

Goosey tutorial 4: Phase separation in multicomponent systems

ICFP M2 – Advanced Biophysics

1 Phase diagram of a symmetrical, incompressible 3-components mixture

To get a sense of the possible phase behaviors of fluids with multiple components, we study the topology of the phase diagram of a system with three fluids with respective volume fractions ϕ_1 , ϕ_2 and ϕ_3 constrained by the condition $\phi_1 + \phi_2 + \phi_3 = 1$. Its free energy density is given by

$$f(\phi_1, \phi_2, \phi_3) = T [\phi_1(\ln \phi_1 - 1) + \phi_2(\ln \phi_2 - 1) + \phi_3(\ln \phi_3 - 1)] + \phi_1\phi_2 + \phi_2\phi_3 + \phi_3\phi_1. \quad (1)$$

We choose this free energy as the simplest, most symmetrical free energy that is the sum of standard entropic terms and quadratic terms. As shown in the following, it nevertheless gives rise to a rather nontrivial phase diagram. Here we wrote f as a function of three variables to emphasize its symmetries, but it can of course also be interpreted as the free energy of a two-component mixture if we replace ϕ_3 with $1 - \phi_1 - \phi_2$.

- 1.1 Observe the plot of the free energy surface corresponding to Eq. (1) in Fig. 1. Sketch a rough phase diagram for each temperature represented. The diagram will show that the system is in a single phase at high temperature. At intermediate temperatures, it will display a coexistence between 2 phases in regions where one of the volume fractions is low. At the lowest temperatures, the concave portion of the free energy surface extends to the region where all three volume fractions are comparable, giving rise to a coexistence between three phases while some 2-phase regions are preserved. In the following we seek to derive a more accurate view of the topology of this phase diagram, and to compute the associated critical temperatures.
- 1.2 consider a line along which the concentration of phase 3 is constant: $\phi_1 = \bar{\phi} + \delta\phi$, $\phi_2 = \bar{\phi} - \delta\phi$, with $\bar{\phi} = (1 - \phi_3)/2$ constant and $\delta\phi \in [-\bar{\phi}/2, \bar{\phi}/2]$. Show that $f(\delta\phi)$ is fully convex at high temperature for all $\bar{\phi}$, then develops a concave region at a critical temperature T_4 which you will determine.
- 1.3 Now consider the line $\phi_1 = \phi_2 = \phi$. Show that $f(\phi)$ is fully convex at high temperature, then develops a concave region at a critical temperature T_3 which you will determine.
- 1.4 Following the appearance of this convex region, $f(\phi)$ develops a secondary minimum. Using the images of Fig. 2, indicate the temperature T_1 at which a single-phase system ceases to be the most stable option at $\phi_1 = \phi_2 = \phi_3$.

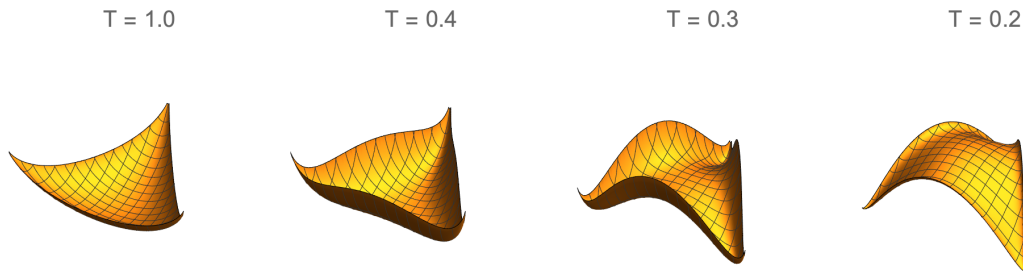


Figure 1: Free energy surface Eq. (1) for four different temperatures. The plotting domain is an equilateral triangle whose vertices correspond to pure phases ($\phi_1 = 1$, $\phi_2 = 1$ and $\phi_3 = 1$, respectively). For each point of the triangle, the concentration of phase i is proportional to the distance between the point and the side opposite to the vertex corresponding to the pure phase i . All points in the triangle have $\phi_1 + \phi_2 + \phi_3 = 1$.

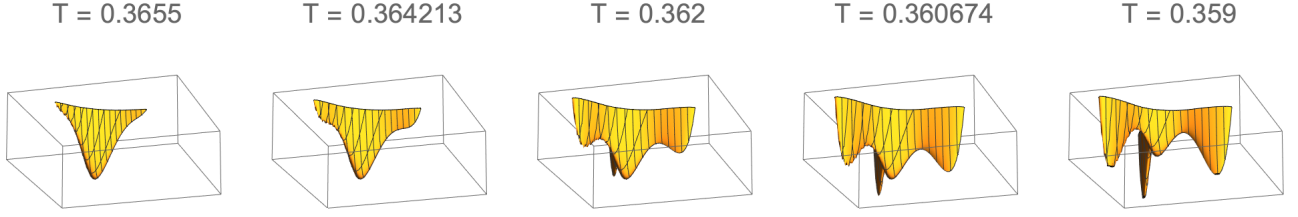


Figure 2: Close-ups of the bottom of the energy surface of Eq. (1).

- 1.5 Using the results from the last questions, order the phase diagram topologies of Fig. 3 and indicate the critical temperatures where you switch from one to the next. To this end you will introduce a new temperature T_2 not discussed above.
- 1.6 Assuming you follow a dilution line $\phi_1/\phi_2 = \text{constant}$, plot the two types of cloud curve/shadow curve couples that you can obtain when the phase diagram has the topology of the rightmost picture of Fig. 3.
- 1.7 What is the equation of the spinodal at any given temperature T ? Conclude just like in a single-component system, the spinodal of a multicomponent system is much easier to find than the various lines required to understand phase coexistence.

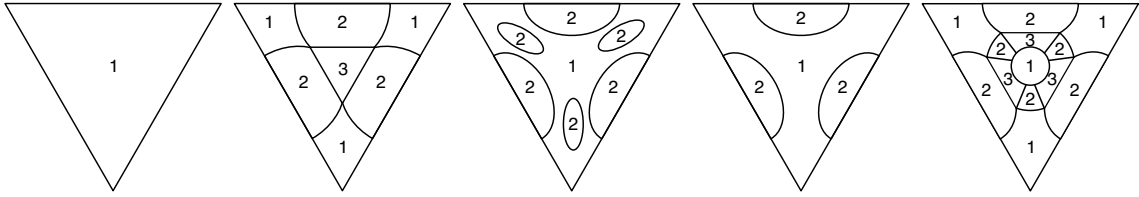


Figure 3: Schematics showing the successive topologies of the phase diagram in the wrong order.

[Optional] Microscopic expression of the surface tension

Here we derive the surface tension between phases in a phase-separated one-component system. We denote the volume fraction of the particles by $\phi \in [0, 1]$ and its free energy density by $f(\phi)$. We assume that f is such that a homogeneous fluids with initial density ϕ phase separates if and only if $\phi \in [\phi_a, \phi_b]$. To lowest order in gradient (just like in a Landau theory), the free energy of an inhomogeneous system reads

$$F = \int \frac{1}{2} [\nabla \phi(\mathbf{r})]^2 + f[\phi(\mathbf{r})] - \mu \phi(\mathbf{r}) \, d\mathbf{r}, \quad (2)$$

where μ is a Lagrange multiplier enforcing the mass conservation condition $\int \phi(\mathbf{r}) \, d\mathbf{r} = \text{constant}$. Here we consider a one-dimensional interface between the two phases of the fluid, meaning that ϕ only depends on the horizontal coordinate x and that $\phi(x) \xrightarrow{x \rightarrow -\infty} \phi_a$ and $\phi(x) \xrightarrow{x \rightarrow +\infty} \phi_b$.

First show that the Euler-Lagrange equation for the volume fraction reads $\Delta \phi + \Pi'(\phi) = 0$, where Π' is the derivative of the osmotic pressure, which you will express as a function of f and μ . Then integrate this equation to show that when the coordinate x changes by a small increment dx , then the change in ϕ is given by

$$dx = \frac{d\phi}{\sqrt{2[\Pi^* - \Pi(\phi)]}}, \quad (3)$$

where you will explain how the coexistence osmotic pressure Π^* can be computed from the function f . Finally show that the surface tension, *i.e.*, the cost of the interface per unit surface, reads

$$\sigma = \int_{\phi_a}^{\phi_b} \sqrt{2[\Pi^* - \Pi(\phi)]} \, d\phi. \quad (4)$$