Graded problems – As usual, try as much as possible to explain in a *narrative form* your reasoning (as opposed to writing down bare equations).

1. **Think outside the box.** Let us suppose that an electron is confined to a 3-dimensional sphere of radius L. The potential inside the sphere is 0, and it is infinite outside the sphere. Write down explicitly the Schrödinger equation in the appropriate coordinate system, discuss what are the solutions for the angular part of the wavefunction, and write down the radial Schrödinger equation. What are the boundary conditions for this problem ? (Not graded: can you say anything on the radial solutions, e.g. for l=0 ?).

2. **Why be exact ?** Calculate the ground state energy of an electron in a 1-dimensional harmonic potential ½ k x^2 using the variational principle with the trial function $A/(b^2+x^2)$, where b is a variational parameter. If you are not familiar with Mathematica or Macsyma, leave the integrals in their indefinite form, but outline all the steps of your procedure.

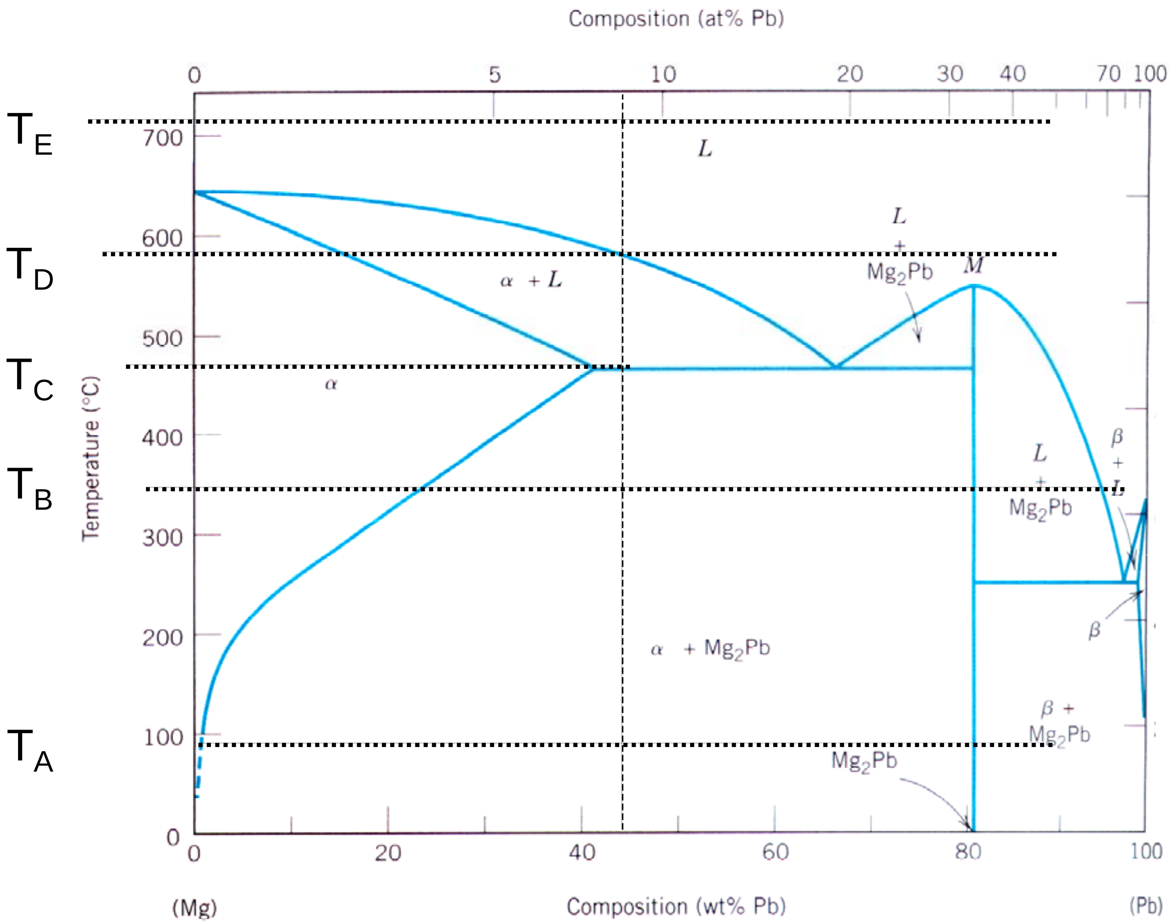
3. **Become a Quantum Wizard (@3.012-2003-MIT).** Prove an extended variational principle: if a trial wavefunction is orthogonal to the exact ground state, the expectation value of the energy for this trial wavefunction cannot be lower than the exact energy of the first excited state.

4. **Analysis of equilibrium phases with a binary phase diagram**. Shown below is the phase diagram for the binary system magnesium-lead at 1 atm pressure. Supposing a sample initially at temperature T_A is slowly heated to temperature T_E, prepare a list of the phase equilibria at each of the noted temperatures A-E. At each temperature, give:

    a. Which phases are present.

    b. The phase fraction of each phase.

    c. The composition of each phase.



5. **Construction of a phase diagram from free energy data.** A new material comprised of an *A-B* binary system is being studied. The free energy of the solid phase of this system is described by the regular solution model, while the liquid phase forms an ideal solution.

<u>Thermodynamic data:</u>

$$\mu^L_{A,o} = -175 \frac{J}{mole} \qquad \mu^S_{A,o} = -5{,}000 \frac{J}{mole}$$

$$\mu^L_{A,o} = -1{,}000 \frac{J}{mole} \qquad \mu^S_{B,o} = -4{,}000 \frac{J}{mole}$$

$$\Omega = 20{,}000 \frac{J}{mole}$$

a. Derive an expression for the molar free energy of the solid solution phase as a function of composition (X_B) and temperature. *Note that the free energy of mixing is not equivalent to the free energy of the solid solution*.

b. Prepare a plot of the free energy of the solid phase and of the liquid phase vs. composition X_B at the following 3 temperatures: 900 K, 700 K, 500 K.

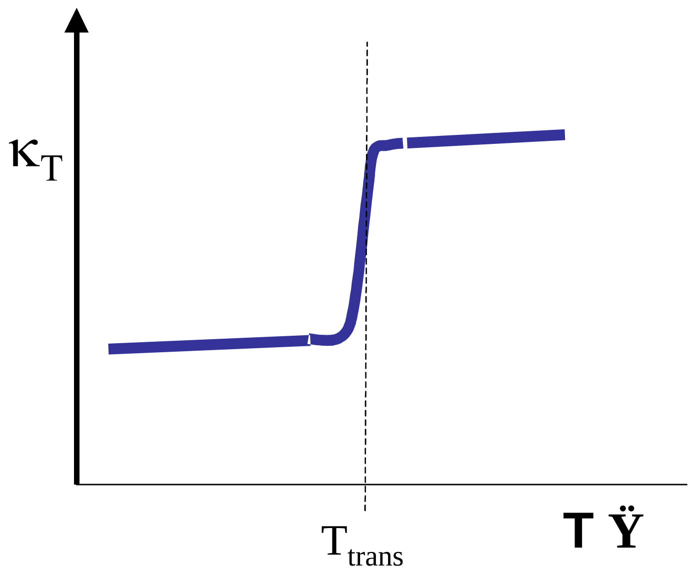
c. Using your 3 plots, graph common tangents and identify the stable phases as a function of X_B at each temperature.

d. From this data, suggest what the complete phase diagram of this system must look like.

Optional problems:

6. **Atoms, atoms everywhere:** Calculate $<z>$, $<p_z^2>$, and $<p_z>^2$ for the 1s state of the He+ ion. Sketch a picture of the radial part, and separately of the angular part, of all its empty 4d orbitals, paying particular care to the nodal surfaces.

7. **Characterizing phase transitions.** Shown below is a sketch of the isothermal compressibility of a new material vs. temperature. Is the discontinuity shown a characteristic of a first-order phase transition, a second-order transition, or a higher-order transition? Show why.



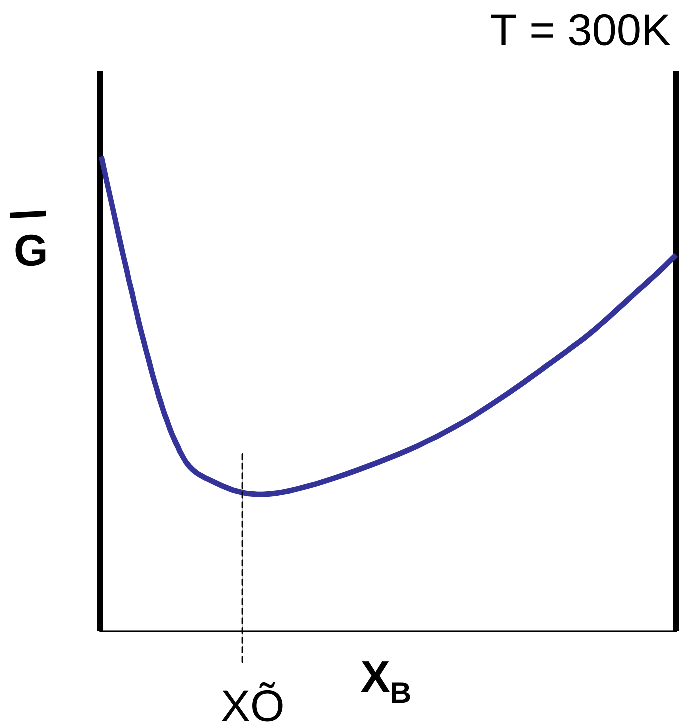
8. **Thermodynamic quantities derived from free energy-composition diagrams**. On the solution free energy diagram for a binary system given below, sketch or identify the following quantities:

   a. The standard state chemical potentials of *A* and *B* at 300 K.

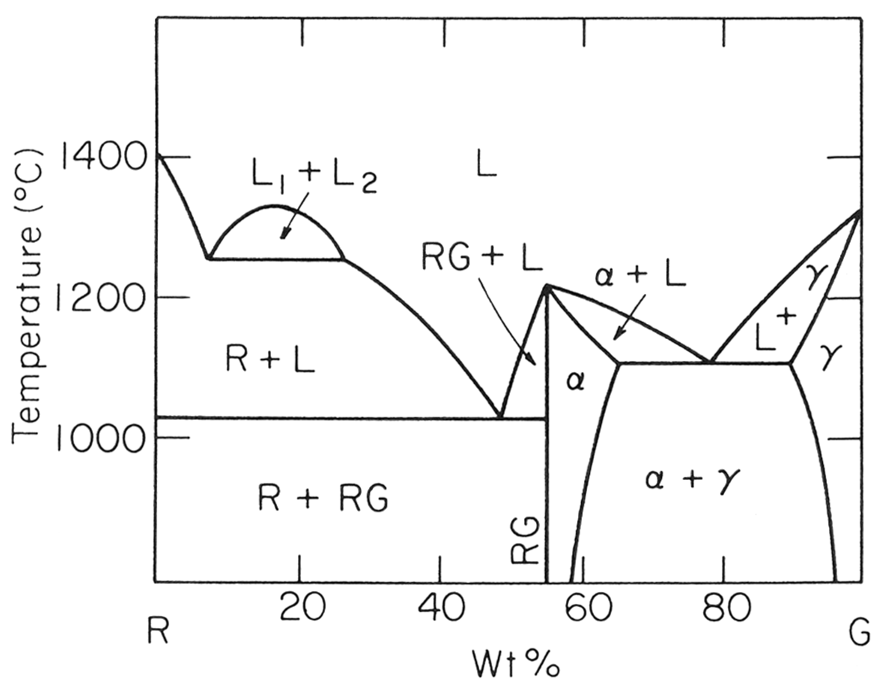
   b. The free energy of a heterogeneous mixture of *A* and *B* with overall composition X'.

   c. The chemical potentials of A and B at 300 K in the solution.

   d. The free energy change $\Delta\overline{G}^{mix}$ obtained when the heterogeneous mixture of A and B forms a homogeneous solution.



9. **Invariant points and congruent transitions.** On the following hypothetical phase diagram, mark and label the class of the invariant points, and identify the congruent transitions.



10. **Free energy of ideal solutions.** Prove that the enthalpy of mixing for an ideal solution is zero, and derive an expression for the entropy of mixing for an ideal solution.

11. **Spinodals in binary systems.** For the regular solution solid phase of the problem 'Construction of a phase diagram from free energy data', make the following calculations:

    a. Determine the critical temperature at which the solid solution would phase separate. (Note that we don't see the critical temperature on the phase diagram since the liquid phase in this system is present at temperatures above the eutectic isotherm; we would have to superheat the solid phase to see the critical temperature where the phase-separated solid becomes a homogeneous solid).

    b. Calculate the composition of the spinodal points at T = 500 K. Qualitatively, how would the spinodals be plotted onto the phase diagram of this system?