Solution to Problem Set 4

We consider a system of Ising spins ($S_i = \pm 1$) with the partition function $Z[J]$ defined as,

$$Z[J] = \mathrm{Tr} e^{-(J_{ij}S_iS_j + J_iS_i)} = e^{-W[J]}. \tag{1}$$

$W[J]$ is the free energy of the system. We will follow the convention that when not mentioned explicitly, all repeated indices are to be summed.

The average magnetization is defined as,

$$\frac{\partial W[J]}{\partial J_i} = \frac{1}{Z}\mathrm{Tr} S_i e^{-(J_{ij}S_iS_j + J_iS_i)} = \langle\, S_i \,\rangle = m_i. \tag{2}$$

The free energy with fixed magnetization $\Gamma[m]$ is defined by the Legendre tranform,

$$\Gamma[m] = W[J] - J_i m_i. \tag{3}$$

Using equations (2) and (3) we find that,

$$\frac{\partial \Gamma[m]}{\partial m_i} = \frac{\partial W[J]}{\partial J_k}\frac{\partial J_k}{\partial m_i} - J_i - m_k\frac{\partial J_k}{\partial m_i} = -J_i. \tag{4}$$

The term J_{ij} in equation (1) defines interaction between the spins. We want to treat this term perturbatively. For this we multiply J_{ij} by α, and expand relevant quantities in successive orders in α. Here α is a parameter which will be set equal to one, like the charge of the electron in DFT. The purpose of this exercise is to demonstrate that since magnetization is the interesting quantity for the spin system, it is meaningful to make a perturbative expansion of the thermodynamic quantity which keeps magnetization fixed, namely $\Gamma[m]$. Mathematically, as α is tuned from zero to one, from the point of view of $\Gamma[m]$, $J_i(\alpha)$ has the role of a Lagrange multiplier which varies with α to satisfy the constraint $\langle\, S_i \,\rangle = m_i$. This is the same principle that motivates DFT. In DFT, density of the electrons is the important quantity that must be kept fixed. The equivalent of J_i in DFT is the effective potential $V(r)$, while the zeroth order approximation to it, which is equivalent to $J_i(0)$ is the Kohn-Sham potential.

1. **Zeroth Order**

   For $\alpha = 0$ we are dealing with free Ising spins. The partition function factorizes and is given by,

   $$Z_0[J] = \prod_i \left(e^{-J_i} + e^{J_i}\right) = \prod_i \left(2\cosh(J_i)\right). \tag{5}$$

   The free energy $W_0[J]$ is,

   $$W_0[J] = -\ln Z_0 = -\sum_i \ln\left[2\cosh(J_i)\right]. \tag{6}$$

Since, $m_i = \langle S_i \rangle$ for all values of α, in particular this is true for $\alpha = 0$. Then, using equation (2), the relation between m_i and $J_i(0)$ is given by,

$$m_i = -\tanh(J_i(0)). \tag{7}$$

We can use the above equation to express $J_i(0)$ in terms of m_i. Using the definition of $\Gamma[m]$ we can write,

$$\Gamma_0[m] = \sum_i \frac{1+m_i}{2} \ln(\frac{1+m_i}{2}) + \sum_i \frac{1-m_i}{2} \ln(\frac{1-m_i}{2}) \tag{8}$$

This is nothing but the entropy of free Ising spins with average magnetization m_i at each site.

2. **First Order**

After introducing the parameter α, the partition function has the form

$$Z[J,\alpha] = \mathrm{Tr} e^{-(\alpha J_{ij} S_i S_j + J_i S_i)}.$$

We get,

$$\frac{\partial W}{\partial \alpha} = -\frac{1}{Z}\frac{\partial Z}{\partial \alpha} = J_{ij}\langle S_i S_j \rangle, \tag{9}$$

and

$$\frac{\partial \Gamma}{\partial \alpha} = \frac{\partial W}{\partial \alpha} + \frac{\partial W}{\partial J_i}\frac{\partial J_i}{\partial \alpha} - m_i \frac{\partial J_i}{\partial \alpha} = \frac{\partial W}{\partial \alpha}. \tag{10}$$

Then, $(\frac{\partial \Gamma}{\partial \alpha})_{\alpha=0} = J_{ij}\langle S_i S_j \rangle_0$, where $\langle \cdots \rangle_0$ means average with Boltzman weight for free spins. We note that for $i \neq j$, $\langle S_i S_j \rangle_0 = \langle S_i \rangle_0 \langle S_j \rangle_0 = m_i m_j$. While for $i = j$, $\langle S_i^2 \rangle = 1$ (for Ising spins). Thus, ignoring a constant term, we have,

$$\Gamma_1[m] = \left(\frac{\partial \Gamma}{\partial \alpha}\right)_{\alpha=0} = \sum_{i \neq j} J_{ij} m_i m_j. \tag{11}$$

We identify this term, together with the zeroth order term, as the free energy of the system within Weiss mean field approximation.

3. **Second Order**

To calculate the second order term we have to work a little more. But the strategy is similar to what we did for the first order. We note that,

$$\frac{\partial^2 W}{\partial \alpha^2} = J_{ij} J_{kl} \left[\langle S_i S_j \rangle \langle S_k S_l \rangle - \langle S_i S_j S_k S_l \rangle\right], \tag{12}$$

and that

$$\begin{aligned} \frac{\partial^2 \Gamma}{\partial \alpha^2} &= \frac{\partial^2 W}{\partial \alpha^2} + \frac{\partial}{\partial J_i}\left(\frac{\partial W}{\partial \alpha}\right)\frac{\partial J_i}{\partial \alpha} \\ &= J_{ij} J_{kl} \left[\langle S_i S_j \rangle \langle S_k S_l \rangle - \langle S_i S_j S_k S_l \rangle\right] \\ &+ J_{ij} \left[\langle S_i S_j \rangle \langle S_k \rangle - \langle S_i S_j S_k \rangle\right] \frac{\partial J_k}{\partial \alpha}. \end{aligned} \tag{13}$$

In the above equation we know, in principle, how to calculate all the terms for $\alpha = 0$, except for the term $\partial J_k/\partial\alpha$. We will calculate this term in two ways. The first method, though longer, sheds light on the mathematics of the formalism. For this we note that $J_i(\alpha)$ varies to satisfy the constraint $m_i = \langle S_i \rangle$. Thus $\partial\langle S_i \rangle/\partial\alpha = 0$, and this condition should give how $J_i(\alpha)$ varies. We get,

$$\left(\frac{\partial\langle S_i \rangle}{\partial\alpha}\right)_{\alpha=0} = J_{kl}\left[\langle S_i \rangle_0\langle S_k S_l \rangle_0 - \langle S_i S_k S_l \rangle_0\right] + \left[\langle S_i \rangle_0\langle S_j \rangle_0 - \langle S_i S_j \rangle_0\right]\left(\frac{\partial J_j}{\partial\alpha}\right)_{\alpha=0} = 0. \tag{14}$$

We note that $\langle S_i \rangle_0\langle S_j \rangle_0 - \langle S_i S_j \rangle_0 = (m_i^2 - 1)\delta_{ij}$. Then, from the above equation we have,

$$\left(\frac{\partial J_i}{\partial\alpha}\right)_{\alpha=0} = -\frac{1}{(m_i^2-1)}\sum_{kl} J_{kl}\left[\langle S_i \rangle_0\langle S_k S_l \rangle_0 - \langle S_i S_k S_l \rangle_0\right].$$

In the above equation, the expression on the right hand side has contribution only for $i = k \neq l$ and for $i = l \neq k$. Thus,

$$\begin{aligned}\left(\frac{\partial J_i}{\partial\alpha}\right)_{\alpha=0} &= -\frac{1}{(m_i^2-1)}\sum_{i\neq j} 2J_{ij}(m_i^2-1)m_j \\ &= -2\sum_{i\neq j} J_{ij}m_j. \end{aligned} \tag{15}$$

We can also derive the above equation very easily using equations (4) and (11). Thus,

$$\begin{aligned}\left(\frac{\partial J_i}{\partial\alpha}\right)_{\alpha=0} &= -\left[\frac{\partial}{\partial\alpha}\left(\frac{\partial\Gamma}{\partial m_i}\right)\right]_{\alpha=0} = -\frac{\partial}{\partial m_i}\left(\frac{\partial\Gamma}{\partial\alpha}\right)_{\alpha=0} \\ &= -\frac{\partial}{\partial m_i}\sum_{i\neq j} J_{ij}m_i m_j \\ &= -2\sum_{i\neq j} J_{ij}m_j. \end{aligned}$$

The above is nothing but an application of Maxwell relation. Note that we can write $\frac{\partial}{\partial\alpha}\frac{\partial}{\partial m_i} = \frac{\partial}{\partial m_i}\frac{\partial}{\partial\alpha}$ because m_i is independent of α.

Now we can evaluate the right hand side of equation (13). The first term, $\langle S_i S_j \rangle_0\langle S_k S_l \rangle_0 - \langle S_i S_j S_k S_l \rangle_0$ is nonzero for $i = l \neq j = k$. There are two such terms. Also, it is nonzero for $i = k \neq j \neq l$. There are four such terms. Thus,

$$J_{ij}J_{kl}\left[\langle S_i S_j \rangle_0\langle S_k S_l \rangle_0 - \langle S_i S_j S_k S_l \rangle_0\right] = 2\sum_{i\neq j} J_{ij}^2\left(m_i^2 m_j^2 - 1\right) + 4\sum_{i\neq j\neq l} J_{ij}J_{jl}\left(m_j^2-1\right)m_i m_l. \tag{16}$$

The second term in equation (13) gives,

$$J_{ij}\left[\langle S_i S_j \rangle_0\langle S_k \rangle_0 - \langle S_i S_j S_k \rangle_0\right]\left(\frac{\partial J_k}{\partial\alpha}\right)_{\alpha=0} \tag{17}$$

$$\begin{aligned} &= -4\sum_{i\neq j} J_{ij}m_i\left(m_j^2-1\right)\sum_{k\neq j} J_{jk}m_k \\ &= -4\sum_{i\neq j\neq l} J_{ij}J_{jl}\left(m_j^2-1\right)m_i m_l - 4\sum_{i\neq j} J_{ij}^2 m_i^2\left(m_j^2-1\right). \end{aligned} \tag{18}$$

Using equations (13), (16) and (18) we finally get,

$$\begin{aligned}
\Gamma_2[m] &= \left(\frac{\partial^2 \Gamma}{\partial \alpha^2}\right)_{\alpha=0} \\
&= 2\sum_{i\neq j} J_{ij}^2 \left(m_i^2 m_j^2 - 1\right) - 4\sum_{i\neq j} J_{ij}^2 m_i^2 \left(m_j^2 - 1\right) \\
&= -2\sum_{i\neq j} J_{ij}^2 \left(1 - m_i^2\right)\left(1 - m_j^2\right).
\end{aligned} \tag{19}$$

This is the famous Onsager correction to the mean field free energy.