**Dielectrics**

**Atoms in Electric Field**

Now let’s look at some dielectric problems. We worked out a dielectric problem earlier, from the perspective of a single atom in the material. Now let’s look at it from a more wholistic perspective, studying the entire material. If there are significant interactions between molecules in the material, then I think we *must* treat it this way. So way back in the Quantum Mechanics/Multiple Particles/Identical Particles/Stark-Zeeman file, we derived the following Hamiltonian for a homogeneous dielectric/dimagnetic material in a uniform external electric/magnetic field:



We don’t have a B field though, so:



HCFA is the Hamiltonian of the individual atoms. is the polarization (density) operator,



where i is implicitly measured from the nucleus of the atom, and *i* runs over all electrons in the atom. Could write the polarization operator as:



where the sum in **P**atom runs over only the electron in a given atom (same as it did before, really). So we could write H as:



The way we’d formally proceed, I imagine, to get the polarization and susceptibility is to solve for the energy levels of our H, then form Z(T,ΔV,**E**f) (ΔV is the volume, by the way). Once we have that, then **P** = -(1/ΔV)∂F/∂**E**f, where F = -kTlnZ of course. Now the susceptibility, χ, is the defined via: **P** = ε0χ**E**, where **E** is the total electric field **E** = **E**f + **E**b = **E**f – **P**/ε0. So then we have:



So whatever proportionality we would find between **P** and **E**f from our ∂F/∂**E**f calculation above, we could then equate it to ε0χ/(1+χ) and get the susceptibility. But that’s more work than we want to put in, because H, via the P2 term, involves interactions between *all* atoms, which makes H hard to solve. A simplification is to use mean field theory, whereby we split the polarization operator into its (thermally averaged) mean value, and fluctuations about that. We don’t know what the thermally averaged mean value is, but will worry about that later. So,



And then we fill this into our H.



The approximation comes in when we neglect the (δP)2 term as being small. And once we do, we then replace all the remaining δP’s with P - <P> again.



Might bother to write this fully in terms of **P**atom:



So the advantage of what we’ve done is that now we’ve eliminated the term describing the interaction between atoms, though at the cost of putting things in terms of the unknown <Patom> guy. And of course this will work only if the (δP)2 is small.

**Classical Atoms in Electric Field**

Let’s start from a classical perspective. We’ll model our atom as positively charged nucleus surrounded by a negatively charged spherical electron ‘shell’, basically like we did in the EM folder when discussing dielectrics. The electron ‘shell’ will have kinetic energy we can describe via just p2/2m and potential energy approximately (1/2)mω2r2, where r is deviation of shell from center. And of course the electric field part will just be e**E**f·**r**. I’m going to designate e as q instead, and call Ef, h instead. Then N identical (but distinguishable) 3D classical harmonic oscillators of charge q in a free electric field h would have the following partition function,



where atom = <**P**atom>. And I guess I’ll define a new quantity **h**eff = **h** – natom/ε0. This would just be the bulk electric field, FWIW. So now,



(guess I’m just leaving off the ΔV argument in F) So setting ℏ = 1 for units sake again, we have:



And calculating the Free energy we get,



So,



Now atom is implicitly a function of T,N,h itself. So we don’t really know what F is yet, until we get atom. It’s defined via (see Thermodynamics/Equilibrium Systems at least):



which we can solve to get:



One (me) might ask, ‘why didn’t we also differentiate atom w/r to h, since we said it’s an implicit function of it?’ I guess there’s two ways of looking at it, as far as I can tell. One is…go back to our implicit statistical definition of atom.



where in the last line we just use the fact that our H describes a bunch of independent particles so the average of this operator over the whole system is the same the average over just one particle. So now we have:



And so,



From which it once again follows that:



So there’s that. Another way is to suppose we *do* implicitly differentiate our thermodynamic relation:



where **1** is the unit tensor. Now we’ll go back to our statistical result for atom, and implicitly differentiate *it*:



And plug it into our thermodynamic relation:



which is the same result. I guess I won’t think about it much anymore, but there is clearly a deeper reason why we don’t need to think of it as an implicit function when we’re differentiating it. So now we can construct the overall **P** = n**P**atom,



Comparing to:



from above, we see the susceptibility is:



This is actually the simple result we got in our dielectric file in the EM folder, and in this folder, priorly. Anyway, we can go back to F and plug in our result,



So we have:



**Quantum Atoms in Electric Field**

Let’s go back to,



and now instead of approximating HCFA as a classical harmonic oscillator, let’s approximate it rather as a Li ion Hamitonian, like we did when we studied the Stark Effect in the QM folder. Then we’d have:



where Z = 3, and **P**atom = e**r.** Anyway, comparing to the Stark Hamiltonian in the QM folder:



we see it’s of the same form, just with the replacement **h** → **E**f – (n/ε0)<**P**atom>, and the addition of an energy constant –(n/2ε0)|<**P**atom>|2. Since the energy levels of the Stark atom, at least in the low energy limit were:



(and each energy level was two-fold degenerate) we can straight away take our energy levels to be (using bar notation to indicate average, instead of brackets):



I guess we’ll now call **E**f to be **h**, like we did in the previous section. And also, as above, define an effective **h**eff, which we will recognize as the bulk interstitial field, to write:



Then, the partition function would be, setting the irrelevant energy constant E1/22 to zero:



and we have F = -kTlnZN, where ZN = Z1N. So,



and then,



What is average polarization? First we need to self-consistently work out <Patom>. So like we said above,



So we’d have to solve this transcendental equation for atom. And once we do, we’d plug it into heff and get F(T,ΔV,N,h). But I’m not going to proceed with this, since our model is that realistic anyway. Maybe I will just note that this equation, which says,



is equivalent to the one we found in the prior Dielectrics file, once we recognize **h** – (n/ε0)**atom** to be the bulk interstitial field, **E**. Going through the motions, we recognize that at low fields this reduces to:



with a concommitant susceptibility:



So basically, our previous single-atom treatment (much earlier file) is equivalent to a mean field analysis of the ‘real’ treatment.