1. **Phase behavior of associating fluids.**

   (a) Consider a fluid of "patchy particles", i.e., colloidal particles that interact via associative interactions between binding site on their surfaces. The patchy particle model is widely used as a simple description of globular proteins that associate via reversible protein–protein interactions at specific binding sites. Assume that the fluid can be described by the associating polymer model with degree of polymerization $L = 1$ and $f \geq 1$ binding sites per particle. The excess chemical potential is

$$\mu^{\text{ex}} = -k_{\text{B}}T \ln(1 - \phi) + k_{\text{B}}T f \ln X,$$

   where ϕ is the volume fraction occupied by the patchy particles and X is the fraction of binding sites that are unbound. Find an expression for the critical association parameter Δ^* as a function of f.

   (b) Using your result from (a), numerically evaluate the critical association parameter for $f = 3, 4, 5,$ and 6, and comment on the physical basis for the observed trend. Can any of these critical points be considered to reside within the weak association regime?

   (c) Explain why phase separation requires $f > 2$. Does this result depend on the degree of polymerization, L?

   (d) Does the critical point computed in (a) reside at a higher, lower, or equal volume fraction to that of the gel point, ϕ_{gel}, which separates the sol and gel phases? Would the answer change if the degree of polymerization, L, were increased?

2. **Predicting instabilities in multicomponent polymer solutions.** Instabilities occur in multicomponent mixtures when the second derivative matrix of the free energy with respect to the component concentrations, $(\partial\mu_i/\partial\rho_j)_{V,T}$ (i.e., the Hessian matrix), has one or more negative eigenvalues. In this case, a spontaneous concentration fluctuation along an unstable eigenmode $\{\delta\rho_i\}$—which increases the local concentration of some components in one region of the system and decreases their concentrations elsewhere—will cause the free energy to decrease,

$$\sum_{ij} \delta\rho_i \left(\frac{\partial\mu_i}{\partial\rho_j}\right) \delta\rho_j < 0,$$

leading ultimately to demixing. Identifying an instability in an initially well-mixed system is sufficient (but not necessary) to predict that a multicomponent mixture will phase separate.

In what follows, use the multicomponent Flory–Huggins expression for the Hessian matrix,

$$\beta v^{-1}\frac{\partial\mu_i}{\partial\rho_j} = \frac{\delta_{ij}}{v\rho_i} + \frac{L_i L_j}{1-\phi_{\mathrm{T}}} + L_i L_j \epsilon_{ij},$$

to explore the dependence of the unstable region of concentration space, $\{\rho_i\}$, on the pairwise interaction matrix, $\{\epsilon_{ij}\}$, and the degree of polymerization, $\{L_i\}$, of the various molecular species. Consider the following scenarios, and use numerical calculations to predict the typical behavior of a multicomponent mixture with the prescribed interaction and polymer length distributions.

(a) *Length polydispersity.* Consider a 16-component mixture in which $\epsilon_{ij} = \bar{\epsilon}$ for all $i, j = 1, \ldots, 16$. Assume that the degree of polymerization is exponentially distributed with mean $\bar{L}$. Further assume that the parent concentrations are uniform (i.e., equimolar), such that $\rho_i^{(\mathrm{parent})} = \bar{\rho}$ for all $i = 1, \ldots, 16$. By sampling many realizations of this random mixture, investigate how the number of unstable eigenmodes depends on $\bar{\epsilon}$, $\bar{L}$, and $\bar{\rho}$, and discuss your observations. Do you expect that the behavior would change qualitatively if the parent concentrations were not uniform?

(b) *Gaussian interactions.* Consider a 16-component mixture in which $L_i = 1$ for all $i = 1, \ldots, 16$. Assume that the elements of the symmetric $\{\epsilon_{ij}\}$ matrix are Gaussian distributed with mean $b = -5$ and variance σ^2. Further assume that the parent concentrations are uniform, such that $\rho_i^{(\mathrm{parent})} = \bar{\rho}$ for all $i = 1, \ldots, 16$. Investigate how (i) the number of unstable eigenmodes and (ii) the cosine similarity between the most unstable eigenmode and the parent concentration vector $(\bar{\rho}, \bar{\rho}, \ldots, \bar{\rho})$ depend on σ^2 and $\bar{\rho}$. Discuss the influence of these two parameters on the stability of the mixture.

(c) *Nonuniform parent concentrations.* Repeat your investigation from (b), but assume a nonuniform parent concentration in which the majority of the total macromolecular volume fraction, ϕ_{T}, is concentrated in a single component $i = 1$. Do your conclusions from (b) change qualitatively? Consider the relationship between the parent concentration vector and the most unstable eigenmode in your answer.