**Paramagnet**

**Atoms in Magnetic Field**

Now let’s look at the corresponding paramagnet problem, treating the entire material at once. We worked out a paramagnet problem earlier, from the perspective of a single atom in the material. Now let’s look at it from a more holistic 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:



where HCFA is the central field approximation to an atom’s Hamiltonian, M and P are the magnetization and polarization (per unit volume), and Bf, Ef are the free external fields.



where ri is implicitly measured from the nucleus of each respective atom. Okay well for paramagnets, we can neglect that r⊥2 in the smallish B limit, and so that’s what we’ll do. And we don’t have an E field, so eliminating that part, and also eliminating the HCFA guy, which really just serves to define the degenerate ground state subspace, whose degeneracy is lifted by the external fields. And I’m going to make the replacement γ(**L**T + g**S**T) → gLγ**J**T, which is accurate as long as we stick within the HCFA ground state subspace |LTSTJTmJT> (see Central Field Approximation and Stark-Zeeman Hamiltonian in Quantum Mechanics folder). So then we have:



So we could write H as:



Now like in the dielectric file, we want to get the energy levels so we can solve for the thermodynamic functions. But the M2 complicates things because it involves interactions between atoms. Even so, the energy levels are actually exactly solvable, and so we could get the exact partition function, in principle (see the Ferromagnet files e.g.). But it’s not easy to work with. So like before, and like we’ll do with Ferromagnets, we’ll simplify things by using mean field theory. So we split the magnetization 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.



Or in other words,



where of course the <> term is to be ascertained self-consistently. Would like to observe that if we did not have that M2 term in the Hamiltonian, then our application of MFT would not have resulted in JT being multiplied by Bf + μ0<M>; rather it would’ve been Bf + 2μ0<M>. So the M2 term does seem kind of critical to getting that correct. Like I’ve done elsewhere, I’m going to write this as:



Also going to write <> as just **M**. So now,



Now notation matches up with dielectric file, basically. Well so the eigenbasis of T is just the usual |LTSTJTJTz> states, so energy levels are just:



So partition function is:



So the Free Energy is, switching notation to γ = -μB:



Then at this point we’d self-consistently solve for M by taking derivative w/r to h (not treating M as dependent upon h yet if want to do it the simple way – otherwise go for it – see Weiss file for such a calculation) and setting equal to M. So,



where



and by **M**atom we mean its statistical average, **M**atom = <atom>. We’ll recognize this equation as the same as what we found in the previous paramagnet file, when we analyzed just a single atom, since our heff here is the total interstitial magnetic field, which is the same as the one we had in that previous file (and which we called simply h, back then). And our result for M is obviously,



So again, our previous analysis (of just the single atom in the sample) is equivalent to a mean field treatment of the whole sample at once. Anyway, this equation is an implicit one for M, and we’d have to solve it upon plugging in **h**eff = **h** + μ0**M**. If we were to include the fluctuations we neglected here at the top of the page, then we’d get a better result. But not sure how we’d include them….

**High T limit**

Let’s work out the potentials in various regimes. So first the sort of classical regime, high T, low h (this makes it classical because the quantized energy spacings are much smaller than kBT). In this limit, the argument of BJ(x) is small, and so can make Taylor series approximation:



So we have approximately,



Taking a derivative we can get (an equation for) the magnetization again,



Solving for M, we get:



and that T0 is…



really small. So χm is practially T0/T. So we can write, recognizing h = Bf = μ0H for solenoidal geometry, homogeneous substance, etc., and that M = χmH:



What about the entropy? First let’s work on F a little more,



Now,



And I’m just going to keep first non-zero order of T0/T.



Makes sense that the entropy should saturate at high T’s, as the energy spectrum is bounded. Also makes sense that it should decrease as we increase h. To this same order, the heat capacity would be:



So,



**Low T limit**

Well, I’d just like to see if this model supports spontaneous magnetization. So basically, we want to see if there exists a non-zero solution for M when h = 0. So let’s examine,



Recall that BJ starts out linear with slope (J+1)/3. So the whole RHS starts out linear with slope (w/r to M), ngLμBJ(J+1)βgLμBμ0/3. And thereafter BJ decreases. So there will only be a non-zero solution if the slope on the LHS (w/r to M) is smaller than the slope on the RHS (w/r to M). So we need:



where we recognize T0, basically our critical temperature, as the thing we calculated up above. This was like 0.02K. So technically yes. But very weak, and I’m not sure it’d remain if we included the other interactions present. On the other hand, the ferromagnetic models we’ll study later do have a robust spontaneous magnetization response and a much higher critical temperature.

**Atoms in Magnetic Field + Classical Field**

The result of our MF analysis seems coincident with what we’d get if did a simple statistical mechanics analysis of the substance + external field. So let’s look into that real fast. Okay, so recall that the Hamiltonian for a bunch of atoms in a classical magnetic field is (see Quantum Mechanics/Many Particles/Zeeman)



For paramagnets we can neglect the r⊥2 in the smallish B limit as r⊥2 is bounded (basically atomic radius). Also going to neglect HCFA – it just defines the ground state space within which we’ll be operating. And I’ll make the replacement γ(**L**T + g**S**T) → gLγ**J**T, as appropriate if we stay within the degenerate ground state space |LTSTJTmJT> of the CFA Hamiltonian. Then we have:



Following our analysis in the previous file, we can work out the free energy:



So partition function is:



So the Free Energy is, switching γ = -μB:



Then at this point we’d calculate M via the differential relation dF = -SdT + HΔVdB (maybe see Thermodynamics/Equilibrium systems, or EM/Insulators Energy). And H = B/μ0 – M. So M = -(1/ΔV)dF/dB + B/μ0. So,



This is the equation we’ve found above, and in many other contexts.

**High T limit**

Let’s work out the potentials in various regimes. So first the sort of classical regime, high T, low h (this makes it classical because the quantized energy spacings are much smaller than kBT). In this limit, the argument of BJ(x) is small, and so can make Taylor series approximation:



So we have approximately,



Taking a derivative we can get (an equation for) the magnetization again,



What about the entropy? Now,



Makes sense that the entropy should saturate at high T’s, as the energy spectrum is bounded. Also makes sense that it should decrease as we increase h. To this same order, the heat capacity would be:



Follows also that:

