**Thermal Equilibrium Properties**

Gonna look at the thermal occupancy of the bands and donor, acceptor levels now. For point of reference, it’s useful to have the following values in mind, for Si, say, which could be doped with Al, or P, to make it a p-type or n-type semiconductor.



Also keep in mind these rough energy scales.



Moving on,

**Thermal Occupancy**

So let’s consider again one of those band diagrams, say of Ge. This time we’ll suppose that our sample is doped with Nd n-type impurities per unit volume, and Na p-type impurities per unit volume. These will establish Nd and Na donor and acceptor levels, per unit volume, just below and above the conduction and valence bands respectively. These are illustrated in red.

Diagram

Description automatically generated

And recall the energy gap Eg ~ 5eV, while the donor and acceptor levels sit below and above the conduction and valence bands by around 0.1eV. We’d like to figure out what the population of the bands and levels will be as a function of T. Well at T = 0, the valence band is full with nv = 2Nv electrons per unit volume, where Nv is number of levels (which can each hold two electrons) per unit volume in valence level. And the conduction band is empty with nc = 0 electrons per unit volume. And we have nd electrons per unit volume that would ostensibly occupy each of those Nd donor levels per unit volume (well, half occupy, as in 1 electron per level). And we have na acceptor electrons per unit volume that would likewise half-occupy (1 electron per level) each of the Na acceptor levels. But we’ll observe that the system can lower its energy if some of those donor electrons drop into the acceptor levels. The number of electrons that will drop down is min(Na, Nd). So we have:



So then at non-zero T, when we have some excitations of electrons from the valence band, acceptor band, or donor band, into bands/levels higher than themselves, they must leave holes where they came from.



Well altogether, the total number of particles must remain the same. So adding up all the particles per unit volume and setting equal to the T = 0 result, we have:



So,



So then all we need to figure out the chemical potential is work out the thermal occupancy of the conduction/valence bands, and donor/acceptor levels. In the free electrons file we worked out the former, and found,



where in the ellipsoidal approximation, the Nc(T), Pv(T) guys were:



Again, the formulas for the occupation #’s follow what we’d expect from Classical Maxwellian statistics, but with holes having a ‘negative’ temperature. So now let’s look at the thermal population of the donor levels, making reference to the diagram we drew in the previous file.

A picture containing chart

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We can consider a single level at a time, as they’re all independent. Consider the single level as a system. And states are n = 0, ε = 0; n = ↑, ε = εd; n = ↓, ε = εd (double occupancy is forbidden because energy is really high). Then form L and differentiate w/r to μ.



And differentiating,



And note that if two electrons were allowed on that level, and the consequent energy were 2εd, then this distribution would reduce to the usual nF(εd). Now we can get the thermal expectation of na, making reference to the diagram from the previous file,

A picture containing diagram

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And again we’ll do this one acceptor level at a time, as the levels are independent. Well the states for our level are: n = 0, ε = ∞ (double hole occupancy is forbidden as energy is really high); n = ↑, ε = εa; n = ↓, ε = εa; n = ↓↑, ε = 2εa. Then form L and differentiate w/r to μ.



And differentiating,



Number of holes would be:



Now our results are for a single level. We must multiply them by Nd and Na respectively to get the thermal population of the entire set of levels. Finally, since we expect μ to be far away from both εa and εd, we can make the same ‘Boltzman’ approximation that we did for the conduction and valence band levels. Then we have:



These formulas are evocative of the ones for the conduction and valence bands. Nd and 2Na are the degeneracies of the donor and acceptor levels. And e-β(ε\_d-μ) is the classical thermal occupation factor in the grand canonical ensemble. And then like with the valence band occupation number, we can get the acceptor ‘band’ number by negating the temperature. And we’d fill our highlighted formulas into the boxed particle conservation equation…



…to solve for μ. Once we have μ, then we have the thermal occupations of all bands/levels at any temperature. And we can calculate stuff. In general, we’d have to solve this equation numerically. Well actually, it looks like its just a quadratic equation in eβμ. Still, let’s simplify. For one, due to the attached exponential factors, nd and pa are pretty small compared to Nd and Na themselves. If we neglect them (and this is tantamount to saying that all donor electrons will be in the conduction band, and all acceptor holes will be in the valence band – seems we will always be making the assumption), we can say,



Now we can actually get around having to solve for μ at all, by taking advantage of the fact that:



So we see that the product of nc(T) and pv(T) is still ni(T)2, from the pure semiconductor file, even though nc(T) and pv(T) are not both equal to ni(T) anymore. This is apparently called the ‘Law of Mass Action’.



I’ll highlight it, because we’ll use it again, later. So altogether, our equations are:



We can solve these guys of course. Plug the first into the second,



Choosing the appropriate signs, we come to:



**case: |ΔN| << ni**

Now say the number of donors and acceptors is small, or large but closely matched. Then (ΔN)/ni will be small, and these reduce to:



Do note that ΔN = Nd – Na can be small, while Nd and Na are *individually* large. It’s interesting that if ΔN = 0, then we go back to the intrinsic case. I guess this is because all the Nd’s drop into the Na’s. So then the Na’s are full and the Nd’s are empty. And since since the Nd’s are so close to the conduction band, and Na’s so close to the valence band, this is basically identical to the intrinsic case.

**case: |ΔN| >> ni**

Now let’s look at when ΔN is large.



where θ() gives 1 if the constraint is satisfied, but 0 otherwise. Going to highlight the result:



I think this case would be expected to prevail, since doping Si, say, has an intrinsic carrier density of 1016 at room temperature. But has atomic density of 1028. So a mild doping concentration of 1/106 (well, assuming either Nd or Na ~ 1/106 and the other is zero) would result in an impurity carrier density of…



So,



whereas we saw in the previous folder that Si’s intrinsic carrier density was ni ~ 1016 carriers/m3. So I think we can presume ΔN >> ni.

So then note that our highlighted equation implies that, if Nd >> Na, then three things happen.

1. if there are Na electrons in the acceptor levels, then there are Na holes in the acceptor levels too, and so Na of the Nd electrons drop into the acceptor levels and fill it completely up (thereby making it impossible for the valence band electrons to thermally jump into the acceptor levels) and make holes for itself.
2. the rest of donor electrons (Nd - Na of them) thermally populate the conduction band.
3. and we can say that an additional ni2/(Nd – Na) electrons jump from the valence band to the conduction band.

I tried to depict this below. 2) corresponds to the third picture, and 3) corresponds to the fourth picture. There probably should be some electrons in the fourth picture’s donor levels, but whatever.

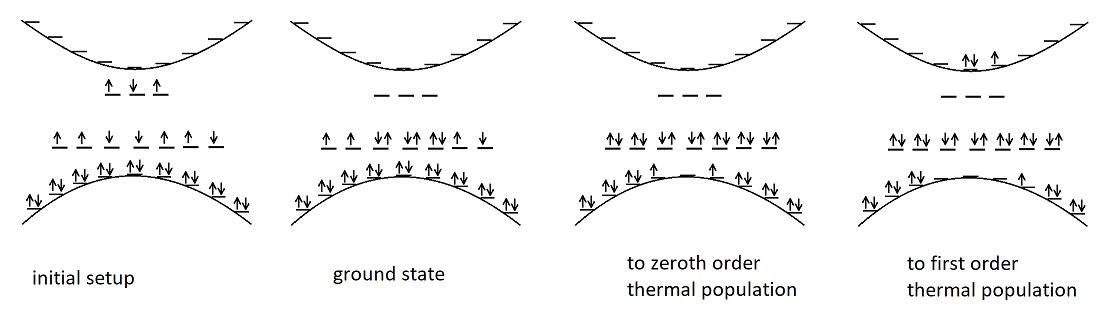
Diagram

Description automatically generated

But if Na >> Nd, then,

1. All of the Nd electrons will completely empty from the donor level into the acceptor level (thereby making it impossible for any donor level electrons to thermally jump into the conduction band)
2. The acceptor level will now have Na – Nd holes, and these will be completely filled up by electrons jumping from the valence band into the acceptor level. And so we’ll have Na – Nd holes in the valence band.
3. and we can say that an additional ni2/(Na – Nd) electrons jump from the valence band to the conduction band.

I tried to depict this below. 2) corresponds to the third picture, and 3) corresponds to the fourth picture. There probably should be some electrons in the fourth picture’s donor levels, but whatever.



**Chemical potential**

Moving on, we can solve for the chemical potential of course, now that we have pv and nc. One nice formula comes from doing it this way. We’ll start by noting we can write nc and pv in terms of the intrinsic concentrations:



where ni is the intrinsic semiconductor electron/hole density, and μi is the intrinsic semiconductor chemical potential.



Now fill these into:



So,



Can see, trivially, that the chemical potential for n-type semiconductors is higher than that for p-types. And we’d expect so since n-types have more electrons.

**case: |ΔN| >> ni**

In the |ΔN| >> 2ni case, we’ll note that sinh-1(x) ~ inverse[e|x|/2] = ln(2|x|). So then,



And we’ll use,



to say,



For later reference, we’ll note that the first three terms don’t depend on impurity concentrations (*this* formula doesn’t reduce to μi when ΔN = 0 because we’re presuming the ΔN >> ni limit, but the exact highlighted one does). The last term is where the doping concentration comes in. And it goes up, the greater the difference in doping types, ΔN. For some perspective, a mild doping concentration is 1/106 (atoms), while ni is about 1/1012 (atoms). So ΔN/ni ~ 106. This makes μ ~ μi ± 6kBT. And room temperature 300kBT ~ 0.02eV. So μ ~ μi ± 0.1eV. Now μi sits almost exactly halfway between the valence and conduction bands. And this energy gap Eg ~ 5eV. And since the donor and acceptor levels are just around 0.1eV away from the conduction and valence bands, this means the chemical potential is still roughly directly inbetween the gap, well away from either the donor or acceptor levels. So going back to those formulas for the donor and acceptor occupations,



we can see that since μ is very far away from the levels, these ought to give something like,



And really, I used a pretty mild energy gap of 1eV. If I used 2eV, then this would have been really, really small. While for comparison nc, pv are, at least in the |ΔN| >> ni case of interest:



So this means that our results are entirely consistent with our presumption that the donor and acceptor levels are empty/fully occupied, so that all the donor electrons are effectively in the conduction band, and all the acceptor holes are in the valence band.