case of aiming an electric field along a reciprocal lattice vector, **G** (it doesn’t have to be a RLV in the 1st BZ, but can be *any* RLV). And let **G**min be the shortest RLV along that direction. Then we have:



Now every time the electron strays from the first BZ traverses, it will be kicked back inside, as discussed. But in our minds, we can just let the electron’s trajectory unfold uninterupted in k-space until the end, and at that time, find the combination of RLV’s necessary to place it back in the first BZ. Keeping that in mind, let’s consider the amount of time it will take for the electrons to travel a distance in k-space equal to Δk = Gmin. This,

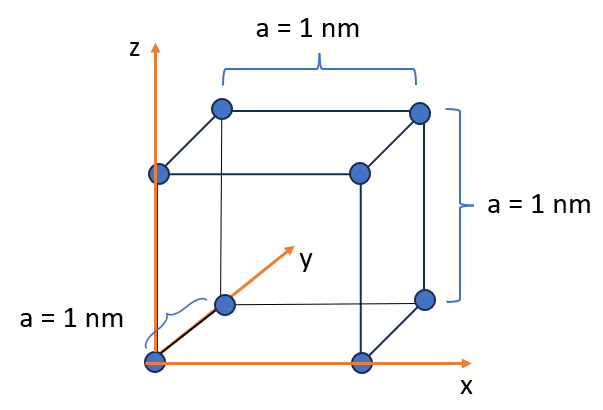


After this amount of time, to locate the electron we would just displace them all backwards by -**G**min. And thus, the electrons will be right back where they started. And so we will get oscillatory motion with period Δt, or in other words, frequency,

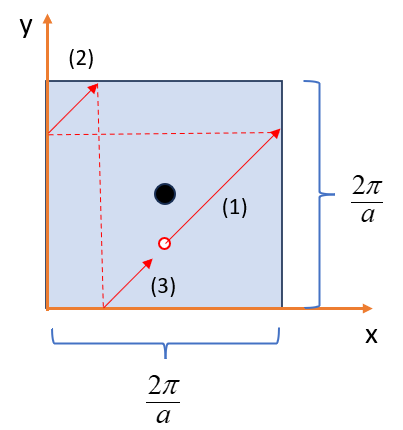


**Example**

Consider a metal which has the simple lattice structure shown in the diagram. Further, let the energy spectrum of the electrons in the conduction band to be something of the tight binding sort ε(k) = -2t[cos(kxa) + cos(kya) + cos(kza)] with no band gaps, but otherwise obeying the symmetry of the crystal. Say we immerse this crystal in an electric field **E** = -E0(+). Consider the trajectory of a single hole in the conduction band, with initial position **k**0 = -ℏπ/2a. What wil be **k**(t)? What will be its period of motion?



The hole’s trajectory will look like this, roughly (the black dot is a RLV point). Note that in k-space, the hole moves just as an electron would.



The hole’s initial trajectory will be:



It will hit the right face of the BZ when:



And will have k-value,



Thereupon it will be reflected to the opposite side of the BZ, and will now have k-value with opposite x-component:



It will proceed as follows,



It will hit the top of the BZ at t2 given by:



Thereupon, its k-value will be:



At which point it will reflect, and become,



And thereupon, its k-value will become,



We can see it will return to its initial position when,



Come to think of it, it looks like all holes will follow the same length of trajectory (one complete diagonal), before returning to their initial positions. And so the current would oscillate with this period, tr. This accords with our Bloch oscillations formula above, noting that E = E0√2, and G = √2(2π/a). Let’s work out the velocity at some point in time,



What will be the velocity at time:



This places it in the middle of the upper left trajectory. Let’s fill it in. So first we need k,



And so the velocity is:



So there.

**Example**

Silver has an FCC lattice structure with lattice constant *a*. Let’s say the primitive basis vectors are:



Now suppose we immerse an ultrapure sample in a DC electric field, **E**, pointing in the direction. What will be the period of oscillation of the current? Well the RLV will be:



The smallest RLV pointing in the z direction is,



The evolution of the electrons will be:



where **G** is the RLV necessary to place **k** back in the first BZ. So every time the electrons traverse a distance Gmin = |**b**1 + **b**2| in k-space, they will be reflected back into the first BZ. The amount of time required for this, i.e., the period of oscillation is:



So the frequency of oscillation is:



**Motion in a constant B field**

What if we take out our electric field and replace it with a magnetic field? Then our equations of motion are:



where **v** = ∂ε/∂**k** of course. Note ε(k) is constant of the motion, since:



Also in direction of B is constant, since:



Thus the motion of **k**(t) along **B** is constant, and in any event, along a constant energy contour. So say we have a nearly free electron band, with magnetic field pointing upward.

Chart, surface chart

Description automatically generated

And then we’ll look at an electron at a k-point on a nearly circular constant energy contour. The magnetic field will make it execute the following motion. We can tell it goes CCW because at, say, the top of the trajectory, **v** goes up the page (since that is the direction of the energy gradient), and **B** goes out of the page, so **v**×**B** points right, and since e is negative, that makes point left.

Chart, diagram, bubble chart

Description automatically generated

If the Fermi surface is indeed spherical, and we do have a circular orbit, as depicted, then we can get the period of motion,



Can take derivative:



General solution is:



where αx,y and βx,y are arbitrary constants. Initial conditions require,



And also have that x(t) = eB/m\*ky, so that requires,



So,



Presumably we’re dealing with electrons so that sgn(e) = -1. Anyway, we’ll recognize ωc as the cyclotron frequency from Electrodynamics, or Quantum Mechanics, or the Free Day/Excitations in a B field file from a neighboring folder. In fact the trajectories of the electrons *should* (?) just be described in some sense by the electrons’ time-independent wavefunctions in a constant B-field. We can get an equation for the orbit in position space, at least in the plane perpendicular to B. Let’s cross both sides of the momentum equation by .



Now we’ll recognize that **v** – (**·v**) is **v** projected onto the plane perpendicular to **B**. So we’ll call it **v**⊥.



And now we’ll integrate both sides from 0 to t.



So,



Graphically then, if we take our **k**(t) trajectory, and rotate it CW (because e is negative) 900 about an axis passing through **k**(0) (the red dot) and parallel to **B**, we will get our **r**⊥(t) – **r⊥**(0) trajectory (the blue guy). And the blue guy is scalled by 1/|e|B as well. Tried to illustrate a little below:

Shape

Description automatically generated

So for a spherical Fermi surface we get circular orbits, as expected since we know that’s what happens in the free electron case. If our Fermi surface were a bit higher, then it’s possible we wouldn’t get closed orbits at all. An electron starting at the red dot would traverse the Fermi surface upwards (1), till it got to the edge, and subsequently kicked back down to the bottom (i.e., displaced by a reciprocal lattice vector), whereupon it would continue on path (2).

Diagram, histogram

Description automatically generated

This orbit is also closed, but if the surface were not spherical, then it’s easy to see that we could get orbits that weren’t closed. Keep in mind that introduction of the magnetic field here doesn’t bring about a net current. The electrons on the other side would be going in the other direction.

**Motion in E and B fields**

So let’s say we add an electric field to this situation, perpendicular to the B field.

Chart, surface chart

Description automatically generated

The equations of motion of our electrons are:



Now ε(k) is not a constant of the motion:



(really should be dε/dt = ∂ε/∂**k**·d**k**/dt – I’m being pretty sloppy with derivative notation) But we’d still have that in the direction of **B** is constant, for this given orientation of fields,



Thus the motion of (t) along **B** is constant, which means the acceleration of **k**(t) along the B field is constant, which is just as is the case for free electrons in and **E**, **B** field. In the EM folder/Charge Dynamics file we examined in detail the motion of a charged particle in an **E**, **B** field. We found generally that **k**(t) precessed about the **B** field lines, while increasing up (or down) the **B** field lines, and simultaneously drifting across them in the **E**×**B** direction. The same should be found here, at least for a spherical Fermi surface, with the exception that if the electron should cross the 1st BZ, it will be Umklapp scattered back into the 1st BZ. But let’s look at position space. Let’s cross both sides of the momentum equation by again,



Again we’ll recognize that **v** – (**·v**) is **v** projected onto the plane perpendicular to **B**. So we’ll call it **v**⊥.



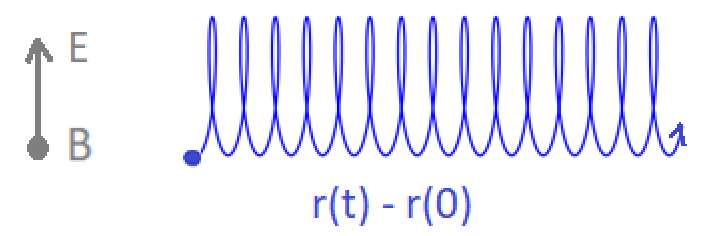
And now we’ll integrate both sides from 0 to t.



So,



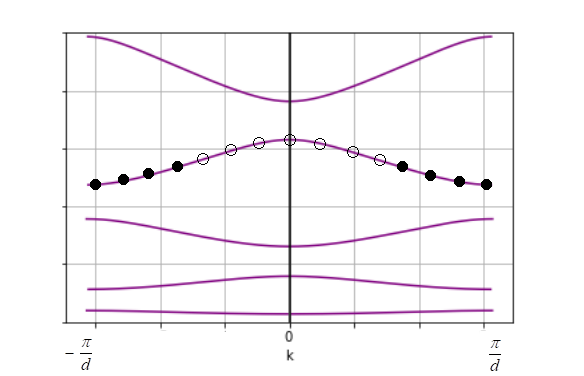
This is the same expression we got before, except for the addition of the last term, the drift velocity term. So instead of circles, we’ll now have something like this:



(B coming out of page) Well, also have to account for the fact that the **k**(t) trajectory is not quite what is was before, w/o the **E** term. Accounting for this, I imagine that the particle is also accelerating up the magnetic field lines, as in free space.

**Conduction in terms of holes**

As we saw when we were looking at excitations, when we have a nearly filled band, it’s more convenient to formulate excitations in terms of holes, rather than electrons.



We can do the same thing here.



Now the first term is zero, as filled bands contribute nothing to the current (adds up to zero due to periodicity of v(**k**)). The right term sums over unoccupied levels, i.e., the number of holes. So we have:



But eh = -e is also the charge of the hole. So we can write:



I’ll content myself with just taking a qualitative view describing conduction with holes. Let’s consider a band that looks like this:

Chart, line chart

Description automatically generated

So if apply field to the right, then electrons will move left in k space.

Chart, line chart

Description automatically generated

Moreover the net current of the electron distribution will be positive, as more electrons will be on the right side now, and so more will be moving with negative velocity (∂ε/∂k < 0), and so more will have positive current. If we look at it from the hole perspective, then the initial distribution will look like,

Chart, line chart

Description automatically generated

Again there is zero current, but with a rightward electric field, we now have a short time later,

Chart, line chart

Description automatically generated

So now there are more holes on the left than right. So there are more holes with positive velocity than negative velocity, and so we’ll have a rightward current, which is the same conclusion we had before. The motion of the holes is a little counter-intuitive, because one might think the holes should move to the right along the k-axis, being positively charged in a sense. But by looking at the electron picture, you can clearly see that the holes do move left along the k-axis. So hole dynamics is the same as electron dynamics, as far as the k-axis is concerned. But…the holes will be accelerated to the right, in position space, as we saw, since their velocities have become more positive. So in position space, the holes do behave as positive particles, and the motion in position space *is* reversed from that of the electrons. As another indication of the fact, we can calculate the acceleration of a particle/hole in an EM field,



This splits into two cases,



So we get the customary N2L in both cases. And clearly holes would have the opposite trajectory to electrons. Now want to look at the Boltzman equation for holes. The electron distribution function nσ follows the usual function.



where v = dr/dt. The hole distribution function must follow the same equation, as this follows for any function (see Stat Mech folder/Relaxation Time Approximation):



[We could come to the same conclusion by using nσ(h) = 1 - nσ] We just need to fill in what v and ∂k/∂t are. Well these should still be given by what they were for electrons. So,



and more specifically,



But e = -e(h), and ε(k) = -ε(h)(k) [see Excitations/Properties file]. So we can say,



So that puts the Boltzman equation in terms of purely hole properties. If we say that ε(h)(k) = (1/2)k2/2m, then this would be:



This equation will get some use in the Semiconductors/pn junction folder.

**Factoid**

Don’t know where else to put this so….consider the case of Aℓ. This is a metal. As discussed in the Excitations folder, we can consider it to have 3 electrons fit into a free-electron spectrum. The Fermi sphere would extend out into parts of the 2nd, 3rd, and 4th BZ (1st BZ completely filled). Band gaps eliminate the 4th BZ occupation. So just 2nd and 3rd BZ’s are partially occupied. And these are occupied by the 1 electron left (first two completely fill the 1st). So we have ne(2) + ne(3) = n, where ne is electron density, nh is hole density, and n is atomic density. But then also ne(2) + nh(2) = 2n. So ne(2) – nh(2) = -n. So this indicates Aℓ would have negative the Hall coefficient you’d think it would have, i.e., it acts as if it’s a positive charge carrier (with one ‘positron’ per atom), instead of a negative charge carrier. And this is confirmed by experiments.

**Appendix**

Would like to get the actual units of vd. So we’ve implicitly been using the Natural + Gaussian fake unit system whereby we set ℏ = 4πε0 = μ0/4π = 1. So we have to restore these factors in vd. I doubt we have an ℏ in there. So just going to do (refer to units file)



Oh so apparently E/B does have units of velocity already. So it really is just vd = E/B. Oh yeah that makes sense, since for EM waves, we have E = Bc.