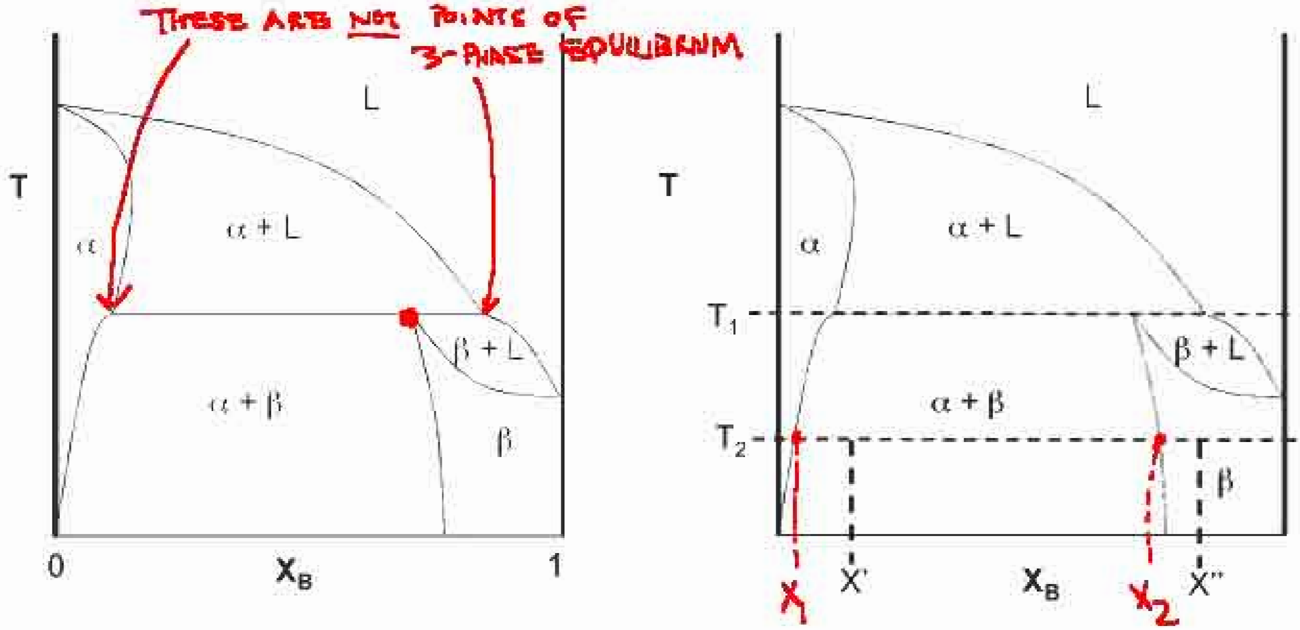
Thermodynamics. (50 points)

6. Shown below on the left is a binary phase diagram, and on the right the same diagram with annotation. Use these diagrams to answer the questions below:



a. (3 points) On the left-hand diagram, mark the invariant point(s) and write the equilibrium that exists at each in the space below.

$\alpha + L \rightleftarrows \beta$ (THIS IS A <u>PERITECTIC</u> INVARIANT POINT)

b. (4 points) **For temperature T_2, identify the phases** present, the **composition** of the phases, and the **phase fraction** of each phase present at the composition **X'** and at the composition **X''**. (Identify additional points on the diagram as needed.)

	PHASES	COMPOSITION	PHASE FRACTION f
AT X':	α	X_1	$(X_2 - X')/(X_2 - X_1)$
	β	X_2	$(X' - X_1)/(X_2 - X_1)$
AT X'':	β	X''	1 (SYSTEM IS ALL β)

c. (4 points) What is the difference between the phase rule for a single component T/P diagram and the phase rule for a binary T/X_B phase diagram? Explain your answer with 1-2 sentences.

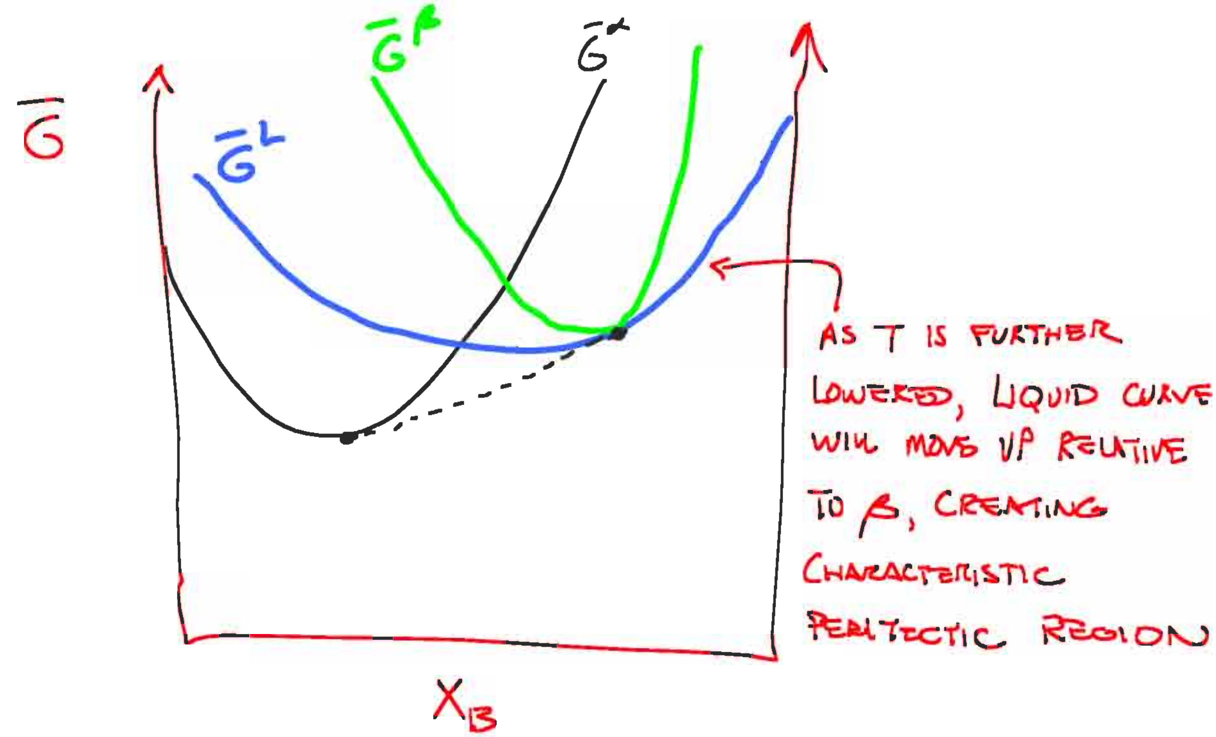
SINGLE COMPONENT T/P DIAGRAM: $D + P = C + 2$

BOTH T AND P ARE VARIABLES

2-COMPONENT T/X_B DIAGRAM: $D + P = C + 1$

PRESSURE IS FIXED

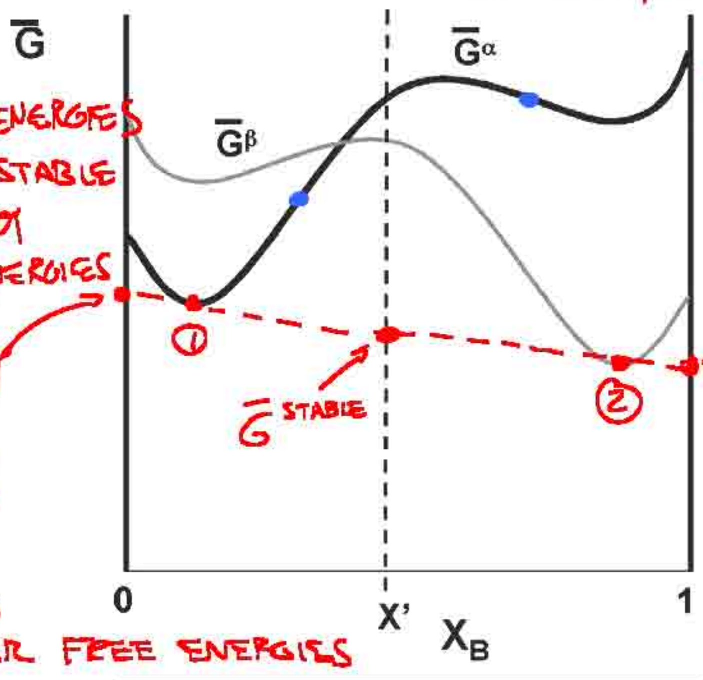
d. (4 points) In the space below, sketch a reasonable set of molar free energy vs. composition curves for each phase of the binary system at the temperature marked T_1 above.



7. Shown below is a free energy vs. composition diagram for a binary system that has two different solid phases α and β, each of which behaves as a regular solution. Use this diagram to answer the questions below:

STABLE STATE IS $\alpha + \beta \rightarrow$ COMMON TANGENT FROM ① TO ②

NOTE THAT ① AND ② ARE THE MOLAR FREE ENERGIES OF α AND β IN THE STABLE STATE, BUT THEY ARE NOT PARTIAL MOLAR FREE ENERGIES



$\mu_A^\alpha = \mu_A^\beta$

$(\bar{G}_A^\alpha = \bar{G}_A^\beta)$

CHEMICAL POTENTIALS ARE PARTIAL MOLAR FREE ENERGIES

$\mu_B^\alpha = \mu_B^\beta$

$(\bar{G}_B^\alpha = \bar{G}_B^\beta)$

Composition bar:

a. (6 points) **For the composition marked X'** above:

   i. Mark the free energy of the stable state of the system on the diagram above. If the stable state of the system is a multi-phase equilibrium, mark the partial molar free energies of each phase present.

   ii. Minimization of the Gibbs free energy at constant temperature and pressure for a closed system occurs if the chemical potential of A is the same in every phase present, and if the chemical potential of B is the same in each phase. Show on the graph how this condition is met for the stable phases at this composition and temperature.

b. (4 points) Suppose the β phase did not exist in this system. Would homogeneous α phase with a composition X' transform to a phase separated state by nucleation and growth or spinodal decomposition? Explain your answer.

MARKED AS BLUE POINTS ABOVE

WE ARE 'INSIDE' THE SPINODALS, THUS THE SYSTEM WILL TRANSFORM BY SPINODAL DECOMPOSITION.

8. A system of N distinguishable molecules that each have 3 possible energy states (with energies $-\varepsilon$, 0, and $+\varepsilon$) is equilibrated at a temperature T.

   a. (6 points) What is the partition function of the **entire system** of N molecules?

$$q = e^{\epsilon/kT} + 1 + e^{-\epsilon/kT}$$

$$Q = q^N = \left(e^{\epsilon/kT} + 1 + e^{-\epsilon/kT}\right)^N$$

   b. (6 points) Show that the ratio $\frac{p_{\varepsilon}}{p_{-\varepsilon}}$, the probability to find one molecule of the system in the E = ε state over the probability of one molecule residing in the E = - ε state can be determined without knowledge of the partition function, and calculate this ratio.

$$\frac{p_\epsilon}{p_{-\epsilon}} = \frac{e^{-\epsilon/kT}}{e^{\epsilon/kT}} = e^{-2\epsilon/kT}$$

   c. (7 points) Show that the free energy of this system becomes a linear function of T at very high temperatures.

$$F = -kT\ln Q = -kTN\ln\big(\underbrace{e^{\epsilon/kT} + 1 + e^{-\epsilon/kT}}_{\text{NONLINEAR T DEPENDENCE}}\big)$$

AS $T \to \infty$:

$$F = -kTN\ln\big(\overset{1}{\cancel{e^{\epsilon/kT}}} + 1 + \overset{1}{\cancel{e^{-\epsilon/kT}}}\big)$$

$$F \to -kTN\ln 3$$

9. (6 points) In our work on binary solution phase behavior, we showed that **some** degree of mixing (homogeneous solution formation on addition of a small amount of the component B to pure A and vice versa) is **always** favored if the components form a regular solution- even though the two components may be very chemically incompatible (i.e., they have a very large interaction parameter Ω). Mixing in this situation is driven by a favorable entropy change. Using arguments based on the statistical mechanical definition of entropy, explain in a few sentences why entropy favors mixing. (You may invoke a lattice model description of the binary solution to help with your explanation).

THE ENTROPY OF A SYSTEM MAY BE REPRESENTED AS:

$$S = k_b \ln W$$

WHERE W IS THE NUMBER OF STATES AVAILABLE TO THE SYSTEM. IN A SIMPLE LATTICE MODEL OF MATERIALS, THE STATES AVAILABLE CAN BE ENUMERATED AS TRANSLATIONAL CONFIGURATIONS OF THE MOLECULES ON A LATTICE. PURE COMPONENTS HAVE A SINGLE (OR VERY LOW NUMBER OF) UNIQUE CONFIGURATION(S). HOWEVER, ADDITION OF A SMALL AMOUNT OF A SECOND COMPONENT CREATES A LARGE NUMBER OF UNIQUE TRANSLATIONAL STATES. THIS SIGNIFICANT INCREASE IN ENTROPY CAN OVERCOME THE CHEMICAL INCOMPATIBILITY OF EVEN VERY DISSIMILAR COMPOUNDS WHICH DO NOT FORM HOMOGENEOUS SOLUTIONS AT HIGH A:B RATIOS.