MSE-483 ADVANCED PHASE TRANSFORMATIONS
FALL 2024

QUESTION 1 : EQUILIBRIUM IN OPEN SYSTEMS

In this problem, we will derive the equilibrium criteria for multicomponent alloys. Consider a binary alloy that is placed in an environment at fixed pressure (p), and temperature(T). The number of moles of A (N_A) and number of moles of B (N_B) are also held constant. The phase diagram of the A-B alloy is shown in fig. 1. Partial molar quantities for this alloy are defined as :

$$g = \frac{G}{N_A + N_B} \tag{1}$$

$$x_i = \frac{N_i}{N_A + N_B} \tag{2}$$

where G is the Gibbs free energy, g is the Gibbs free energy per mole of alloy, x_i and N_i are the mole fraction and number of moles of specie i.
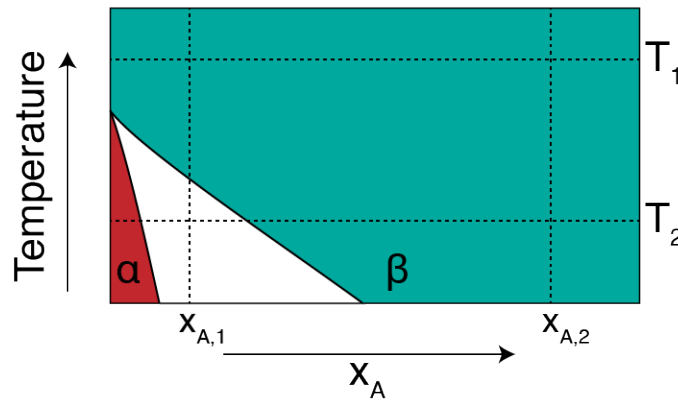

Figure 1: Phase diagram for an A-B alloy

1. Express the characteristic potential $(G(T, p, N_A, N_B))$ under these boundary conditions as a Legendre transform of the internal energy (U). Write down the equations of state for G.
2. Derive an expression relating the chemical potential of specie i to the molar free energy g, the derivative of the molar free energy with respect to the species mole fraction $((\frac{\partial g}{\partial x_i})_{x_j \neq i, T, p})$ and the mole fraction x_i of specie i.
3. Sketch the molar free energy, g of phase β at temperature T_1 as a function of x_A. Use your results from the previous question to identify the chemical potentials μ_A, μ_B at a composition $x_{A,1}$, on the $g - x_A$ plot.
4. Sketch the molar free energies of α and β at temperature T_2.
5. Derive equilibrium conditions for the system at a temperature T_2, and composition $x_{A,1}$. How would your results differ if you were at the composition $x_{A,2}$?

QUESTION 2 : THE REGULAR SOLUTION MODEL

A binary mixture of two chemical species (denoted A and B) is found to have the following free energy function:

$$G^m(x, T) = \Omega x(1 - x) + k_B T(x \log(x) + (1 - x) \log(1 - x))$$

where $G^m = \frac{G}{N}$ is the molar Gibbs free energy of the solid, $x = N_B/N$ is the mole fraction of specie B, T is the temperature, $N = N_A + N_B$ is the total number of atoms, Ω is a positive number and $k_B = 8.617 \times 10^{-5}$eV/K/atom is Boltzmanns constant.

1. Derive an expression for the enthalpy $(H^m(x, T) = H/N)$ and entropy $(S^m(x, T) = S/N)$ of the mixture
2. Express the chemical potential of B in terms of x, Ω, T, k_B

3. Assuming $\Omega = 0.1eV/atom$, plot G^m, H^m and S^m as a function of composition at $T = 400K$ and $T = 800K$ using your favorite plotting program.
4. Analytically, show that the free energy is at an extremum when $x = \frac{1}{2}$ for any positive value of Ω
5. Using the second derivative of the free energy with respect to composition, find the temperature above which the free energy at $x = \frac{1}{2}$ is always a minimum. Notice that above this temperature, the free energy is convex, while below this temperature the free energy will contain concave regions.
6. Sketch the $T - x$ phase diagram of the binary mixture.

QUESTION 3

Titanium forms an hcp phase (α) at room-temperature. At elevated temperatures, titanium transforms into the bcc phase (β) at 1155K. The β phase is found to melt at 1943 K. Calculate the metastable melting point of α. The metastable melting point is the temperature at which α would melt assuming that the β phase is never formed. You can assume that the enthalpies and entropies of the individual phases are insensitive to temperature.

Data
$\Delta S^{\beta \rightarrow \text{liquid}} = 9.6$J/mol-K
$\Delta S^{\alpha \rightarrow \beta} = 3.43$J/mol-K

QUESTION 4

Epitaxially grown thin films are extensively used in solid-state electronic devices. Techniques such as physical vapor deposition, chemical vapor deposition etc. can be used to epitaxially grow thin films on large substrates. The epitaxial growth constrains the lattice parameter of the thin film to be equal to the lattice parameter of the substrate. You can think of the epitaxial growth of thin films as one mechanism of experimentally controlling the strain applied to a material along the x and y directions as indicated below in fig. 2. The thin film is kept within an environment that is at constant temperature (T), pressure (p) and electric field ($\vec{E}$).
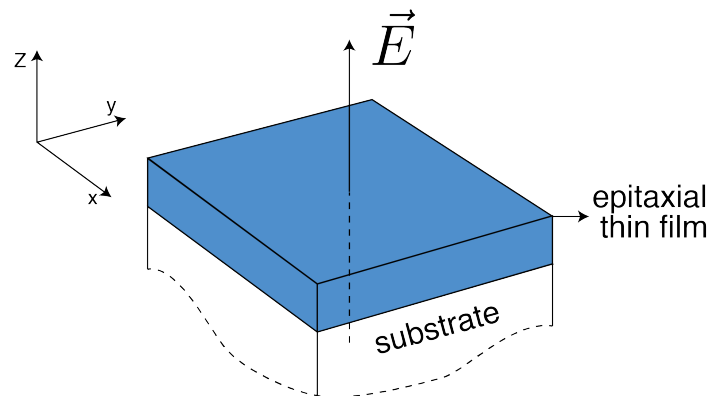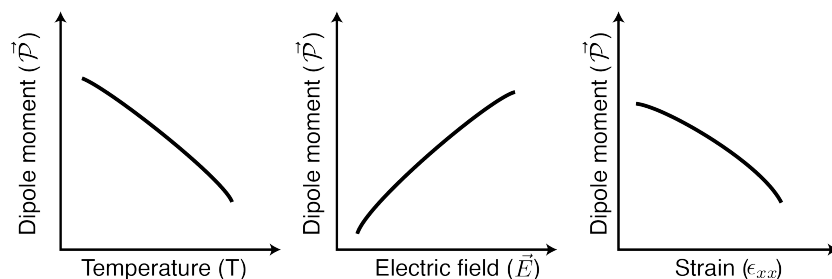

Figure 2

Figure 3

1. What are the thermodynamic state variables of the film that we can experimentally control?
2. Write down an expression for the characteristic potential and equations of state of the film.
3. The thin film is grown such that it is under tensile stress along the x axis. You are worried that as you increase the electric field applied on the film, the internal stress within the film σ_{xx} may increase beyond the critical fracture stress. Based on the measurements shown in fig. 3, should you be worried about the film developing internal cracks?

QUESTION 5

A magnetic material that undergoes a ferromagnetic (α-phase) to paramagnetic (β-phase) phase transition is clamped along the x and y directions as shown in fig. 4. The stress acting on the material (σ_{zz}) is controlled by varying the pressure of the gas surrounding the material.
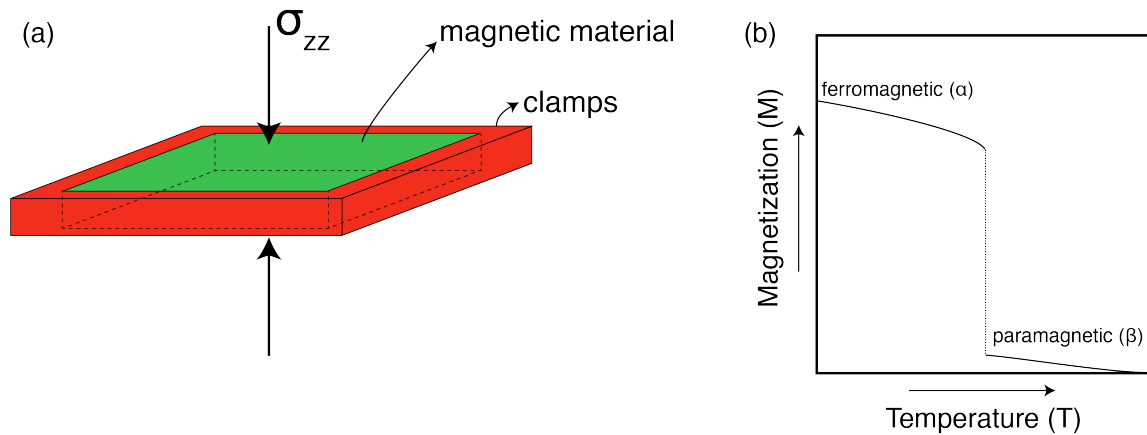

Figure 4

1. Sketch the magnetic field (H) versus temperature (T) phase diagram for this material. Clearly indicate the single-phase and two-phase regions.
2. Experiments on this material reveal that the material expands along the z-direction when it undergoes a phase transition from $\alpha \to \beta$. Draw the stress (σ_{zz}) versus magnetic field (H) phase diagram for this material
3. The paramagnetic (β) phase is enclosed in an *adiabatic* chamber and a magnetic field is applied to it. Would the temperature of the material increase or decrease if the magnetic field applied to the material is reversibly switched off?

QUESTION 6

A colleague has asked you to verify the phase diagram shown in fig. 5. The phase diagram is constructed using a series of experiments where a metal substrate was exposed to a gaseous environment of oxygen at varying oxygen partial pressures and temperatures. Oxygen is found to adsorb on the surface of the metal. At low chemical potentials of oxygen, a *disordered* phase (α) is formed. In the α phase, the oxygen atoms are randomly distributed on the metal's surface. The β phase, formed at higher chemical potentials, is comprised of an ordered arrangement of oxygen atoms. The β phase is known to be very intolerant to any defects - leading to very high energies for any arrangement other than the perfectly ordered state. Could the phase diagram in fig. 5 be correct? Justify your answer with thermodynamic arguments.
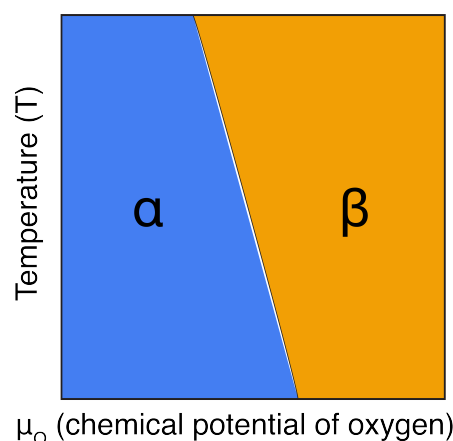

Figure 5