UBC Physics Circle

Session 1: Solutions

October 17, 2019

1. The cost of free energy

Solutions

1. (a) The minimal energy is $N_d = 0$ defects. With no defects, the there is only one configuration, meaning that $S = k_B \log(1) = 0$.

   (b) The energy is $E = \varepsilon$. Since the defect could be at any of the N positions, there are a total of $N = \binom{N}{1}$ configurations. The entropy is then $S = k_B \log N$.

   (c) For the 0 defect state to be favoured, we need:

   $$0 < \Delta F = \Delta E - T\Delta S = \varepsilon - k_B T \log N.$$

   Rearranging, the zero-defect state is favoured when

   $$T < \frac{\varepsilon}{k_B \log N} = \frac{1.4 \times 10^{-19}}{1.38 \times 10^{-23} \log(8.5 \times 10^{22})} \approx 192 \text{ K}.$$

2. (a) The number of possible arrangements is given by the number of ways to choose N_d vacancies from N sites, or $W = \binom{N}{N_d}$. The entropy is therefore

   $$S = k_B \log \binom{N}{N_d}.$$

   Since each vacancy costs an energy ε, the free energy at temperature T is

   $$F = E - TS = N_d \varepsilon - k_B T \log \binom{N}{N_d}.$$

   (b) From the previous question, adding a single defect will lead to a change in entropy. Using the formula for binomial coefficients, and log laws, we find that

   $$\begin{aligned} \Delta S &= k_B \log(\binom{N}{N_d + 1} - \log \binom{N}{N_d})) \\ &= k_B \log \left[\frac{N_d!(N - N_d)!N!}{(N_d + 1)!(N - (N_d + 1))!N!} \right] \\ &= k_B \log \left(\frac{N - N_d}{N_d + 1} \right). \end{aligned}$$

When $N_d \gg 1$ (many defects), then we can express this difference in terms of the density of defects, $n = N_d/N$:

$$\Delta S = k_B \log\left(\frac{n^{-1} - 1}{1 + 1/N_d}\right) \approx k_B \log(n^{-1} - 1).$$

The change in energy is just $\Delta E = \varepsilon$, since we add a single defect. The change in free energy is then

$$\Delta F = \Delta E - T\Delta S \approx \varepsilon - k_B T \log(n^{-1} - 1).$$

The equilibrium concentration, n_{eq}, is given by setting the change in free energy to zero and solving for n:

$$0 = \Delta F = \varepsilon - k_B T \log(n_{\text{eq}}^{-1} - 1) \quad \Longrightarrow \quad n_{\text{eq}} = \frac{1}{1 + e^{\varepsilon/k_B T)}}.$$

(c) Room temperature is around $T = 20^\circ$ C ≈ 300 K. Using the parameters from question 1(c), and assuming the upper bound from the previous question gives a good estimate of the density, the number of defects in a single cubic centimetre of iron is

$$N_d \approx \frac{N}{1 + e^{\varepsilon/k_B T)}} = \frac{8.5 \times 10^{22}}{1 + \exp[\frac{1.4\times 10^{-19}}{300(1.4\times 10^{-23})}]} \approx 2.8 \times 10^8.$$

There are around 300 million vacancies!

2. Ising into phase transitions

Solutions

1. (a) We just take pairs of consecutive spins, multiply them together, then add up the results and multiply by $-J$. The products of consecutive spins are

$$\begin{aligned}
s_1 \cdot s_2 &= -1 \cdot -1 = 1 \\
s_2 \cdot s_3 &= -1 \cdot -1 = 1 \\
s_3 \cdot s_4 &= -1 \cdot 1 = -1 \\
s_4 \cdot s_5 &= 1 \cdot 1 = 1 \\
s_5 \cdot s_6 &= 1 \cdot -1 = -1 \\
s_6 \cdot s_7 &= -1 \cdot -1 = 1 \\
s_7 \cdot s_8 &= -1 \cdot -1 = 1 \\
s_8 \cdot s_9 &= -1 \cdot 1 = -1 \\
s_9 \cdot s_{10} &= 1 \cdot -1 = -1.
\end{aligned}$$

Adding up all the terms in the last column, and multiplying by $-J$, gives

$$-J(1 + 1 - 1 + 1 - 1 + 1 + 1 - 1 - 1) = -J.$$

(b) Since aligning consecutive spins gives energy $-J$, and anti-aligning them gives $+J$, we *minimise* the total energy by aligning all spins, an *maximise* total energy by anti-aligning them. For minimum energy, we have all spins aligned, $\uparrow\uparrow \cdots \uparrow$ or $\downarrow\downarrow \cdots \downarrow$. The total magnetisation is $M = \pm N$. For anti-aligned spins, we have $\uparrow\downarrow\uparrow\downarrow \cdots$ or $\downarrow\uparrow\downarrow\uparrow \cdots$. The total magnetisation depends on N. If N is even, then the up and down spins cancel, and $M = 0$. If N is odd, then they cancel except for the last spin, and hence $M = \pm 1$.

2. (a) Since aligned spins have energy $-J$, and we have $N - 1$ pairs, the total energy is $E_1 = -J(N-1)$. There is a single way of aligning all spins up, so the entropy is $S_1 = k_B \log 1 = 0$.

   (b) Each pair of anti-aligned spins gives $+J$ rather than $-J$. Compared to the state where all spins align, each misalignment therefore adds $+J - (-J) = 2J$ energy. Since we have introduced two misalignments, the energy is

$$E_2 = E_1 + 2(2J) = -J(N-1) + 4J.$$

   The leftmost of the N_1 negative spins can start in any of $N - N_1$ positions, so there are $N - N_1$ configurations, and hence the entropy is $S_2 = k_B \log(N - N_1)$.

   (c) We can calculate the change in free energy, at temperature T, from the results of the previous question:

$$\Delta F = (E_2 - E_1) - T(S_2 - S_1) = 4J - Tk_B \log(N - N_1) = 4J - Tk_B \log(N/2),$$

   where we set $N_1 = N/2$ in the last step. If the chain is long, $N \gg 1$, then $\log(N/2)$ is very large. Provided the temperature is nonzero, $T > 0$, then the second term will beat the first, and the "island" of $N/2$ spins has smaller free energy than all spins up. It is therefore favoured over all spins up! Since "all spins up" is the definition of a magnetic material, it appears we cannot have these materials in one dimension.

3. (a) In the previous question, we noted that going from an aligned to a misaligned spin incurs an energy cost of $2J$. For a straight wall of length L, the number of misalignments is L, and hence the energy cost is $\Delta E = 2JL$. This result remains approximately true for a wall which mostly consists of straight segments, $\Delta E \approx 2JL$. If the wall reaches from one side of the grid to the other, it must be have length $L \geq N$, so this is our lower bound.

   (b) Let's just consider walls going from the left to the right. These walls can start at any of N sites on the left boundary, so $C = N$. Let's imagine the boundary wall can't double back on itself, so every time we proceed, we can only go three directions. That means $A = 3$. So the number of configurations $N_L \approx N3^L$.

   (c) Recall that a single domain of aligned spins can only occur in one way, so the entropy vanishes. Using the previous two questions, the change in free energy going from a single spin domain to two domains separated by a wall of length L is approximately

$$\Delta F = \Delta E - TS \approx 2JL - k_B T \log(CA^L) = (2J - k_B T \log A)L - k_B T \log A,$$

(d) If we plug in our choices $A = 3$ and $C = N$, and the lower bound $L = N$, we obtain

$$\Delta F \approx (2J - k_B T \log 3)N - k_B T \log N.$$

As hinted at, the function N grows much faster than $\log N$ for large N, so only the first term is relevant. We get

$$\Delta F \approx (2J - k_B T \log 3)N.$$

If T_c is the value of temperature for which this change in free energy is zero, we find

$$T_c \approx \frac{2J}{k_B \log(3)} \approx 1.8 \frac{J}{k_B}.$$

This is reasonably close to the exact result, obtained using much more mathematics:

$$T_c = \frac{2J}{\log(1+\sqrt{2})} \approx 2.3 \frac{J}{k_B}.$$

3. Mean field theory

Solutions

1. (a) Assuming that each state with energy E is independent and equally likely, if there are $W(E)$ of them, and each has probability $e^{-E/k_B T}/Z$, then the total probability is just

$$P(E) = \text{total number of states} \times \text{probability of each state} = \frac{1}{Z} W(E) e^{-E/k_B T}.$$

(b) Recall that entropy is defined as $S(E) = k_B \log W(E)$. We can therefore write $W(E)$ as

$$W(E) = e^{S(E)/k_B} = e^{TS(E)/k_B T}.$$

This means we can rewrite our answer to the previous question as

$$P(E) = \frac{1}{Z} W(E) e^{-E/k_B T} = \frac{1}{Z} e^{(ST-E)/k_B T} = \frac{1}{Z} e^{-F(E)/k_B T},$$

where we used the definition of free energy, $F = E - TS$. The larger F is, the smaller the probability $P(E)$! So the state minimising the free energy is the most likely, as we have been claiming all along.

2. (a) The *average* or *expected spin* m is the sum of outcomes weighted by their probabilities. We have probability p of pointing up (spin $s = +1$) and hence probability $1 - p$ of pointing down (spin $s = -1$) so the average spin is

$$m = p \cdot (+1) + (1 - p) \cdot (-1) = 2p - 1.$$

(b) First, observe that

$$e^{-E_1/kT} = e^{-(E_2+\Delta E)/kT} = e^{-E_2/kT}e^{-\Delta E/kT}.$$

We can use this to rewrite the probabilities solely in terms of energy differences:

$$P(s_1) = \frac{e^{-E_1/kT}}{e^{-E_1/kT} + e^{-E_2/kT}} = \frac{e^{-E_2/kT}e^{-\Delta E/kT}}{e^{-E_2/kT}(e^{-\Delta E/kT}+1)} = \frac{e^{-\Delta E/kT}}{e^{-\Delta E/kT}+1}$$

$$P(s_2) = \frac{e^{-E_2/kT}}{e^{-E_1/kT} + e^{-E_2/kT}} = \frac{e^{-E_2/kT}}{e^{-E_2/kT}(e^{-\Delta E/kT}+1)} = \frac{1}{e^{-\Delta E/kT}+1}.$$

(a) Let's use cardinal directions N, E, S, W to index neighbors. The energy difference is then

$$\Delta E = -J(s_N + s_E + s_S + s_W)\cdot(1-(-1)) = -2J(s_N + s_E + s_S + s_W).$$

To get the *average* difference, we can replace each spin with its average, m. This gives

$$\Delta E_{\text{av}} = -2J(m+m+m+m) = -8Jm.$$

(b) Plugging the result from 3(a) into 2(b) gives

$$P(s=\uparrow) = \frac{e^{8Jm/kT}}{e^{8Jm/kT}+1}.$$

(c) In the previous question, $P(s=\uparrow)$ is exactly the probability p that a spin points up. So we have two equations related m and p:

$$m = 2p-1, \quad p = \frac{e^{8Jm/kT}}{e^{8Jm/kT}+1}.$$

We can eliminate p:

$$m = 2p-1 = \frac{2e^{8Jm/kT}}{e^{8Jm/kT}+1} - 1 = \frac{e^{8Jm/kT}-1}{e^{8Jm/kT}+1} = \tanh\left(\frac{4Jm}{k_BT}\right).$$

This is the *mean field self-consistency* equation.

(d) Recall that m is the *average* spin. It $m = 1$, it tells us that almost all spins point up, and the material is magnetised. A similar story is true for $m = -1$. If, on the other hand, $m = 0$, it means that spins are equally likely to point up or down, so as in previous questions, we are in a phase with *no magnetism*. Now let's consider the limits $T \to 0, \infty$.

(i) As $T \to 0$, the term $8Jm/k_BT$ gets very large, and approaches $\pm\infty$ depending on the sign of m. If m is positive, it approaches $+\infty$, and hence e^{8Jm/k_BT} also blows up, so

$$m = \frac{e^{8Jm/kT}-1}{e^{8Jm/kT}+1} \approx \frac{e^{8Jm/kT}}{e^{8Jm/kT}} = 1.$$

In other words, one possibility is all spins pointing up. But if m is negative, then as $T \to 0$, $8Jm/k_BT$ approaches $-\infty$, and hence $e^{8Jm/k_BT} \to 0$. It follows that

$$m = \frac{e^{8Jm/kT} - 1}{e^{8Jm/kT} + 1} \approx \frac{0-1}{0+1} = -1.$$

Thus, it is also possible that all spins point down! In either case, we are rediscovering that at low temperatures, the material can be magnetised, with all (or almost all) spins pointing in the same direction.

(ii) Now, in the limit $T \to \infty$, $e^{8Jm/k_BT} \to 1$, and hence

$$m = \frac{e^{8Jm/kT} - 1}{e^{8Jm/kT} + 1} \to 0.$$

At high temperatures, there is no magnetism, just as we discovered for the 2D Ising model in the previous question!