General Considerations

• *Idea:* Atoms have a permanent μ_i and they interact with each other, so in this case $Z \neq \zeta^N/N!$. Now the thermal effect has to compete not just with the possible aligning effect of an external magnetic field, but with the intrinsic aligning effect of the interactions as well.
• *Hamiltonian:* If we neglect the translational degrees of freedom and just look at the spins, the degrees of freedom are the values of the spin $\vec{s}_i$ at all lattice sites. Their interaction with each other is described by a symmetric matrix J^{ij}, so their total Hamiltonian in an external magnetic field is

$$H = -\sum\nolimits_{i,\, j\neq i} J^{ij}\, \vec{s}_i \cdot \vec{s}_j - \sum\nolimits_i \vec{\mu}_i \cdot \vec{B}_{i,\,\rm ext} = -\sum\nolimits_i \vec{\mu}_i \cdot \vec{B}_i\;, \qquad \vec{B}_i := \vec{B}_{i,\,\rm ext} + \sum\nolimits_{j\neq i} J^{ij}\, \vec{s}_j\;.$$

• *Mean-field approximation:* Model the material as a lattice at each site of which there is a spin $\vec{s}_i$. Although in principle any two spins interact with each other, and $\vec{s}_i$ feels the actual value of all other spins, we will approximate the situation by an interaction of each $\vec{s}_i$ with the mean field produced by the other ones, i.e.,

$$B_i \mapsto \vec{B}_{i,\,\rm ext} + \sum\nolimits_{j\neq i} J^{ij}\, \langle \vec{s}_j\rangle = \langle \vec{B}_i\rangle\;, \qquad \text{and use as Hamiltonian} \qquad H' = -\sum\nolimits_i \langle \vec{B}_i\rangle \cdot \vec{s}_i\;.$$

Notice that this has actually changed the physical problem; we are now ignoring correlations.

Quantitative Treatment

• *Setup:* Choose again coordinate axes such that $\langle \vec{B}_i\rangle = \langle B_i\rangle\,\hat{\mathbf{z}}$, and $|\!\uparrow\rangle$, $|\!\downarrow\rangle$ as spin basis.
• *Magnetization:* In this case it is convenient to use the density matrix to write down the mean i-th spin,

$$\langle s_i\rangle = \frac{\mathrm{tr}\, s_i\, \mathrm{e}^{-\beta H}}{\mathrm{tr}\, \mathrm{e}^{-\beta H}} = \frac{\mathrm{tr}\, s_i\, \mathrm{e}^{\beta \langle \vec{B}_i\rangle\cdot \vec{s}_i}}{\mathrm{tr}\, \mathrm{e}^{\beta \langle \vec{B}_i\rangle\cdot \vec{s}_i}} = \tfrac12 \tanh\big(\tfrac12\, \beta\, \langle B_i\rangle\big) = \tfrac12 \tanh\big(\tfrac12\, \beta \sum\nolimits_{j\neq i} J^{ij} \langle s_i\rangle\big)\;.$$

If we assume that $\langle s_i\rangle$ is homogeneous (which is not always the case—see antiferromagnetism), then

$$\bar{M} = N\langle s\rangle\;, \qquad \text{with} \qquad \langle s\rangle = \tfrac12 \tanh\big(\tfrac12\, \beta J \langle s\rangle\big)\;, \qquad J := \sum\nolimits_{j\neq i} J^{ij}\;.$$

• *Solution, graphically:* [∗ plot the equation above ∗] Introduce $x := \frac12\,\beta J\langle s\rangle$. For a fixed value of β, $\langle s\rangle$ corresponds to the value of x such that the two curves $(4/\beta J)\,x$ and $\tanh x$ intersect. The possibilities are:
– High temperature, $4/\beta J \geq 1$: there is 1! solution, $x = 0$ (paramagnetism).
– Low temperature, $4/\beta J < 1$: there are three solutions, $x = 0$, $x_\pm$, where the two new ones correspond to spontaneous magnetization at $T < T_{\rm c} = J/4k_{\rm B}$, the Curie temperature. To determine which solutions actually occur and are physical, we study the susceptibility χ, below. (Another approach would be to use general thermodynamical considerations on phase transitions and stability; we will cover those later.)
• *Remark:* When $B = 0$, the set of solutions for $\langle s\rangle$ must be symmetric about $\langle s\rangle = 0$, but not each value.

The Phase Transition

• *Susceptibility:* To calculate $\chi \propto \partial\langle s\rangle/\partial B$ for a single atom, we need to introduce an external B field. Then the implicit expression above for $\langle s\rangle$ becomes (to simplify the plotting, we can also define $x := \frac12\,\beta(J\langle s\rangle + B)$)

$$\langle s\rangle = \tfrac12 \tanh\big(\tfrac12\, \beta(J\langle s\rangle + B)\big)\;, \qquad \text{and} \qquad \chi = \frac{\partial\langle s\rangle}{\partial B} = \frac14\, \frac{\beta\,(J\chi + 1)}{\cosh^2\big(\tfrac12\, \beta(J\langle s\rangle + B)\big)}\;.$$

• *The $\langle s\rangle$ solution for $B = 0$:* Setting $B = 0$ and $\langle s\rangle = 0$ in the last equation and simplifying, we find that

$$\chi(T) = \frac{1}{4k_{\rm B}}\, \frac{1}{T - T_{\rm c}}\;, \qquad T_{\rm C} = \frac{J}{4k_{\rm B}}\;.$$

Thus, for $T < T_{\rm c}$ the susceptibility χ would be negative, which is not allowed, indicating that $\langle s\rangle = 0$ is not a physical solution. As T approaches $T_{\rm c}$, the $(T - T_{\rm c})^{-1}$ behavior of χ denotes a phase transition with order parameter T and critical exponent -1 (associated with a SO(3) $\mapsto$ SO(2) phase transition).
• *Remark:* The mean-field approximation predicts a phase transition in every dimensionality. We will see...

Relevant Sections: PHY 731, 22-23; Chandler, 131-138; [Halley]; Reif, §10.6-10.7; Schwabl.