**Dielectrics**

Now let’s look at some dielectric problems. So way back in the Quantum Mechanics/Multiple Particles/Identical Particles/Stark-Zeeman file, we derived the following Hamiltonian for an atom in a uniform external electric/magnetic field:



where HCFA is the central field approximation to the atomic Hamiltonian, and the other terms account for the influence of the magnetic and electric fields. The sum runs over all electrons in the atom. And **E**f, **B**f are the ‘free’ external fields, which would, from the point of view of our atom, simply be the fields due to any charges external to the atom. And so these fields would be the bulk interstitial fields running throughout the dielectric (those due to charges external to the substance and the other N-1 charges *within* the substance). So I’ll just call them **B** and **E** respectively, coincident with our parlance in the EM folder. We don’t have a B field though, so:



is the polarization operator,



So we could write H as:



We can calculate the energy levels of the Hamiltonian, and then construct Z, and then F = -kTlnZ, and then get **Patom** = -∂F/∂**E** (see Thermodynamics folder/Equilibrium Systems for ‘proof’ of this statement). So now we’d have the polarization. And the proportionality between the polarization density **P** = (N/ΔV)**P**atom and **E** would just be ε0χe, according to our analysis in the EM folder. N = number of atoms in dielectric, and ΔV is its volume.

**Classical harmonic oscillator in a 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)mω2x2, where x is deviation of shell from center. And of course the electric field part will just be eEx. I’m going to designate e as q instead, and call E, h instead. Then N identical (but distinguishable) 1D classical harmonic oscillators of charge q in an electric field h would have the following partition function:



So setting ℏ = 1 for units sake again, and to avoid confusion with the field, we have:



And calculating the Free energy we get,



So,



Basically it’s the same as the field-less harmonic oscillator system, but with the addition of a ‘ground state’ energy term. Can calculate <x>. This is:



Polarization is:



And so the polarization density would just be:



where n = N/ΔV. And so the susceptibility is:



which is just as we surmised in the EM folder. Heat capacity is just as it was for the simple harmonic oscillator:



Entropy as a function of T is,



Energy can be ascertained from F = E – TS → E = F + TS,



So it’s just the usual virial theorem result, with an additional ‘ground state’ energy term coming from the displaced equilibrium position. Don’t know why to bother, but we could get S(E,h) now by solving for T in terms of E and plugging into S,



So yay. Could solve for E in terms of S,



So when keep entropy constant, the energy changes by what is expected – just the change in energy as the dipoles adjust to their new equilibrium points. For instance when adiabatically change field h(t): 0 → h, then xeq(t): 0 → qh/k. Then new potential energy is defined to be (1/2)kxeq2 – qhxeq. = (1/2)k(qh/k)2 – qh(qh/k) = -(qh)2/2k = -(qh)2/2mω2.

**Quantum Harmonic Oscillator in a field**

Would things change if we modelled the atom as a quantum harmonic oscillator?



(why did I change sign of h – whatever) Writing this as:



we can tell this will merely shift the GS energy. And the energy levels will be:



The partition function is:



and the free energy is F = -kBTlnZ. So,



Entropy is:



as before. Anyway, given k = mω2, can see that this won’t change susceptibility.

**Actual atom in a field**

Let’s go back to the QM folder where we studied the Stark Effect in the context of atomic Li. The Hamiltonian was:



where e is the absolute value of the electron charge, and **h** the ambient electric field near the atom. And we found that the approximate energy levels of the outer electron (assumed spinless) were:



and each energy level was two-fold degenerate. The 2-fold degeneracy of each energy level probably is accounted for in the different ways the electron can traverse its orbit (CCW or CW). Well, the partition function would be, setting the irrelevant energy constant E1/22 to zero:



and we have:



Entropy would be:



Looks like entropy goes to zero when T does, since:



And this is good. What is average polarization?



And for the polarization density:



So here we see the polarization saturates at high fields. This is not likely the case as at super-high fields, the electron would begin to populate states at higher energy levels than we’ve allowed it to within our model. At low fields this reduces to:



with a concommitant susceptibility:



This is the first result that has temperature dependence, and it makes sense that higher T’s would result in lower susceptibility.