[pex58] Interface width in phase-separated polymer blend

Consider a blend of two homopolymers with large and roughly equal degrees of polymerization N and roughly equal monomeric length a. The phase separation is driven by an unfavorable (meaning more repulsive or less attractive) interaction energy between unlike polymers, characterized by a dimensionlss interaction constant χ (see [pln48]). A sharp interface would minimize that interaction energy, producing an enthalpic gain ($\Delta H < 0$) but at too high an entropic cost ($\Delta S < 0$). A compromise minimizes the free energy $G = H - TS$. An interface of width w has loops of contour length $N_\mathrm{L} a$ from one species of polymer protruding into the space occupied by polymers from the other species. If the conformation can be assumed to take on the shape of a random walk we have

$$\frac{w}{a} \sim \sqrt{N_\mathrm{L}}. \tag{1}$$

It is reasonable to assume that at thermal equilibrium the (positive) interaction energy of a protruding loop is of the order of $k_\mathrm{B}T$.

(a) Show that the estimated width w of the interface then depends on the interaction constant χ as follows:

$$\frac{w}{a} \sim \frac{1}{\chi}. \tag{2}$$

(b) The interfacial energy density γ (interfacial energy per unit area) of the phase boundary can now be estimated from these ingredients. An additional assumption is that monomers are compact, implying that their cross section has area a^2. Show that the estimate is

$$\gamma \sim \frac{k_\mathrm{B}T}{a^2}\sqrt{\chi}. \tag{3}$$

[adaptd from Jones 2002]

Solution: