Ising model

From our Ising model, where our spins can be +1 and -1, the Hamiltonian could be written as:

$$H(\mathbf{s}) = -\frac{1}{2}J\sum_{i}\sum_{j}^{n.n.} s_i s_j$$

If we try to find out average Hamiltonian:

$$\langle H(\mathbf{s})\rangle = -\frac{1}{2}J\sum_{i}\sum_{j}^{n.n.} \langle s_i s_j\rangle$$

If we assume that the spins are decoupled, then:

$$\langle H(\mathbf{s})\rangle = -\frac{1}{2}J\sum_{i}\sum_{j}^{n.n.} \langle s_i\rangle\langle s_j\rangle = -\frac{1}{2}Nzm^2$$

Where z is the coordination number and the magnetization, m:

$$m = \langle s_i\rangle = \frac{1}{N}\sum_{i} s_i$$

To find the Gibbs entropy, we know:

$$S = -Nk\sum_{s} p(s)\ln p(s)$$

Given our probabilities must have the properties:

$$p(+1) + p(-1) = 1$$

And:

$$m = (+1)p(+1) + (-1)p(-1) = p(+1) - p(-1)$$

We must then have:

$$p(+1) = \frac{1+m}{2}$$
$$p(-1) = \frac{1-m}{2}$$

Thus:

$$S = -Nk\left[\frac{1+m}{2}\ln\left(\frac{1+m}{2}\right) + \frac{1-m}{2}\ln\left(\frac{1-m}{2}\right)\right]$$

From here, our variational free energy is simply given by:

$$G_R = \langle H(\mathbf{s})\rangle - TS = -\frac{1}{2}Nzm^2 + NkT\left[\frac{1+m}{2}\ln\left(\frac{1+m}{2}\right) + \frac{1-m}{2}\ln\left(\frac{1-m}{2}\right)\right]$$

BEM model

In this case, a few things have changed. For one, our spins can now have three possible values ($\tau_i = +1, -1, 0$) and two types of particles (A and B). Particle A can have spins ± 1 and particle B only has spin 0. As we are dealing with the grand canonical ensemble, we must write out our Hamiltonian as:

$$H(\boldsymbol{\tau}) = -\frac{1}{2}J\sum_{i}\sum_{j}^{n.n.} \tau_i\tau_j - N_A\mu_A - N_B\mu_B$$

Where $N_A + N_B = N$. We can also define the variable x as:

$$x = \frac{N_A}{N}$$

Allowing us to somewhat simplify our Hamiltonian:

$$H(\boldsymbol{\tau}) = -\frac{1}{2}J\sum_{i}\sum_{j}^{n.n.}\tau_i\tau_j - Nx\Delta\mu$$

Where $\Delta\mu = \mu_A - \mu_B$. There is a constant we are neglecting above but, for the purposes of solving for phase equilibrium, it will cancel out and, therefore, can be neglected.

Obtaining the average Hamiltonian and assuming that the spins are once again decoupled:

$$\langle H(\boldsymbol{\tau})\rangle = -\frac{1}{2}J\sum_{i}\sum_{j}^{n.n.}\langle\tau_i\tau_j\rangle - Nx\Delta\mu = -\frac{1}{2}J\sum_{i}\sum_{j}^{n.n.}\langle\tau_i\rangle\langle\tau_j\rangle - Nx\Delta\mu$$

We now need to find a value for $\langle\tau_i\rangle$. We know it will be given by:

$$\langle\tau_i\rangle = (0)p(0) + (+1)p(+1) + (-1)p(-1)$$

Unfortunately, we cannot reuse our values from the Ising model *directly*. We know that, if a lattice site is particle A, then:

$$p(+1|A) = \frac{1+m}{2}$$
$$p(-1|A) = \frac{1+m}{2}$$

From conditional probabilities:

$$p(+1|A) = \frac{p(+1\cap A)}{p(A)} = \frac{1+m}{2}$$

Given the probability of a site being particle A is just x, then:

$$p(+1\cap A) = x\frac{1+m}{2}$$

Noticing that only particles A can be spin +1, we have:

$$p(+1\cap A) = p(+1) = x\frac{1+m}{2}$$

Similarly:

$$p(-1) = x\frac{1-m}{2}$$

And:

$$p(0) = 1 - x$$

As such:

$$\langle\tau_i\rangle = mx$$

Substituting into our expression for the average Hamiltonian:

$$\langle H(\boldsymbol{\tau})\rangle = -\frac{1}{2}JzNm^2x^2 - Nx\Delta\mu$$

We can also obtain our Gibbs entropy as:

$$S = -Nk[p(0)\ln p(0) + p(+1)\ln p(+1) + p(-1)\ln p(-1)]$$
$$S = -Nk\left[(1-x)\ln(1-x) + x\frac{1+m}{2}\ln x\frac{1+m}{2} + x\frac{1-m}{2}\ln x\frac{1-m}{2}\right]$$

From these two expressions, we can obtain the variational free energy as:

$$G = \langle H(\boldsymbol{\tau})\rangle - TS$$

$$G = -\frac{1}{2} J z N m^2 x^2 - N x \Delta\mu$$
$$+NkT\left[(1-x)\ln(1-x) + x\frac{1+m}{2}\ln x\frac{1+m}{2} + x\frac{1-m}{2}\ln x\frac{1-m}{2}\right]$$