[pex52] Phase separation in polymer blend

Consider a polymer blend composed of two kinds of monodisperse polymers with degrees of polymerization N_A and N_B, respectively. Under the assumption that the volume of monomers of either kind are of very similar size we can adapt the mean-field lattice model used in [pex47] to this case. The free-energy density then reads

$$f(T,\phi,N_A,N_B) = \frac{k_BT}{v_c}\left[\frac{1}{N_A}\phi\ln\phi + \frac{1}{N_B}(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right], \quad \chi = -\frac{z\Delta\epsilon}{2k_BT} > 0,$$

where ϕ is the volume fraction of the type-A polymer and $1-\phi$ the volume fraction of the type-B polymer. All monomers have volume v_c, the coordination number of the model lattice is z, and $\Delta\epsilon$ is a measure of the (attractive) interaction between type-A and type-B polymers.
(a) Derive the critical-point coordinates in the phase diagram: $\phi_c(N_A,N_B)$, $\chi_c(N_A,N_B)$ from the function $f(T,\phi,N_A,N_B)$.
(b) Show that the spinodal line in the phase diagram, the locations of inflection points in the free-energy-density, has the following dependence on ϕ for any given N_A, N_B:

$$\chi_{sp}(\phi,N_A,N_B) = \frac{1}{2}\left[\frac{1}{N_A\phi} + \frac{1}{N_B(1-\phi)}\right].$$

Plot $\chi_{sp}(\phi,50,20)$ with the vertical scale ranging from zero to 0.3 and the horizontal scale ranging from zero to one. Identify the location of the critical point on that line.
(c) Derive the coexistence line $\chi_{co}(\phi,N_A,N_B)$ for the special case $N_A = N_B \doteq N$. Plot $\chi_{sp}(\phi,50,50)$ and $\chi_{co}(\phi,50,50)$ versus ϕ in the same diagram with the vertical scale ranging from zero to 0.3 and the horizontal scale ranging from zero to one.

Solution: