3.012 Quiz 3 **3.012**
12.20.05 **Fall 2005**
100 points total (50 in thermo + 50 in bonding)

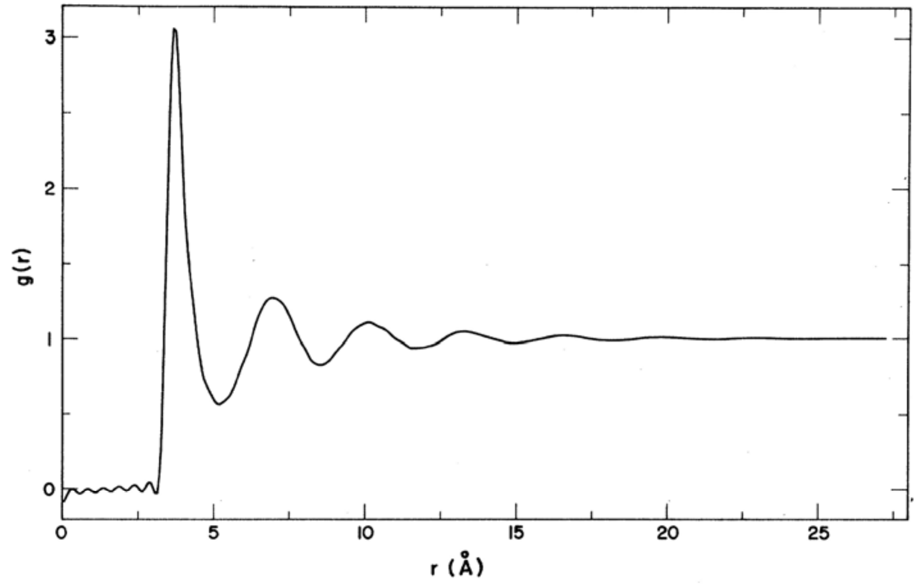
Give as much written explanation as possible of your reasoning, and write clearly and legibly. There is plenty of space in between questions, and more blank space at the end.

Time yourself carefully – do not spend most of your time on a single question. Remember, you have three hours (from 1.30pm to 4.30pm). You can start with thermo, or start with bonding.

Write your name here: ____

BONDING (4 problems, 50 points total)

1. **Local structure:** in 1973 Yarnell and co-workers determined the structure of argon at 85 K. The pair correlation function g(r) they found for this monoatomic substance is shown below:



   a. What is the definition of the pair-correlation function ? Why does it tend to 1.0 at large r ?

   b. What is the state of argon at 85 K ? Is it a solid, a liquid, or a gas, and why ?

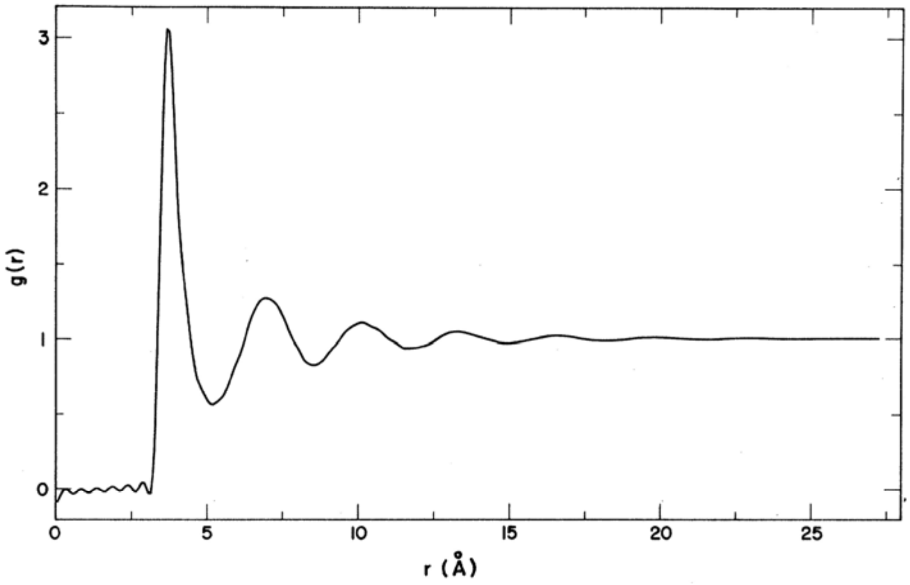
c. What is your estimate for the diameter of an argon atom ?

d. What do the different peaks in the g(r) shown above represent ?

e. Why does the pair-correlation function flatten beyond 15-20 Å ?

f. How can you calculate the number of first-neighbors around an argon atom at 85 K ?

g. In which ways would the g(r) (reproduced below) change, if the temperature were to increase by a small amount (small enough that the system doesn't undergo a phase transition) ?



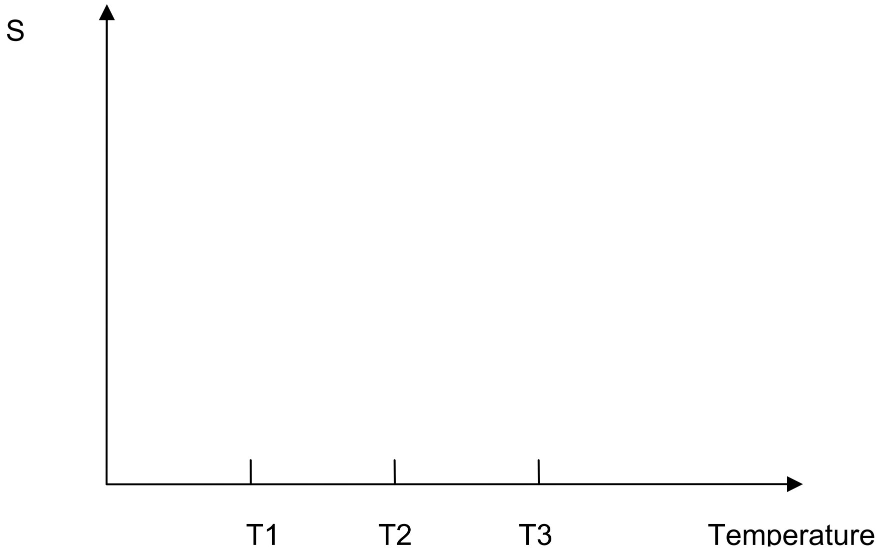
h. How would the pair-correlation functions for argon look like for the two other states not considered in point b. ? (label each of the two pair-correlation functions either as solid, liquid, or gas)

2. Nematic liquid crystals:

a. What characterizes a nematic liquid crystal ? How is it different from a cholesteric liquid crystal, or from a smectic one? Discuss these differences in terms of orientation and translation order parameters, both long-range and short-range.

b. The orientation order parameter S for a nematic liquid crystal is given by $S = \frac{3\left\langle \cos^2 \theta \right\rangle - 1}{2}$, where θ is the angle between a mesogen and the average preferred orientation $\hat{n}$, and the angular brackets represent an average over all the mesogens in the sample. Show what the order parameter S will be if all the mesogens are oriented perfectly in the direction of $\hat{n}$, and what will it be if they are randomly oriented (derive explicitly your result).

c. Suppose that a material goes through 4 phases as temperature is increased: first it is a solid, then a smectic liquid crystal, then a nematic liquid crystal, and finally an isotropic liquid. How will the orientation order parameter change with temperature (the phase-transition temperatures are labeled as T1, T2, and T3) ?



3. **X-ray diffraction:**
   a. Suppose we have a real space Bravais lattice with principal crystallographic vectors $\vec{a}_1, \vec{a}_2,$ and $\vec{a}_3$. What condition does the wavector $\vec{k}$ of a plane wave $A\exp\left(i\vec{k}\cdot\vec{r}\right)$ must satisfy, so that the planewave has the same value at every point $(l,m,n) = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$ of the Bravais lattice ? (As always, demonstrate your statement)

b. Explain how the Laue conditions arise for constructive interference of a plane wave incident on a monoatomic crystal that has one atom at each point of the Bravais lattice $(l,m,n) = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$.

c. The Ewald construction can be used to determine if Laue diffraction will be present or not in a given sample. Describe, first in words, and only at the end with a figure, the Ewald construction, its relation to the incoming and outgoing versors for the diffracted X-beams, and the reciprocal lattice of the crystal you are investigating.

d. Why do we use monochromatic X-rays in a Debye-Scherrer experiment ?

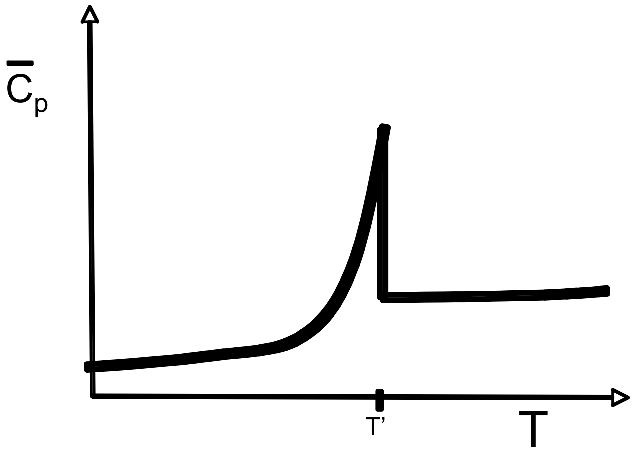
4. **Symmetry constraints of physical properties:** at a well-known Insitute of Technology in the Northeast of the United States, Prof. Superman, Prof. Laue, and two UROP students are busy at work. Prof. Superman has brought a crystal of kryptonite, and gone off to greater glories. Prof. Laue has given it a glance (Prof. Laue emits X-rays, in his spare time), and proclaimed that kryptonite is metallic, and has a point-group made only by a 4-fold rotation axis and a mirror plane perpendicular to that axis. The UROPs are asked to figure out what the symmetry properties of the electrical conductivity tensor $\underline{\underline{\sigma}}$ are ($\underline{\underline{\sigma}}$ relates an applied field to a current density via $\vec{j} = \underline{\underline{\sigma}}\vec{E},\ \text{i.e.}\ j_i = \sigma_{ik} E_k$), write a convincing explanation for it, and invoke a clear statement of the Neumann principle in the process. Can you help them out, and grant them a well-deserved break ?

THERMODYNAMICS (4 problems, 50 points total).

Physical Constants:
Gas constant: R = 8.3144 J/mole-K = 0.082057 L-atm/mole-K

1. **Short Answer. [3 parts, a-c] Answer with 1-3 brief sentences.**

    a. A new material shows a variation in heat capacity with temperature as shown in the diagram below. Is the phase transition at T = T' a first- or second-order transition? Briefly explain your answer.



b. The Flory-Huggins statistical mechanics model for polymer solutions models the internal energy change on mixing polymer and solvent by the following expression:

$$\Delta\overline{U}^{mix} = \chi k_b T \phi_s \phi_p$$

…where χ is the interaction parameter, and ϕ_s and ϕ_p are the volume fractions of solvent and polymer, respectively. Explain in a few sentences why this expression for the internal energy change breaks down if the polymer and solvent do not mix randomly in space.

c. Briefly explain why reasonably accurate calculations of the free energy change on mixing in solutions are possible using lattice models that neglect all degrees of freedom in the system except translational degrees of freedom.

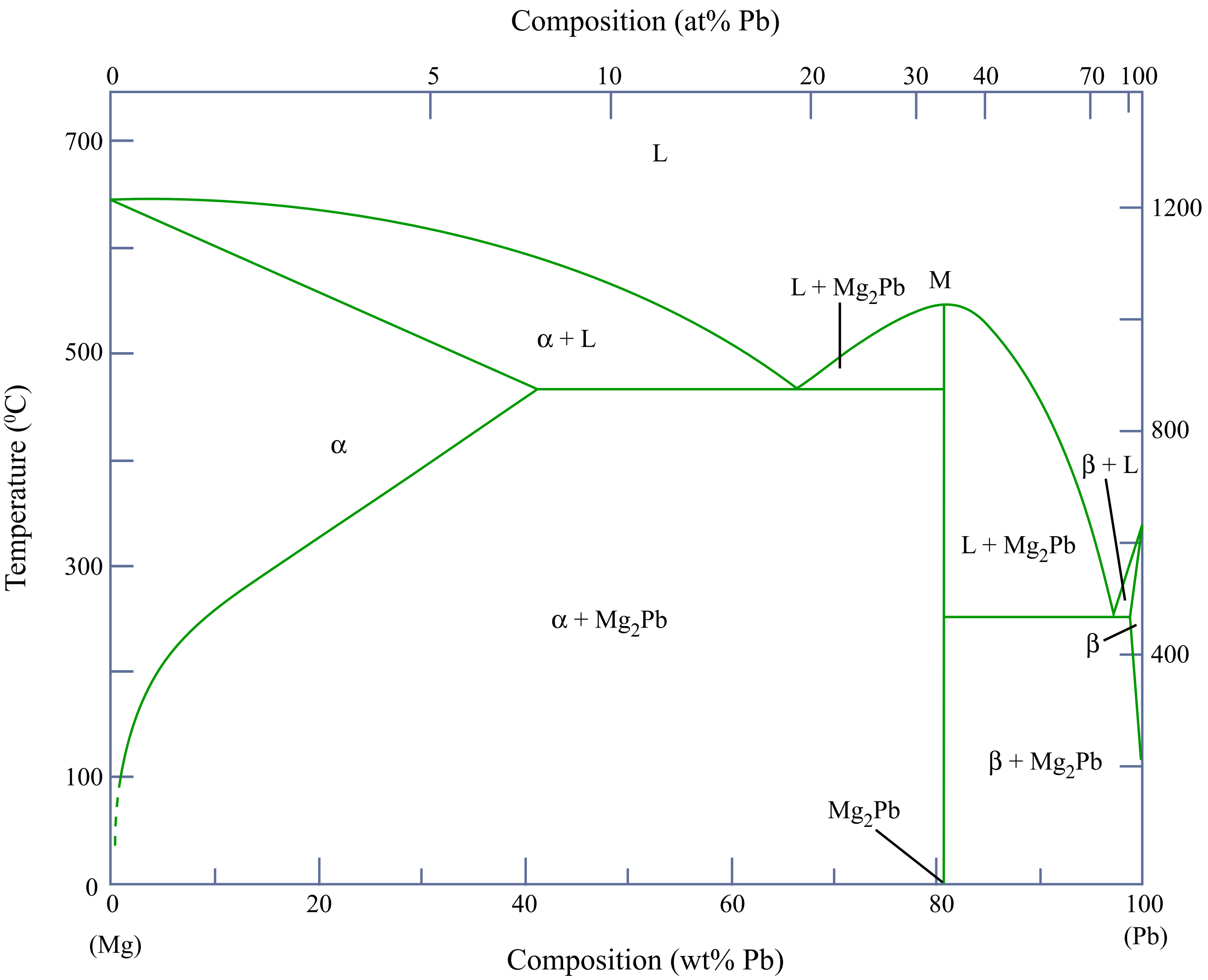
2. **Interpreting binary phase diagrams. [4 parts, a-d]** Shown on the following page is the binary phase diagram for magnesium-lead alloys. Use the diagram to answer the questions below:

   a. A Mg-Pb solution with 60 wt% Pb is equilibrated at 400°C. What are the approximate phase fractions of α and Mg_2Pb?

   b. Mark the location(s) of congruent phase transitions on the diagram with a filled circle.

   c. What are the (approximate) compositions of the α, L, and Mg_2Pb phases in the eutectic mixture present at ~470°C?

   d. Why does the eutectic mixture exist at only a single temperature?



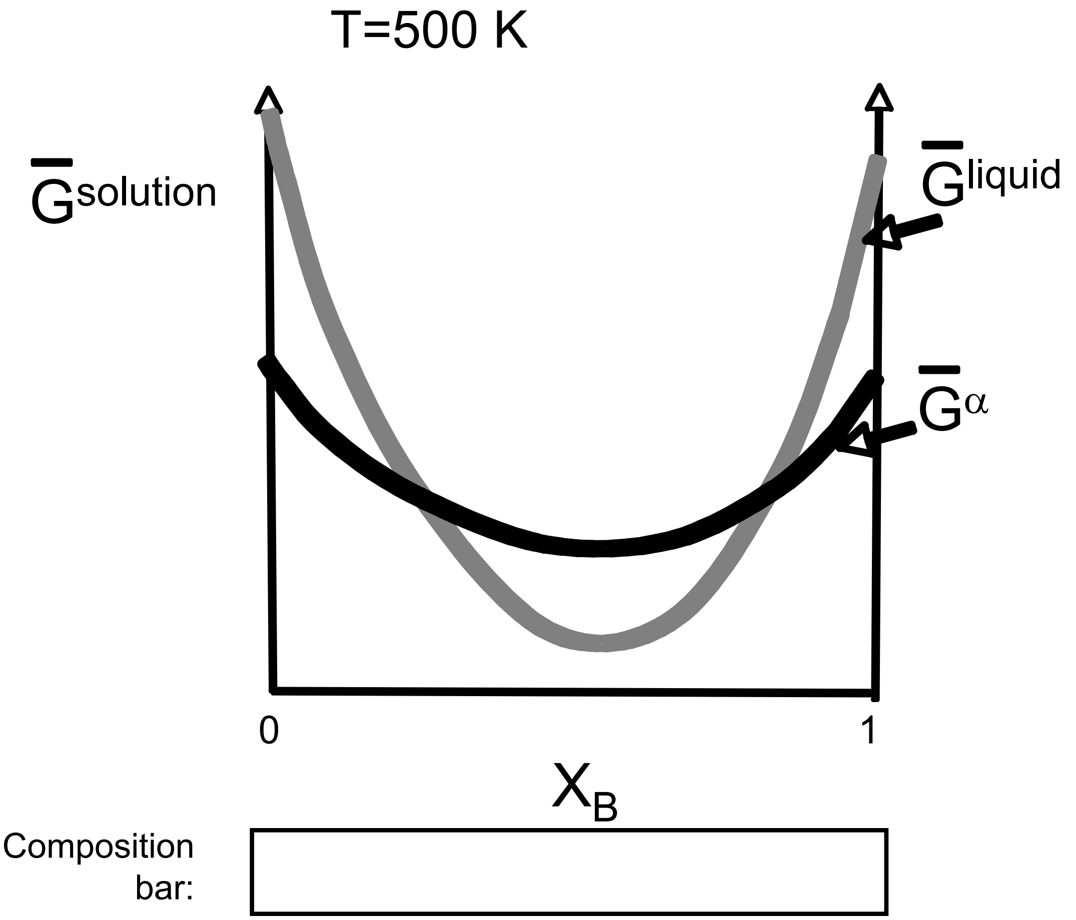
The magnesium-lead phase diagram.

Figure by MIT OCW.

(Phase diagram from W.D. Callister, Jr. Materials Science and Engineering an Introduction 6th Ed., Wiley, New York (2003))

3. **Free energy diagrams**. **[2 parts, a and b]** Consider a binary A-B system, which has a solid solution phase α with regular solution behavior (solid black curves) and a liquid phase (gray curves).

   a. Draw any common tangents on the T = 500 K diagram with a dashed line and mark which phases are present as a function of composition in the 'composition bar' below the diagram.

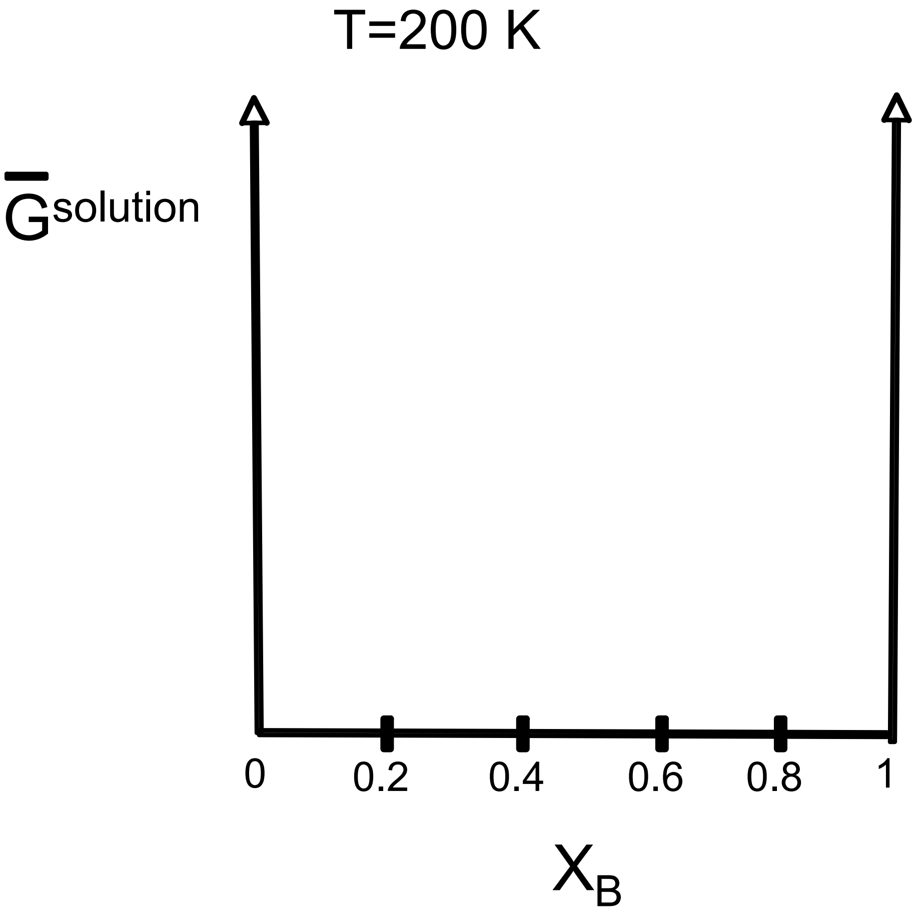


b. At T = 200K, the system is in the solid state at all values of X_B. Further, the regular solution α phase exhibits a miscibility gap, splitting into α_1 and α_2 phases with compositions $X_B^{\alpha_1} = 0.2$ and $X_B^{\alpha_2} = 0.8$.

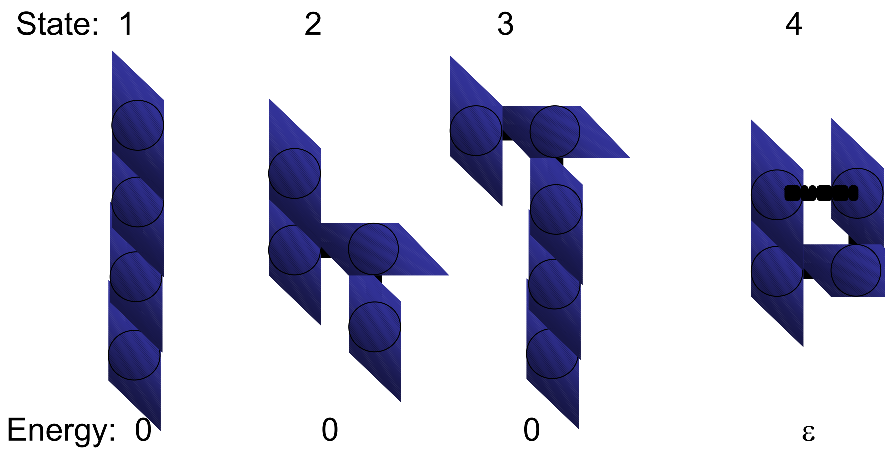
  i. Draw a qualitatively reasonable free energy vs. composition diagram for the system at this temperature, based on the given information.

  ii. Draw vertical SOLID lines on the diagram to denote boundaries between values of X_B where the system is phase separated vs. homogeneous, and **label the phases present across the diagram**.

  iii. Draw vertical DASHED lines to denote approximate boundaries between regions where the homogeneous α phase is ***metastable*** and where it is ***unstable***. **Label the diagram to indicate which ranges of X_B give α solutions that are metastable and which give α solutions that are unstable**.



4. **Statistical mechanics of a collapsing polymer chain. [3 parts, a-c]** Consider a simple model of a polymer chain confined to a two-dimensional surface, where the possible unique states (and their associated energies) are as shown below:



   a. What is the entropy of a single polymer chain in this simple model? (You do not need to plug in numbers for the physical constants).

   b. Write the molecular partition function for the polymer chain (accounting only for the translational degrees of freedom shown in the states above).

   c. If the energy of the 'collapsed' state of the chain is $\varepsilon = -600k_b$, what is the probability of the collapsed state at room temperature (25°C)?