Problem Set 5

Magnetism and Mean Field Theory

5.1. ‡ **General Magnetism**

(a) Explain qualitatively why some atoms are paramagnetic and others are diamagnetic with reference to the electronic structure of these materials.

(b) Define the terms Ferromagnetism, Antiferromagnetism, Ferrimagnetism, and Itinerant Ferromagnetism.

▷ Write down an example of a Hamiltonian which would have each one of these as its ground state.

(c) Use Hund's rules and the Aufbau principle to determine L, S, and J for the following isolated atoms:

(i) Sulfer (S) atomic number = 16

(ii) Vanadium (V), atomic number = 23

(iii) Zirconium (Zr), atomic number = 40

(iv) Xenon (Xe), atomic number = 54

(v) Dysprosium (Dy), atomic number =66

5.2. ‡ **Para and Diamagnetism**

Manganese (Mn, atomic number=25) forms an atomic vapor at 2000K with vapor pressure 10^5 Pa. You can consider this vapor to be an ideal gas.

(a) Determine L, S, and J for an isolated manganese atom. Determine the paramagnetic contribution to the (Curie) susceptibility of this gas at 2000K.

(b) In addition to the Curie susceptibility, the manganese atom will also have some diamagnetic susceptibility due to its filled core orbitals. Determine the Larmor diamagnetism of the gas at 2000K. You may assume the atomic radius of an Mn atom is one angstrom.

Make sure you know the derivations of all the formulas you use!

5.3. ‡ **Weiss Mean Field Theory of the Ferromagnet** Consider the spin-1/2, ferromagnetic Heisenberg Hamiltonian on the cubic lattice

$$\mathcal{H} = -\frac{J}{2} \sum_{<i,j>} \mathbf{S_i} \cdot \mathbf{S_j} + g\mu_B \mathbf{B} \sum_i \mathbf{S_i} \tag{1}$$

Here, $J > 0$, with the sum indicated with $< i, j >$ means summing over i and j being neighboring sites of the cubic lattice, and $\mathbf{B}$ is the externally applied magnetic field, which we will assume is in the $\hat{z}$ direction for simplicity. The factor of $1/2$ out front is included so that each pair of spins is counted only once. Each site i is assumed to have a spin $\mathbf{S_i}$ of spin $S = 1/2$. Here μ_B is the conventional Bohr magneton defined to be positive. The fact that the final term has a + sign out front is from the fact that the electron charge is negative, therefore the magnetic moment opposes the spin direction. If one were to assume that these were nuclear spins the sign would be reversed (and the magnitude would be much smaller due to the larger nuclear mass).

(a) Focus your attention on one particular spin $\mathbf{S_i}$, and write down an effective Hamiltonian for this spin, treating all other variables $\mathbf{S_j}$ with $j \neq i$ as expectations $\langle \mathbf{S_j} \rangle$ rather than operators.

(b) Calculate $\langle \mathbf{S_i} \rangle$ in terms of the temperature and the fixed variables $\langle \mathbf{S_j} \rangle$ to obtain a mean-field self-consistency equation.

▷ Write the magnetization $M = |\mathbf{M}|$ in terms of $\langle \mathbf{S} \rangle$ and the density of spins.

(c) At high temperature, find the susceptibility $\chi = dM/dH = \mu_0 dM/dB$ in this approximation.

(d) Find the critical temperature in this approximation.

▷ Write the susceptibility in terms of this critical temperature.

(e) Show graphically that in zero external field ($\mathbf{B} = 0$), below the critical temperature, there are solutions of the self consistency equation with $M \neq 0$.

(f) Repeat parts (a)-(d) but now assuming there is an $S = 1$ spin on each site (meaning that S_z takes the values $-1, 0, +1$).

5.4. **Bragg-Williams Approximation**

This problem provides a different approach to obtaining the Weiss mean-field equations. For simplicity we will again assume spin 1/2 variables on each site.

Assume there are N lattice sites in the system. Let the average spin value be $\langle S_i \rangle = s$. Thus the probability the probability of a spin being an up spin is $P_\uparrow = 1/2 + s$ whereas the probability of any spin being a down spin is $P_\downarrow = 1/2 - s$. The total number of up spins or down spins is then $NP_\uparrow$ and $NP_\downarrow$ respectively where there are N total lattice sites in the system.

(a) Consider first a case where sites do not interact with each other. In the micro-canonical ensemble, we can count the number of configurations (microstates) which have the given number of spin ups and spin downs (determined by s). Using $S = k_b \ln \Omega$ calculate the entropy of the system in the large N limit.

(b) Assuming all sites have independent probabilities $P_\uparrow$ and $P_\downarrow$ of pointing up and down respectively, calculate the probability that two neighboring sites will point in the same direction and the probability that two neighboring sites will point in opposite directions.

▷ Use this result to calculate an approximation to the expectation of the Hamiltonian. Note: This is not an exact result, as in reality, sites that are next to each other will have a tendency to have the same spin because that will lower their energies, but we have ignored this effect here.

(c) Putting together the results of (a) and (b) above, derive the approximation to the free energy

$$F = E - TS = Nk_bT\left[(\frac{1}{2}+s)\log(\frac{1}{2}+s) + (\frac{1}{2}-s)\log(\frac{1}{2}-s)\right] + g\mu_B B_z N s - JNZs^2/2$$

where Z is the number of neighbors each spin has, and we have assumed the external field to be in the $\hat{z}$ direction. (Again we assume the spin is electron spin so that the the energy of a spin interacting with the external field is $+g\mu_b \vec{B} \cdot \vec{S}$.)

(d) Extremize this expression with respect to the variable s to obtain the same mean field equations as above.

▷ Below the critical temperature note that there are three solutions of the mean field equations.

▷ By examining the second derivative of F with respect to s, show that the $s = 0$ solution is actually a maximum of the free energy rather than a minimum.

▷ Sketch $F(s)$ both above and below the critical temperature for $B = 0$. At nonzero B?

5.5. **Mean Field Theory for the Antiferromagnet**

For this exercise we use the Molecular Field (Weiss Mean Field) approximation for the spin-1/2 *Antiferromagnetic* model on a 3 dimensional cubic lattice. The full Hamiltonian is exactly that of Eq. 1 above, except that now we have $J < 0$, so neighboring spins want to point in opposite directions. (Compared to a Ferromagnet where $J > 0$ and neighboring spins want to point in the same direction). For simplicity let us assume that the external field points in the $\hat{z}$ direction.

At mean field level, the ordered ground state of this Hamiltonian will have alternating spins pointing up and down respectively. Let us call the sublattices of alternating sites, sublattice A and sublattice B respectively (i.e, A sites have lattice coordinates (i, j, k) with $i + j + k$ odd whereas B sites have lattice coordinates with $i + j + k$ even).

In Mean field theory the interaction between neighboring spins is replaced by an interaction with an average spin. Let $s_A = \langle S^z \rangle_A$ be the average value of the spins on sub-lattice A, and $s_B = \langle S^z \rangle_B$ be the average value of the spins on sub-lattice B. (We assume that these are also oriented in the $\pm\hat{z}$ direction).

(a) Write the mean field Hamiltonian for a single site on sublattice A and the mean field Hamiltonian for a single site on sublattice B.

(b) Derive the mean-field self consistency equations

$$\begin{aligned} s_A &= \frac{1}{2}\tanh(\beta[JZs_B - g\mu_B B]/2) \\ s_B &= \frac{1}{2}\tanh(\beta[JZs_A - g\mu_B B]/2) \end{aligned}$$

with $\beta = 1/(k_b T)$. Recall that $J < 0$.

(c) Let $B = 0$. Reduce the two self-consistency equations to a single self consistency equation. (Hint: Use symmetry to simplify! Try plotting s_A versus s_B).

(d) Assume $s_{A,B}$ are small near the critical point and expand the self consistency equations. Derive the critical temperature T_c below which the system is antiferromagnetic (i.e., $s_{A,B}$ become nonzero).

(e) How does one detect antiferromagnetism experimentally?

(f) In this mean-field approximation, the magnetic susceptibility can be written as

$$\chi = -(N/2)g\mu_0\mu_B \lim_{B\to 0} \frac{\partial(s_A + s_B)}{\partial B}$$

(why the factor of 1/2 out front?).

▷ Derive this susceptibility for $T > T_c$ and write it in terms of T_c.

▷ Compare your result with the analogous result for a ferromagnet. (Problem 5.3.). In fact, it was this type of measurement that first suggested the existence of antiferromagnets!

(g)* For $T < T_c$ show that

$$\chi = \frac{(N/4)\mu_0(g\mu_b)^2(1-(2s)^2)}{k_b T + k_b T_c(1-(2s)^2)}$$

with s the staggered moment (ie, $s(T) = |s_A(T)| = |s_B(T)|$).

▷ Compare this low T result with that of part f.

▷ Give a sketch of the susceptibility at all T.

5.6. **Ground States**

Consider the spin-1 Heisenberg Hamiltonian from Problem 5.3.. Let us take $\mathbf{B}$ to be in the $-\hat{z}$ direction, and assume a cubic lattice.

It will be useful to remember that

$$\mathbf{S_i} \cdot \mathbf{S_j} = \frac{1}{2}(S_i^+ S_j^- + S_i^- S_j^+) + S_i^z S_j^z$$

(a) For $J > 0$, i.e., for the case of a ferromagnet, intuition tells us that the ground state of this Hamiltonian should simply have all spins aligned. Consider such a state. Show that this is an eigenstate of the Hamiltonian Eq. 1 and find its energy.

(b) For $J < 0$, the case of an antiferromagnet, one might expect that, at least for $\mathbf{B} = 0$ the state where spins on alternating sites point in opposite directions might be an eigenstate. Unfortunately, this is not precisely true. Consider such a state of the system.

▷ Show that the state in question is not an eigenstate of the Hamiltonian.

Although the intuition of alternating spins on alternating sites is not perfect, it becomes reasonable for systems with large spins S. For smaller spins (like spin 1/2) one needs to consider these so-called "quantum fluctuations". (We will not do that here).

5.7. **Itinerant Ferromagnetism**

(a.i) Review 1: For a three dimensional tight binding model on a cubic lattice, calculate the effective mass in terms of the hopping matrix element t between nearest neighbors and the lattice constant a.

(a.ii) Review 2: Assuming the density n of electrons in this tight binding band is very low, one can view the electrons as being free electrons with this effective mass m^*. For a system of spin polarized electrons show that the total energy per unit volume (at zero temperature) is given by

$$E/V = nE_{min} + Cn^{5/3}$$

where E_{min} is the energy of the bottom of the band.

▷ Calculate the constant C.

(b) Let the density of spin-up electrons be $n_\uparrow$ and the density of spin-down electrons be $n_\downarrow$ we can write these as

$$n_\uparrow = (n/2)(1+\alpha) \quad (2)$$
$$n_\downarrow = (n/2)(1-\alpha) \quad (3)$$

where the total net magnetization of the system is given by

$$M = -\mu_b n \alpha$$

Using the result of part (a), fixing the total density of electrons in the system n,

▷ calculate the total energy of the system per unit volume as a function of α.

▷ Expand your result to fourth order in α.

▷ Show that $\alpha = 0$ gives the lowest possible energy.

▷ Argue that this remains true to all orders in α

(c) Now consider adding a Hubbard interaction term

$$H_{hubbard} = U \sum_i N_\uparrow^i N_\downarrow^i$$

with $U \geq 0$ where N_σ^i is the number of electrons of spin σ on site i.

Calculate the expectation value of this interaction term given that the up and down electrons form fermi seas with densities $n_\uparrow$ and $n_\downarrow$ as given by Eqns. 2 and 3 above.

▷ Write this energy in terms of α.

(d) Adding together the kinetic energy calculated in part b with the interaction energy calculated in part c, determine the value of U for which it is favorable for α to become nonzero.

▷ For values of U not too much bigger than this value, calculate the magnetization as a function of U.

▷ Explain why this calculation is only an approximation.

(e) Consider now a two dimensional tight binding model on a square lattice with a Hubbard interaction. How does this alter the result of part (d)?

5.8. **Antiferromagnetism in the Hubbard Model**

Consider a tight binding model with hopping t and a strong Hubbard interaction.

$$H_{hubbard} = U \sum_i N_\uparrow^i N_\downarrow^i$$

(a) If there is one electron per site, if the interaction term U is very strong, explain qualitatively why the system must be an insulator.

(b) On a square lattice, with one electron per site, and large U, use second order perturbation theory to determine the energy difference between the ferromagnetic state and the antiferromagnetic state. Which one is lower energy?