

M04T.3

a) As $T \rightarrow \infty$, entropy dominates and all the atoms are randomly placed, so each additional atom has a probability of being A of x

Probability of getting n A atoms in a row: $P(n) \sim x^n$

$$\begin{aligned} \langle n \rangle &= \frac{\sum_n nP(n)}{\sum_n P(n)} = x \frac{d}{dx} \ln(\sum_n P(n)) = x \frac{d}{dx} \ln(\sum_n x^n) = x \frac{d}{dx} \ln\left(\frac{x}{1-x}\right) \\ &= x \left(\frac{1}{x} - \frac{1}{1-x} \right) = \frac{1}{1-x} \end{aligned}$$

b) As $T \rightarrow 0$, the energy is minimized if all of each type of atom cluster together, so we expect all xN of the A atoms to form a single cluster:

$$\langle n \rangle = xN$$

$$c) F = U - TS$$

We take the bond to the right of each individual atom to account for all the bonds.

The expected energy of a single A atom: $u_A = P_A U_{AA} + P_B U_{AB}$

The expected energy of a single B atom: $u_B = P_A U_{AB} + P_B U_{BB}$

The total expected energy U is then given by:

$$U = (N_A u_A + N_B u_B)$$

If the atoms are independently and randomly distributed, $P_A = x$ and $P_B = 1 - x$

$$U_{AA} = U_{BB} = -\epsilon, U_{AB} = -\epsilon/2$$

$$N_A = xN, N_B = (1-x)N$$

Plugging in for all these values and simplifying, we obtain:

$$U = \epsilon N(-x^2 + x - 1)$$

$$\Delta S = k_B \ln(\Omega)$$

$$\Omega = \frac{N!}{N_A! N_B!}$$

$$\text{And so: } \Delta S = k_B \ln\left(\frac{N!}{N_A! N_B!}\right)$$

We use Stirling's approx: $\ln(x!) \approx x \ln(x) - x$

$$\begin{aligned} \Delta S &= k_B (N \ln(N) - xN \ln(xN) - (1-x)N \ln((1-x)N)) \\ &= k_B N ((x + (1-x)) \ln(N) - x \ln(xN) - (1-x) \ln((1-x)N)) = \\ &= -k_B N (x \ln(x) + (1-x) \ln(1-x)) \end{aligned}$$

Plugging these in, we obtain:

$$F = \epsilon N(-x^2 + x - 1) + k_B N T (x \ln(x) + (1-x) \ln(1-x))$$

d) A variational upper bound as the atoms are assumed to be randomly and independently distributed. In reality, the atoms will tend to form clusters at finite temperatures, decreasing the free energy. Looking at our F equation, we see the TS term is a concave up function. When we factor in that it is finite, U is a concave down function that creates a small bump within the overall F function, causing the probability of an $A-A$ and $B-B$ bond to increase, resulting in clustering.

e) A phase transition occurs when the atoms begin to cluster. This occurs at the temperature where F flips from convex to concave wrt x

$$F''(x = 1/2) = 0$$

$$F'(x) = \epsilon N(-2x + 1) + k_B N T (\ln(x) - \ln(1-x))$$

$$F''(x) = -2N\epsilon + k_B NT(1/x + 1/(1-x))$$

$$-2N\epsilon + 4k_B NT_C = 0$$

$$T_C = \frac{\epsilon}{2k_B}$$

If we again plot F , if $T < T_C$, we get a local maximum at $x = 1/2$ as $abs(U'') > abs(TS'')$ at that point. At that point our probability of getting $A - A$ and $B - B$ bonds will settle into the local minima on each side of the local maximum, resulting in clustering. If $T > T_C$, instead the probabilities will just settle at $1/2$.

f) Shivaji said in class that this part of the question is written wrong, and should be that there is a phase transition at $T = 0$.

If the question is written correctly, if we look at our plot of F it looks identical to U , with a single maximum. However, we will have an unstable equilibrium at $x = 1/2$, and if there is no additional energy to perturb the system from temperature fluctuation, the probabilities will stay at the unstable maximum and there will be no phase transition.

One thought on "M04T.3"



December 11, 2013 at 5:34 pm

Part (a) -- OK, except one typo after the second equality sign -- \sum_n should be under the logarithm.

Part (b) -- OK

Part (c) -- OK. You may notice that your approximation is essentially a mean field approximation. Also you assigned "expected energy" to a single atom, while originally in the problem the energy was assigned to every pair of adjacent atoms, so it would make sense to be more clear on what you mean. However, I agree with your result.

Part (d) -- OK, physically it makes sense. However, I would probably expect to see a more convincing argument on why the free energy decreases after the atoms cluster. It's clear that U decreases (simply from the formula for the Hamiltonian), but why F ?

Part (e) -- it's not clear why the atoms begin to cluster at $F''(x) = 0$. Can you provide more explanation? The answer looks correct though.

Part (f) -- explain more clearly what you mean. What is the expected phase transition at $T = 0$? Why can't it occur?
