**Quantum Paramagnets**

Now let’s look at some examples…

**2-state system**

Consider a two state system, with energy levels E1 and E2. What is the heat capacity? Well, we’d have,



And then F,



The heat capacity, TdS/dT), would be dU/dT, since the system wouldn’t be doing any work – since its internal parameters which determine the energy levels are changing. So then…



And then taking the derivative w/r to T we get,



So we have,



A typical plot is:



where E1 = 2, E2 = 5. We can make sense of this plot in that C(T) is zero for low T since T isn’t high enough for the levels to be thermally populated. As T increases, the levels can be populated and U increases with T. As T get’s larger though, the population of E2 saturates to 100% and higher T’s cannot increase the internal energy any more. So C goes back down.

**Spin in Magnetic Field**

So say we have a spin in a paramagnetic material, immersed in a magnetic field. Then as discussed elsewhere, the Hamiltonian would be given by:



where **B** is the total magnetic field experienced by the spin, i.e., the bulk-interstitial field. Let’s say that we’re dealing with a spin in magnetic field, h. Then the energy eigenvalues are:



Partition function would be (μB = |γ|/ℏ, and we’re evidently using units where ℏ → 1, whatever):



and we have:



Entropy would be:



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



And this is good. Also might note that S → 0 as h → ∞, by same analysis, and this makes sense as all spin would be practically guaranteed to be down. And average energy would be E = F + TS,



Could’ve gotten that from partition function too. So energy is unambiguous function of temperature. Heat capacity is:



And Cv does go to zero as T → 0 (h →∞). So that checks out. What is average magnetization and variance?



(This is same as what we claim to have in the Thermodynamics/Equilibrium Systems file: M = -∂F/∂Bf, as here, the external field, Bf, *is* the bulk-interstitial field, h) And this is:



This makes sense as it would go to -μB in the large h limit, meaning all spins pointing down. The overall magnetization density would be:



where N = total number of spins and ΔV = volume of paramagnet, and n = N/ΔV. Of course n = N/ΔV. The susceptibility is not the proportionality between M and the total field though, rather between M and the ‘free’ field, the part coming from just the ‘free’ currents in the solenoid. But whatever. Looks like as T → ∞, we’d get 0, consistent with all states equally populated. <M2> would be:



And this is:



Huh. The variance would then be:



So when h → ∞ this goes to zero. As T → ∞, this goes to max of μB2, which is pretty big compared to typical value of μB. This seems to suggest that at super-high T, there’s no way of knowing whether its up or down. Could put entropy in terms of energy to get the microcanonical ensemble state function:



For what it’s worth,



So,



So can say,



And further, using tanh-1(x) = (1/2)ln[(1+x)/(1-x)],



Not sure what good that does us, but there. Will point out that even though we are working with a single spin, and by extension N independent spins, if in a closed system, we must have some residual interaction between the spins, some way for them to share energy with each other. Otherwise, if we say take a single spin in some superposition state, increasing the field will not result in it tending to occupy the lower energy state with any more probability. It will just continue precessing about the ever growing field. So this ‘coming to thermal equilibrium’ process does require some residual interactions between members. Kind of a corollary that a single truly independent spin could never come to any sort of ‘thermal equilibrium’ all by itself, at least in a closed system (if connected to a thermal bath, then it can).

**System of N spins**

What if we had a system of N spins. Then Z = Z1N. Can verify that the formula for <M> and <M2> still applies for system of N spins, if we just generalize En and Mn = gμBSn to be total energy and total spin, and n being any allowed state of system. So then we have ZN = Z1N = [2cosh(βμBh)]N, and :



As expected. What about <M2>?



The variance would be:



Well, I guess that follows from probability theory, as any cumulant of N independent variables is the sum of the independent variable cumulants. But anyway, we can see now that the magnetization is self-averaging, ‘cause:



which goes to zero in the thermodynamic limit (large N). So while being at some temperature T would seem to allow a couple spins to have basically any net spin, a large system of spins will have a well defined mean with negligible fluctuations about. Probably can only presume statistical mechanics/thermodynamics to be valid in the large N limit anyway.

**Atom in Magnetic Field**

Let’s look at an atom in an EM field. Then according to our work in Quantum Mechanics Folder/Identical Particles/Stark-Zeeman Interaction, H goes to, absent electric field:



We’ll stay within the degenerate ground state subspace |LTSTJTmJT>, given by Hund’s rules, of HCFA. With this assumption, we can write:



where gL is the Lande´ g factor,



and Bf is the field external to the atom, and so is really the *bulk interestitial field*, same as the **B** in the previous problem. So we may write:



Now remember that for electrons in a particular ℓ shell, the approximate low lying eigenstates will be the aforementioned (in the quantum folder) |LTSTJTJZT>. Now recall as we discussed in the Quantum/Many Particles/Stark-Zeeman file that a paramagnet is typically charactersized by non-zero JT in the ground state of the CFA, and also small r⊥, so that we can approximate the Hamiltonian as:



which has eigenstates |LTSTJTJZT> and energies -gLγJz where Jz runs from -JT to JT. And going to call B, h instead, to match up with previous notation. So,



Let’s calculate the magnetization, from a purely statistical point of view. We have, assuming h is pointing in the **z** direction:



We define the Brilluoin function (there are other definitions out there; namely Wikipedia’s BJ(x) = our BJ(x/J)):



where we recall the geometric sum formula,



So finally, performing the derivative



Might note that for small x,



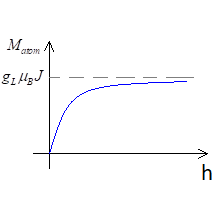
and for large x,



and anyway, we can write,



where gLμBJ is the max magnetization. And plotting this we get,



We’ll note it’s linear in the small h region, which is consistent with Curie’s law, though again, the proportionality wouldn’t be the susceptibility because h here is not the external field (it’s the field external to the atom, but not the field external to the substance as a whole). Maybe go back and get the free energy and stuff. So,



So partition function is:



Switching to γ = -μB, we have:



We can take a derivative w/r to h to get our magnetization, again,



So that agrees with our previous result. Now let’s do entropy,



which we can write as:



FWIW, can see that S is a function of just h/T, and so is M. So could put h/T in terms of M, and therefore write S as a function of M alone.

**Magnetization in the Classical Limit**

Might bother to note that in the large J limit, where the levels the atom can occupy becomes very large, and thereby its quantum nature becomes less salient. Then we’d expect classical behavior,



So let’s take the large J limit of our result:



So that checks out, and we recover the ‘classical’ model in the appropriate limit 😊.