1.   i In Figure 1, the four regions of the phase diagram are identified.
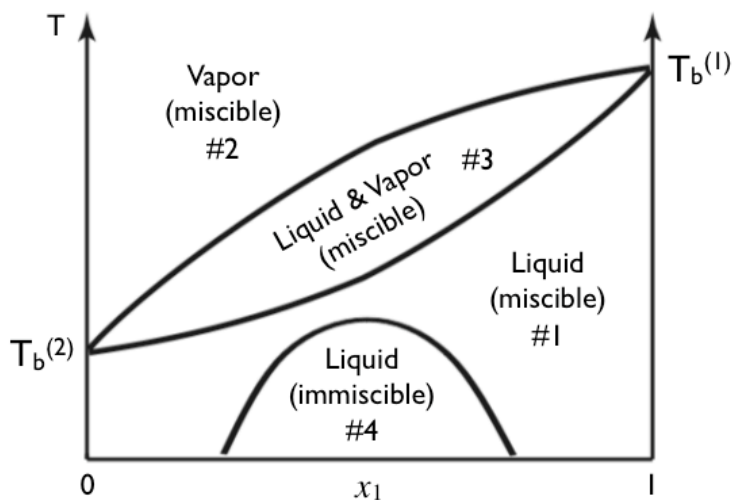

Figure 1: Labeled two-component phase diagram.

   ii Gibbs phase rule gives the number of thermodynamic variables that can be independently
      controlled while preserving coexistence of ν phases of an r-component material: $f = 2 + r - \nu$. We have a two-component material, so $f = 4 - \nu$. Furthermore, we know that
      pressure is fixed, so $f = 3 - \nu$.

      In region #1, we have one phase (liquid), so $f = 3 - 1 = 2$. We can change both tem-
      perature and overall composition (i.e. mole fraction of species 1) independently and still
      maintain coexistence. In region #2, we also have one phase (vapor), so we once again have
      $f = 2$; both temperature and composition can be varied independently. In region #3, we
      have both liquid and vapor phases, so $f = 3 - 2 = 1$. We can vary either temperature
      (moving vertically through the region) or composition (moving horizontally), but not in-
      dependently of each other. If we choose to vary temperature within region #3, the relative
      amounts of the liquid and vapor phases and the amounts of species 1 and species 2 in the
      liquid and vapor phases change in a way that keeps the overall composition (x_1) constant.
      If we choose to vary overall composition by moving along the x-axis, temperature remains
      constant, as well as the amounts of species 1 and species 2 in the vapor and liquid phases.
      However, the relative amounts of the vapor and liquid phases are changing as we change x_1.

      Note: The **composition** of the liquid phase, i.e. the mole fraction of species 1 in the
      liquid phase, is found by drawing a tie line from your location in the two-phase region
      to the right side (the liquid side) of the region. The place along the x-axis where you
      intersect the boundary of the two-phase region gives the x_1 for the liquid phase. The
      composition of the vapor phase is found in a similar way, this time drawing the tie line
      to the left side (the vapor side) of the two-phase region. You can see by looking at the
      diagram that the vapor phase will always be richer in species 2 than the liquid phase is
      for a given temperature; this makes sense because species 2 is more volatile. Also, if you
      want to determine the **relative amounts** of the liquid and vapor phases in the system,
      consider the relative distances from your location in the two-phase region to the left and
      right boundaries. If the tie line to the vapor side is shorter than the tie line to the liquid
      side, you have more vapor than liquid present at that temperature and overall system

composition.

iii On Fig 2., $T_b^{(2)}$ is boiling point of 2, and $T_b^{(1)}$ is the boiling point of 1. Species 2 is more volatile, as it has the lower boiling point.

iv One would capture the more volatile species, species 2 via this distillation.

Starting at some initial composition x_1^*, the mixture is heated to the two-phase region (i.e. to T_1). Then, collect the vapor, which is enriched in the more volatile species 2. (Remember that the composition of the vapor phase is found by drawing a tie line across to the left of the two-phase region; the value of x_1 at point a_1 therefore gives the composition of this vapor.) Condense the vapor you collected so that you once again have a liquid. Heat this liquid to T_2 and collect the vapor. This vapor is even more enriched in species 2 and has a composition corresponding to the point a_2. Condense the vapor. Repeat until you are at the far left of the two-phase region, i.e. at pure species 2.
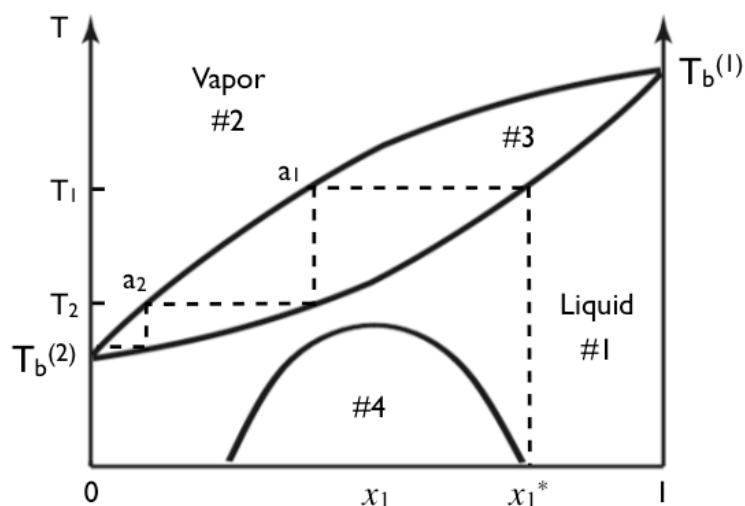

Figure 2: Illustration of distillation process.

v Along the horizontal tie-line, it is evident that T is held constant. Across a horizontal tie-line the composition of the liquid and vapor phases remains the same. The relative proportions of the two phases changes. For example, in Fig. 3, as you move from point A to point B, you begin with an entirely vapor phase with composition χ_A. At point B, you end with an entirely solution phase of composition χ_B. In the middle, there is coexistence with some fraction of vapor phase with composition χ_A, and the corresponding fraction of the liquid phase with composition χ_B. An equation that could describe this is

$$f\chi_A + (1 - f)\chi_B = \chi_1$$

where f is the fraction of material in the vapor phase with composition χ_A.

vi The behavior is analogous to what was described in part v. Instead of a vapor phase with composition χ_A, there is a liquid with composition χ_C (as plotted in Fig. 3), and a different liquid phase with composition χ_D.

2. See solution manual. Remember that at equilibrium, different (usually intensive) properties are equal across both phases, like μ and P.
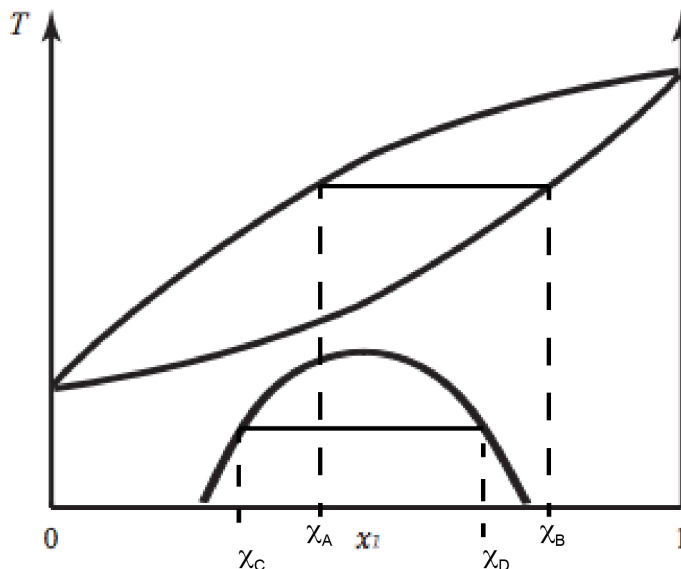
Figure 3: Behavior along horizontal tie-lines.

3. See solution manual. Remember that at equilibrium, different (usually intensive) properties are equal across both phases, like μ and P.

4. i There are two phases of the rubber band, with two different lengths L_1 and L_2. When the force on the band is increased, the length changes according to the equation of state in a particular phase until some force f^*, there is a phase transition to another phase. The behaviour of the rubber band is different in this new phase. This is similar to applying pressure on a system, causing it to transition from a vapour state to a liquid state.

   ii At coexistence, we require the that,

$$A_1 - f^*L = A_2 - f^*L.$$

   Note that the force can also be determined by the derivatives of the Helmholtz free energy.

$$\left(\frac{\partial A_1}{\partial L}\right)_T = f^* = \kappa_1 L_1$$

$$\left(\frac{\partial A_2}{\partial L}\right)_T = f^* = \kappa_2 L_2$$

   Thus, we can substitute for L_1 and L_2 in terms of f^* and κ_i. Solving the resulting equation for f^* yields $\sqrt{2a\Delta\kappa}$.

   iii The isotherm is shown in Fig. 4. It should remind you of the $p-V$ phase diagrams you've seen in class for liquid-vapour transitions. Note that $f = k_1 L_1$ in phase 1 and $f = k_2 L_2$ in phase 2 (obtained by using the fact that $\frac{\partial A}{\partial L} = f$). When $f < f^*$, the rubber band is in phase 1 and thus, has length L_1 but for values of $f > f^*$, we get a transition to phase 2 with length L_2.
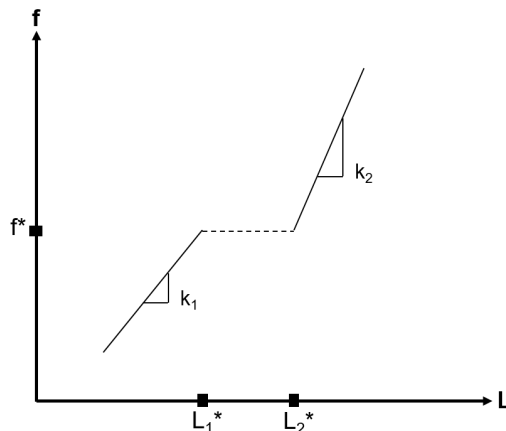
Figure 4: An isotherm in the $f - L$ plane, showing a phase transition.

iv To find the equilibrium partitioning, we need to find the length that minimizes the net free energy. That is, for the free energy,

$$F_i(L) = A_i(L) + \frac{1}{2}kx^2 + a_i,$$

we need,

$$\left(\frac{\partial F_i}{\partial L}\right)_T = 0.$$

Solving this equation, we see that

$$L = \left(\frac{k}{\kappa_i + k}\right)L_{\text{total}}.$$

Thus, when the system transitions from phase 1 to 2, the length also changes discontinuously because the spring constant κ_i changes.

v The function $F_i(L)$ will have a transition at $F_1 = F_2$ i.e., when both phases have the same free energy. Substituting in our equilibrium values of F_1 and F_2 at the transition length L_{tot}^*, we get:

$$\frac{1}{2}(L_{\text{tot}}^*)^2\left(\frac{\kappa_1 k}{\kappa_1 + k}\right) = \frac{1}{2}(L_{\text{tot}}^*)^2\left(\frac{\kappa_2 k}{\kappa_2 + k}\right) + a$$

$$(L_{\text{tot}}^*)^2\left(\frac{\kappa_1}{\frac{\kappa_1}{k} + 1} - \frac{\kappa_2}{\frac{\kappa_2}{k} + 1}\right) = 2a$$

$$(L_{\text{tot}}^*)^2\left(\frac{\kappa_1 - \kappa_2}{\kappa_1 \kappa_2\left(\kappa_1^{-1} + k^{-1}\right)\left(\kappa_2^{-1} + k^{-1}\right)}\right) = 2a$$

A little bit of algebra gets us to:

$$L_{\text{tot}}^* = \sqrt{2a\Delta\kappa(1/k + 1/\kappa_1)(1/k + 1/\kappa_2)}.$$

vi The discontinuous jump is the difference between the equilibrium values of the length at the transition. Using L_{tot}^* from the previous part, we can find values for L_1^* and L_2^*. The difference between these is ΔL.

$$\Delta L = L_2^* - L_1^*$$

$$\Delta L = kL_{tot}^* \left(\frac{1}{\kappa_2 + k} - \frac{1}{\kappa_1 + k} \right)$$

$$\Delta L = kL_{tot}^* \left(\frac{\kappa_1 - \kappa_2}{(\kappa_1 + k)(\kappa_2 + k)} \right)$$

$$\Delta L = \frac{kL_{tot}^*}{\Delta\kappa} \left(\frac{\kappa_1}{\kappa_1 + k} \right) \left(\frac{\kappa_2}{\kappa_2 + k} \right)$$

Substituting in the value of L_{tot}^* found previously we now get,

$$\Delta L = \sqrt{\frac{2a\kappa_1\kappa_2}{(\kappa_1 + k)(\kappa_2 + k)\Delta\kappa}}.$$

vii We can easily obtain the two slopes m_1 and m_2 from the expressions in part (iv).

$$m_1 = \frac{k}{\kappa_1 + k}$$

$$m_2 = \frac{k}{\kappa_2 + k}$$

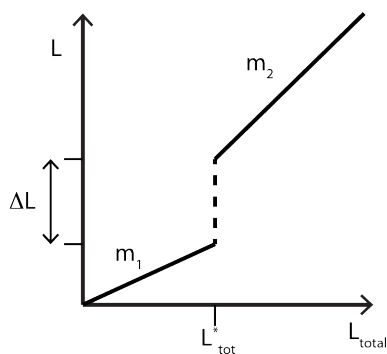viii See Fig. 5.

Figure 5: Partitioning of L as a function of L_{tot}

ix The force on subsystem two is given by $k(L_{\text{total}} - L) = \kappa_i L$, as we know that the force on subsystem 2 should equal the force on the primary subsystem at equilibrium. We know that there will be a discontinuous jump in the force at the jump in L. We can solve for the change in the force constant in terms of the equilibrium length at either side of the jump in L. Note that, at the phase transition

$$L_2^* = \left(\frac{\kappa_1 + k}{\kappa_2 + k} \right) L_1^*.$$

Then, we use a Maxwell construction to compute the slope of the line connecting these two points. That is,

$$\frac{\kappa_2 L_2 - \kappa_1 L_1}{L_2 - L_1} = -k.$$

This is non-monotonic behaviour of the sort normally precluded by stability. However, the values of L in the transition regime are not equilibrium states of the system, so stability guarantees nothing.