

3.942 (Polymer Physics) Problem Sets

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1 The Macromolecule

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Total grade: 100/100

- 9/18: 1. (25 pts) Consider the following distribution of polymer chains with repeat unit molecular weight M_0 :

10 chains with degree of polymerization 100;
 100 chains with degree of polymerization 1000;
 10 chains with degree of polymerization 10 000.

- a) Calculate the number average molecular weight of this distribution.

Answer.

$$\begin{aligned} M_n &= M_0 \cdot \frac{\sum_i i n_i}{\sum_i n_i} \\ &= M_0 \cdot \frac{100 \cdot 10 + 1000 \cdot 100 + 10000 \cdot 10}{10 + 100 + 10} \end{aligned}$$

$M_n = 1675M_0$

□

- b) Calculate the weight average molecular weight of this distribution.

Answer.

$$\begin{aligned} M_w &= M_0 \cdot \frac{\sum_i i^2 n_i}{\sum_i i n_i} \\ &= M_0 \cdot \frac{100^2 \cdot 10 + 1000^2 \cdot 100 + 10000^2 \cdot 10}{100 \cdot 10 + 1000 \cdot 100 + 10000 \cdot 10} \end{aligned}$$

$M_w \approx 5473M_0$

□

- c) What is the polydispersity index of this distribution?

Answer.

$$\begin{aligned} D &= \frac{M_w}{M_n} \\ &\approx \frac{5473M_0}{1675M_0} \end{aligned}$$

$D \approx 3.27$

□

- d) If you randomly chose a monomer in the solution, what is the chance that it belongs to a chain with degree of polymerization 10 000?

Answer. This probability would be equal to the sum of the number of monomers in chains with $N = 10 000$ divided by the total number of monomers in solution. But this is just the weight fraction of a 10 000-mer! Symbolically, we have

$$\frac{10000 \cdot n_{10000}}{\sum_i i n_i} = w_{10000} = \frac{10000 \cdot 10}{100 \cdot 10 + 1000 \cdot 100 + 10000 \cdot 10} = \boxed{49.8\%}$$

□

2. (25 pts) The root mean squared end-to-end distance $\langle R^2 \rangle^{1/2}$ of a poly(methyl methacrylate) (PMMA) molecule (MW = 10^7 g/mol) in tetrahydrofuran (THF) at its Theta temperature was found to be 200 nm.

- a) What is the degree of polymerization for this polymer?

Answer. The molar mass of a methyl methacrylate (MMA) monomer is $M = 100.12$ g/mol. Thus,

$$N = \frac{\text{MW}}{M}$$

$N \approx 99880$

□

- b) Estimate C_∞ for this polymer.

Answer. Since each MMA monomer introduces 2 C–C bonds to the polymer chain, the number n of C–C bonds in the polymer is

$$n = 2N \approx 199760$$

Additionally, the length l of a typical C–C bond is 0.154 nm. Thus, from the symmetric hindered rotations model, the characteristic ratio C_∞ is

$$\begin{aligned} C_\infty &= \frac{\langle R^2 \rangle}{nl^2} \\ &= \frac{(200)^2}{(199760)(0.154)^2} \\ &\boxed{C_\infty \approx 8.44} \end{aligned}$$

□

- c) Estimate the Kuhn length and number of Kuhn segments for this polymer.

Answer. For a polyolefin like PMMA, the straight-chain length R_{\max} is given by

$$R_{\max} = nl \cos(70.5/2) = (199760)(0.154 \text{ nm}) \cos(70.5/2) \approx 25122 \text{ nm}$$

Thus, the Kuhn length l_k is

$$\begin{aligned} l_k &= \frac{\langle R^2 \rangle}{R_{\max}} \\ &= \frac{(200)^2}{25122} \\ &\boxed{l_k \approx 1.59 \text{ nm}} \end{aligned}$$

It follows that the number N_k of Kuhn steps is

$$\begin{aligned} N_k &= \frac{R_{\max}}{l_k} \\ &= \frac{25122}{1.59} \\ &\boxed{N_k \approx 15800} \end{aligned}$$

□

- d) Estimate the persistence length for this polymer.

Answer. Since the Kuhn length is twice the persistence length a ,

$$\begin{aligned} a &= \frac{l_k}{2} \\ &= \frac{1.59}{2} \\ a &\approx 0.795 \text{ nm} \end{aligned}$$

□

- e) Is this PMMA a “flexible,” “semi-flexible,” or “rod-like” polymer?

Answer. Since the chain length is $R_{\max} = 25\,122 \text{ nm}$ and the persistence length is $a = 0.795 \text{ nm}$, the chain length is clearly much greater than the persistence length (indeed, by nearly five orders of magnitude). Therefore, PMMA is a flexible polymer. □

3. (25 pts) Consider a linear copolymer with N_A steps of Kuhn length ℓ_A and N_B steps of Kuhn length ℓ_B . The solvent is such that excluded volume effects are negligible (theta solvent).

- a) Calculate the mean squared end-to-end distance $\langle R^2 \rangle$ of the chain for a linear diblock architecture (all A monomers connected to all B monomers).

Answer. By the definition of $\langle R^2 \rangle$ for a freely jointed chain — regardless of whether or not all steps are the same length — we have

$$\begin{aligned} \langle R^2 \rangle &= \left\langle \sum_{i=1}^{N_A+N_B} \mathbf{l}_i \cdot \sum_{j=1}^{N_A+N_B} \mathbf{l}_j \right\rangle \\ &= \sum_{i=1}^{N_A+N_B} \sum_{j=1}^{N_A+N_B} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= \sum_{i=1}^{N_A+N_B} \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle + \underbrace{\sum_{i=1}^{N_A+N_B} \sum_{\substack{j=1 \\ j \neq i}}^{N_A+N_B} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle}_0 \\ &= \sum_{i=1}^{N_A} \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle + \sum_{i=N_A+1}^{N_A+N_B} \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle \\ \langle R^2 \rangle &= N_A \ell_A^2 + N_B \ell_B^2 \end{aligned}$$

Note that the underbracketed term still goes to zero because for each expected dot product of uncorrelated vectors, regardless of whether the vectors are the same length or different, every possible orientation of \mathbf{l}_i and \mathbf{l}_j (and hence their dot product) is in one-to-one correspondence with an equally probable opposing orientation. □

- b) Will your answer in (a) change if the chain has a random distribution of monomers A and B? Explain why or why not.

Answer. As long as the polymer can still be described by the Kuhn steps laid out in the original problem statement, the commutativity principle postulates that it does not matter in which order we add up the dot products. Thus, the answer in (a) will not change. However, if the new bonding changes the Kuhn steps and length, then we may well obtain a different answer. □

4. (25 pts) Consider a linear polymer with N Kuhn steps of length ℓ_k restricted to a two-dimensional interface (e.g. air/water interface). The Flory free energy terms for chain extension and excluded volume are

$$\frac{F}{k_B T} = \frac{1}{2} \frac{aN^2}{R^2} + \frac{R^2}{N\ell_k^2}$$

where a is the effective excluded area per monomer (analogue to excluded volume in 3D). The first term on the right-hand side is related to excluded volume and the second term related to stretching.

- a) Calculate the scaling for R .

Answer. The polymer will be at its optimal size when there is no force either pushing it apart or pulling it together any more. This condition of zero force is equivalent to the change in free energy with respect to distance being equal to zero, or $\partial F / \partial R = 0$. But this condition implies that

$$\begin{aligned} 0 &= \frac{\partial F}{\partial R} \\ &= k_B T \left(-\frac{aN^2}{R^3} + \frac{2R}{N\ell_k^2} \right) \\ \frac{aN^2}{R^3} &= \frac{2R}{N\ell_k^2} \\ \frac{aN^3\ell_k^2}{2} &= R^4 \\ R &\approx a^{1/4} N^{3/4} \ell_k^{1/2} \end{aligned}$$

□

5. (25 pts) Consider monomers which interact via the following pairwise interaction potential, which is called a square well interaction:

$$\begin{aligned} U &= \infty && (r < b) \\ U &= -\varepsilon && (b \leq r \leq \lambda b) \\ U &= 0 && (r > \lambda b) \end{aligned}$$

- a) Calculate the excluded volume B .

Answer. The excluded volume B is given by

$$\begin{aligned} B &= -4\pi \int_0^\infty r^2 \left[\exp\left(-\frac{U(r)}{k_B T}\right) - 1 \right] dr \\ &= -4\pi \left\{ \int_0^b r^2 [-1] dr + \int_b^{\lambda b} r^2 \left[\exp\left(\frac{\varepsilon}{k_B T}\right) - 1 \right] dr + \int_{\lambda b}^\infty r^2 [0] dr \right\} \\ &= -4\pi \left\{ - \int_0^b r^2 dr + \left[\exp\left(\frac{\varepsilon}{k_B T}\right) - 1 \right] \int_b^{\lambda b} r^2 dr + 0 \right\} \\ &= -4\pi \left\{ -\frac{b^3}{3} + \left[\exp\left(\frac{\varepsilon}{k_B T}\right) - 1 \right] \cdot \frac{b^3}{3} (\lambda^3 - 1) \right\} \\ &= \frac{4}{3}\pi b^3 \left\{ 1 - \left[\lambda^3 \cdot \exp\left(\frac{\varepsilon}{k_B T}\right) - \exp\left(\frac{\varepsilon}{k_B T}\right) - \lambda^3 + 1 \right] \right\} \\ &= \frac{4}{3}\pi b^3 \left[-\lambda^3 \cdot \exp\left(\frac{\varepsilon}{k_B T}\right) + \exp\left(\frac{\varepsilon}{k_B T}\right) + \lambda^3 \right] \\ B &= \frac{4}{3}\pi b^3 \left[(1 - \lambda^3) \exp\left(\frac{\varepsilon}{k_B T}\right) + \lambda^3 \right] \end{aligned}$$

□

- b) Simplify your expression for B by assuming $\varepsilon/k_B T \ll 1$. Hint: Expand the exponential.

Answer. The Taylor series expansion for e^x is

$$e^x = 1 + x + \frac{x^2}{2!} + \cdots + \frac{x^n}{n!} + \cdots$$

Given that $x = \varepsilon/k_B T$ is very small, it is then clear that the higher-order terms in the Taylor series become negligible very quickly. Thus, it is not a bad approximation to say that $e^x \approx 1 + x$ for small x . Applying this line of reasoning to the result from part (a) and simplifying then yields

$$\begin{aligned} B &= \frac{4}{3}\pi b^3 \left[(1 - \lambda^3) \left(1 + \frac{\varepsilon}{k_B T} \right) + \lambda^3 \right] \\ &= \frac{4}{3}\pi b^3 \left[\left(1 + \frac{\varepsilon}{k_B T} - \lambda^3 - \lambda^3 \cdot \frac{\varepsilon}{k_B T} \right) + \lambda^3 \right] \\ &= \frac{4}{3}\pi b^3 \left[1 + \frac{\varepsilon}{k_B T} - \lambda^3 \cdot \frac{\varepsilon}{k_B T} \right] \\ \boxed{B = \frac{4}{3}\pi b^3 \left[1 + (1 - \lambda^3) \frac{\varepsilon}{k_B T} \right]} \end{aligned}$$

□

- c) Using your answer in (b), determine the Theta temperature for this system.

Answer. The theta temperature for a system is the one at which excluded volume effects are negligible, i.e., $B = 0$. Using this constraint and solving the result from part (b) for T yields

$$\begin{aligned} 0 &= \frac{4}{3}\pi b^3 \left[1 + (1 - \lambda^3) \frac{\varepsilon}{k_B T} \right] \\ -1 &= (1 - \lambda^3) \frac{\varepsilon}{k_B T} \\ \boxed{T = \frac{\varepsilon}{k_B} (\lambda^3 - 1)} \end{aligned}$$

□

2 Solution Thermodynamics

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- 9/30: 1. a) Calculate a general expression for chemical potential $\mu - \mu_0$ for species 1 from the Flory-Huggins free energy of mixing that we have seen in class.

Answer. The Flory-Huggins expression for the free energy of mixing is

$$\frac{\Delta G_M}{X_0} = k_B T \left(\chi \phi_1 \phi_2 + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right)$$

Using the identities

$$\phi_i = \frac{X_i}{X_0} \quad X_i = n_i N_A N_i \quad (i = 1, 2)$$

we can rewrite the original expression as

$$\Delta G_M = RT(N_1 \chi \phi_2 n_1 + n_1 \ln \phi_1 + n_2 \ln \phi_2)$$

Since the chemical potential requires us to take a derivative with respect to the number n_1 of moles of species 1, let's also investigate two helpful derivatives.

$$\begin{aligned} \frac{\partial \phi_1}{\partial n_1} &= \frac{\partial}{\partial n_1} \left(\frac{n_1 N_1}{n_1 N_1 + n_2 N_2} \right) & \frac{\partial \phi_2}{\partial n_1} &= \frac{\partial}{\partial n_1} \left(\frac{n_2 N_2}{n_1 N_1 + n_2 N_2} \right) \\ &= \frac{(n_1 N_1 + n_2 N_2) \cdot N_1 - n_1 N_1 \cdot N_1}{(n_1 N_1 + n_2 N_2)^2} & &= \frac{(n_1 N_1 + n_2 N_2) \cdot 0 - n_2 N_2 \cdot N_1}{(n_1 N_1 + n_2 N_2)^2} \\ &= \frac{n_2 N_2 N_1}{(n_1 N_1 + n_2 N_2)^2} & &= -\frac{n_2 N_2 N_1}{(n_1 N_1 + n_2 N_2)^2} \\ &= \frac{\phi_2 N_1}{n_1 N_1 + n_2 N_2} & &= -\frac{\phi_2 N_1}{n_1 N_1 + n_2 N_2} \\ &= \frac{\phi_2 \phi_1}{n_1} & &= -\frac{\phi_2 \phi_1}{n_1} \end{aligned}$$

It follows that

$$\begin{aligned} \mu_1 - \mu_1^\circ &= \left(\frac{\partial \Delta G_M}{\partial n_1} \right)_{T, P, n_2} \\ &= RT \left[N_1 \chi (\phi'_2 \cdot n_1 + \phi_2 \cdot 1) + \left(1 \cdot \ln \phi_1 + n_1 \cdot \frac{\phi'_1}{\phi_1} \right) + n_2 \cdot \frac{\phi'_2}{\phi_2} \right] \\ &= RT \left[N_1 \chi (\phi_2 - \phi_1 \phi_2) + (\ln \phi_1 + \phi_2) - \frac{\phi_1 n_2}{n_1} \right] \\ &= RT \left[N_1 \chi \phi_2 (1 - \phi_1) + (\ln \phi_1 + \phi_2) - \frac{N_1 \phi_2}{N_2} \right] \\ &= RT \left[N_1 \chi \phi_2^2 + \ln \phi_1 + \left(1 - \frac{N_1}{N_2} \right) \phi_2 \right] \\ \boxed{\mu_1 - \mu_1^\circ = RT \left[\ln \phi_1 + \left(1 - \frac{N_1}{N_2} \right) \phi_2 + N_1 \chi \phi_2^2 \right]} \end{aligned}$$

Note that we need μ_1° as a reference because we are taking the partial derivative of the *change* in free energy, as opposed to the partial derivative of free energy *alone* (as in the definition of the chemical potential). \square

- b) Calculate a general expression for χ that satisfies the spinodal criterion of a polymer blend from Flory-Huggins theory. Remember that the spinodal satisfies the expression

$$\frac{\partial^2 \Delta G_M}{\partial \phi_1^2} = 0$$

where ϕ_1 is the volume fraction of one of the species.

Answer. The equation

$$\begin{aligned}\frac{\Delta G_M}{X_0} &= k_B T \left(\chi \phi_1 \phi_2 + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right) \\ \Delta G_M &= X_0 k_B T \left[\chi \phi_1 - \chi \phi_1^2 + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{1 - \phi_1}{N_2} \ln(1 - \phi_1) \right]\end{aligned}$$

can be viewed as generating a family of ΔG_M vs. ϕ_1 curves in 2D space, indexed by the variable χ . To find the set of points in each curve that satisfy the spinodal criterion, we may directly evaluate said criterion and then solve for χ as a function of ϕ_1 . Let's begin.

We have that

$$\begin{aligned}\frac{\partial \Delta G_M}{\partial \phi_1} &= X_0 k_B T \left\{ \frac{\partial}{\partial \phi_1} [\chi \phi_1] - \frac{\partial}{\partial \phi_1} [\chi \phi_1^2] + \frac{1}{N_1} \frac{\partial}{\partial \phi_1} [\phi_1 \ln \phi_1] + \frac{1}{N_2} \frac{\partial}{\partial \phi_1} [(1 - \phi_1) \ln(1 - \phi_1)] \right\} \\ &= X_0 k_B T \left\{ \chi - 2\chi \phi_1 + \frac{1}{N_1} \left[1 \cdot \ln \phi_1 + \phi_1 \cdot \frac{1}{\phi_1} \right] + \frac{1}{N_2} \left[-1 \cdot \ln(1 - \phi_1) + (1 - \phi_1) \cdot \frac{-1}{1 - \phi_1} \right] \right\} \\ &= X_0 k_B T \left[\chi - 2\chi \phi_1 + \frac{1 + \ln \phi_1}{N_1} - \frac{1 + \ln(1 - \phi_1)}{N_2} \right] \\ &= \frac{X_0 k_B T}{N_1 N_2} [(N_1 N_2 \chi + N_2 - N_1) - 2N_1 N_2 \chi \phi_1 + N_2 \ln \phi_1 - N_1 \ln(1 - \phi_1)]\end{aligned}$$

It follows that

$$\frac{\partial^2 \Delta G_M}{\partial \phi_1^2} = \frac{X_0 k_B T}{N_1 N_2} \left[-2N_1 N_2 \chi + \frac{N_2}{\phi_1} + \frac{N_1}{1 - \phi_1} \right]$$

Therefore, the desired general expression is

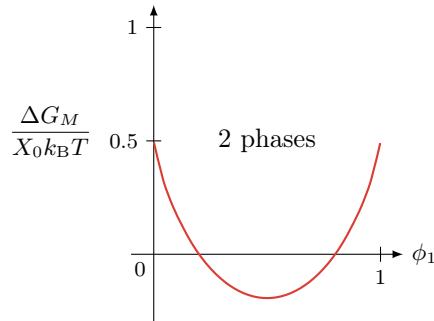
$$\begin{aligned}0 &= -2N_1 N_2 \chi + \frac{N_2}{\phi_1} + \frac{N_1}{1 - \phi_1} \\ \boxed{\chi} &= \frac{1}{2N_1 \phi_1} + \frac{1}{2N_2 (1 - \phi_1)}\end{aligned}$$

□

- c) From your expression for χ above, plot the spinodal line as a function of ϕ_1 for the following cases. Please plot all 4 cases separately, and label which region corresponds to 2 phases (only label the 2 phase/phase-separated region; note that from the spinodal alone you cannot with certainty label a homogeneous/1 phase region). MIT has free student site licenses for Excel, Matlab, and Mathematica that you can use for plotting.

i) $N_1 = N_2 = 1$.

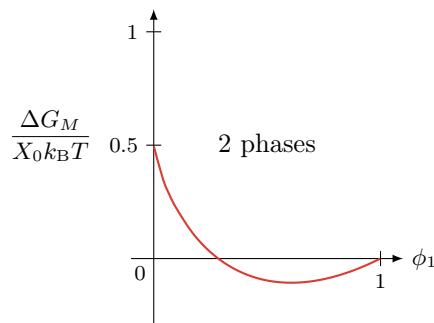
Answer.



□

ii) $N_1 = 1$ and $N_2 = 1000$.

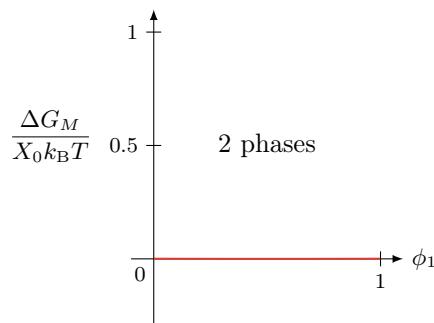
Answer.



□

iii) $N_1 = N_2 = 1000$.

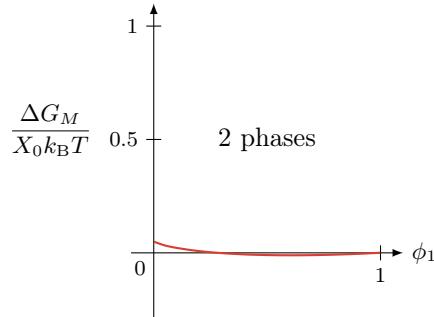
Answer.



□

iv) $N_1 = 10$ and $N_2 = 1000$.

Answer.



□

- d) Please qualitatively explain the differences in the curves for the cases in part (c).

Answer. For case (i), we have the “typical” solution case where relatively strong interspecies attraction will guarantee mixing, but relatively weak interspecies attraction (and/or strong intraspecies attraction) will result in demixing regimes if a sufficient amount of both components are present.

This mostly holds true in case (ii) as well, except that demixing is much more likely the more species 1 we have. Indeed, mixing is only possible if we either have very strong interspecies attractions or very little of 1.

In case (iii), mixing is almost entirely enthalpically controlled. This is because there is a very small increase in entropy when we mix polymer chains that are mostly covalently bonded together (i.e., highly ordered). Thus, whether we form 1 phase or two will really only depend on how much the polymers like each other vs. themselves.

And case (iv) is somewhere in between cases (ii) and (iii). In particular, more ϕ_1 will still make mixing more difficult, and yet whether or not we get mixing is pretty much just down to enthalpy. □

- e) From part (b), continue to derive the table for the critical composition and critical interaction parameter shown in class. In other words, find the critical χ parameter and corresponding volume fraction for the general case, and evaluate it for two low-molecular weight liquids, a solvent-polymer blend, and a symmetric polymer-polymer blend. Show your work.

Answer. Among the family of curves discussed in part (b), the critical interaction parameter χ_c occurs on the curve that switches from being always concave up (for small or negative χ) to having concave and convex regions (for large or positive χ). While curves with lower χ than this one have no inflection points and curves with greater χ than this one have two inflection points, this curve will have just *one* inflection point. But if it has only one inflection point, this means that $\partial^2 \Delta G_M / \partial \phi_1^2$ must have only one root.

When $\partial^2 \Delta G_M / \partial \phi_1^2$ has two roots, the tangent line at each of them has nonzero slope. However, when $\partial^2 \Delta G_M / \partial \phi_1^2$ has only one root, the tangent line has *zero* slope (the original curve is concave up, then just barely neither concave up nor down, then concave up again). Therefore, among all $(\phi_1, \Delta G_M)$ satisfying the spinodal criterion for various χ , $\phi_{1,c}$ satisfies

$$0 = \frac{\partial}{\partial \phi_1} \left(\frac{\partial^2 \Delta G_M}{\partial \phi_1^2} \right) \Big|_{\phi_1=\phi_{1,c}} = \frac{\partial^3 \Delta G_M}{\partial \phi_1^3} \Big|_{\phi_1=\phi_{1,c}}$$

Continuing from part (b), we have that

$$\frac{\partial^3 \Delta G_M}{\partial \phi_1^3} = \frac{X_0 k_B T}{N_1 N_2} [-N_2 \phi_1^{-2} + N_1 (1 - \phi_1)^{-2}]$$

Thus,

$$\begin{aligned}
 0 &= -N_2\phi_{1,c}^{-2} + N_1(1 - \phi_{1,c})^{-2} \\
 N_2(1 - \phi_{1,c})^2 &= N_1\phi_{1,c}^2 \\
 N_2 - 2N_2\phi_{1,c} + (N_2 - N_1)\phi_{1,c}^2 &= 0 \\
 \phi_{1,c} &= \frac{2N_2 \pm \sqrt{4N_2^2 - 4(N_2 - N_1)N_2}}{2(N_2 - N_1)} \\
 &= \frac{N_2 \pm \sqrt{N_1 N_2}}{N_2 - N_1}
 \end{aligned}$$

Suppose for the sake of contradiction that $\phi_{1,c} = (N_2 + \sqrt{N_1 N_2})/(N_2 - N_1)$. Then since — by definition — $\phi_{1,c} \leq 1$ for all $\{N_1, N_2 \in \mathbb{N} \mid N_1 \leq N_2\}$, we have that

$$\begin{aligned}
 \frac{N_2 + \sqrt{N_1 N_2}}{N_2 - N_1} &\leq 1 \\
 N_2 + \sqrt{N_1 N_2} &\leq N_2 - N_1 \\
 \sqrt{N_1 N_2} &\leq -N_1 < 0
 \end{aligned}$$

But the square root of a natural number cannot be less than zero, a contradiction. Therefore,

$$\phi_{1,c} = \frac{N_2 - \sqrt{N_1 N_2}}{N_2 - N_1}$$

Simplifying the above expression yields

$$\begin{aligned}
 \phi_{1,c} &= \frac{N_2 - \sqrt{N_1 N_2}}{N_2 - N_1} \\
 &= \frac{\sqrt{N_2}(\sqrt{N_2} - \sqrt{N_1})}{(\sqrt{N_2} + \sqrt{N_1})(\sqrt{N_2} - \sqrt{N_1})} \\
 \boxed{\phi_{1,c} = \frac{\sqrt{N_2}}{\sqrt{N_1} + \sqrt{N_2}}}
 \end{aligned}$$

as desired.

Given the critical composition, we can plug into the result from part (b) to find the critical interaction parameter χ_c , as follows.

$$\begin{aligned}
 \chi_c &= \frac{1}{2N_1\phi_{1,c}} + \frac{1}{2N_2(1 - \phi_{1,c})} \\
 &= \frac{1}{2} \left[\frac{\sqrt{N_1} + \sqrt{N_2}}{N_1\sqrt{N_2}} + \frac{1}{N_2 \left(1 - \frac{\sqrt{N_2}}{\sqrt{N_1} + \sqrt{N_2}} \right)} \right] \\
 &= \frac{1}{2} \left[\frac{\sqrt{N_1} + \sqrt{N_2}}{N_1\sqrt{N_2}} + \frac{\sqrt{N_1} + \sqrt{N_2}}{N_2\sqrt{N_1}} \right] \\
 &= \frac{1}{2} \left[\frac{\sqrt{N_2}(\sqrt{N_1} + \sqrt{N_2}) + \sqrt{N_1}(\sqrt{N_1} + \sqrt{N_2})}{N_1 N_2} \right] \\
 &= \frac{1}{2} \left[\frac{(\sqrt{N_1} + \sqrt{N_2})^2}{(\sqrt{N_1 N_2})^2} \right] \\
 \boxed{\chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}} \right)^2}
 \end{aligned}$$

To confirm that $(\phi_{1,c}, \chi_c)$ satisfies the spinodal criterion, we can see that

$$\begin{aligned} \left. \frac{\partial^2 \Delta G_M}{\partial \phi_1^2} \right|_{(\phi_{1,c}, \chi_c)} &\propto -2N_1 N_2 \chi_c + \frac{N_2}{\phi_{1,c}} + \frac{N_1}{1 - \phi_{1,c}} \\ &= -N_1 N_2 \left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}} \right)^2 + \frac{N_2(\sqrt{N_1} + \sqrt{N_2})}{\sqrt{N_2}} + \frac{N_1(\sqrt{N_1} + \sqrt{N_2})}{\sqrt{N_1}} \\ &= -\left(\sqrt{N_1} + \sqrt{N_2} \right)^2 + \left(\sqrt{N_1} + \sqrt{N_2} \right)^2 \\ &= 0 \end{aligned}$$

as expected.

We now use the two expressions derived above fill out the table shown in class. Evaluating the case of two low molecular weight liquids (i.e., $N_1 = N_2 = 1$), we obtain

$$\begin{aligned} \phi_{1,c} &= \frac{\sqrt{1}}{\sqrt{1} + \sqrt{1}} & \chi_c &= \frac{1}{2} \left(\frac{1}{\sqrt{1}} + \frac{1}{\sqrt{1}} \right)^2 \\ \boxed{\phi_{1,c}(N_1 = N_2 = 1) = 0.5} & & \boxed{\chi_c(N_1 = N_2 = 1) = 2} & \end{aligned}$$

Evaluating the case of a solvent-polymer blend (i.e., $N_1 = 1 < N_2$), we obtain

$$\begin{aligned} \phi_{1,c} &= \frac{\sqrt{N_2}}{\sqrt{1} + \sqrt{N_2}} & \chi_c &= \frac{1}{2} \left(\frac{1}{\sqrt{1}} + \frac{1}{\sqrt{N_2}} \right)^2 \\ \boxed{\phi_{1,c}(N_1 = 1 < N_2) = \frac{\sqrt{N_2}}{1 + \sqrt{N_2}}} & & \boxed{\chi_c(N_1 = 1 < N_2) = \frac{1}{2} \left(1 + \frac{1}{\sqrt{N_2}} \right)^2} & \end{aligned}$$

Evaluating the case of a symmetric polymer-polymer blend (i.e., $N_1 = N_2 = N$), we obtain

$$\begin{aligned} \phi_{1,c} &= \frac{\sqrt{N}}{\sqrt{N} + \sqrt{N}} & \chi_c &= \frac{1}{2} \left(\frac{1}{\sqrt{N}} + \frac{1}{\sqrt{N}} \right)^2 \\ \boxed{\phi_{1,c}(N_1 = 1 < N_2) = 0.5} & & \boxed{\chi_c(N_1 = 1 < N_2) = \frac{2}{N}} & \end{aligned}$$

□

2. a) Estimate the Flory interaction parameter χ between polystyrene and polybutadiene at room temperature if the solubility parameter of polystyrene is $\delta_{\text{PS}} = 18.7 \text{ MPa}^{1/2}$ and the solubility parameter for polybutadiene is $\delta_{\text{PB}} = 16.2 \text{ MPa}^{1/2}$. For simplicity assume $v_0 = 100 \text{ \AA}^3$.

Answer. From class, the enthalpy of mixing per site for polystyrene and polybutadiene can be shown to be

$$\frac{\Delta H_M}{k_B T} = \chi \phi_{\text{PS}} \phi_{\text{PB}}$$

It follows that the enthalpy of mixing per mole of sites is

$$\frac{\Delta H_M}{RT} = \chi \phi_{\text{PS}} \phi_{\text{PB}}$$

Additionally, the Hildebrand equation (from class^[1]) states that the enthalpy of mixing per mole of sites is

$$\Delta H_M = V_m \phi_{\text{PS}} \phi_{\text{PB}} (\delta_{\text{PS}} - \delta_{\text{PB}})^2$$

where the units are RT . Since V_m is the average molar volume of the monomers, we have by definition that

$$V_m = N_A v_0$$

where N_A denotes Avogadro's number. Thus, equating the first two expressions for ΔH_M and substituting in the above affords

$$\begin{aligned} \chi \phi_{\text{PS}} \phi_{\text{PB}} RT &= N_A v_0 \phi_{\text{PS}} \phi_{\text{PB}} (\delta_{\text{PS}} - \delta_{\text{PB}})^2 \\ \chi &\approx \frac{(6.02 \times 10^{23} \text{ mol}^{-1})(100 \text{ \AA}^3)(18.7 \text{ MPa}^{1/2} - 16.2 \text{ MPa}^{1/2})^2}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} \\ &= \frac{(6.02 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})(6.25 \times 10^6 \text{ Pa})}{2476.38 \text{ J mol}^{-1}} \\ \boxed{\chi \approx 0.152} \end{aligned}$$

□

- b) Show explicitly that Flory's χ parameter is always positive for nonpolar molecules whose interaction can be described by the London dispersion potential (van der Waals interaction) given by

$$\varepsilon_{ij} = -\frac{k\alpha_i\alpha_j}{r^6}$$

where α_i is the polarizability of molecule i , k is a universal constant, and r is the distance between molecules. Explain your assumptions.

Answer. By definition,

$$\chi = \frac{z}{k_B T} \left[\varepsilon_{12} - \frac{1}{2} (\varepsilon_{11} + \varepsilon_{22}) \right]$$

It follows that

$$\begin{aligned} \chi &= \frac{z}{k_B T} \left[-\frac{k\alpha_1\alpha_2}{r^6} - \frac{1}{2} \left(-\frac{k\alpha_1^2}{r^6} - \frac{k\alpha_2^2}{r^6} \right) \right] \\ &= \frac{zk}{2k_B Tr^6} [-2\alpha_1\alpha_2 + (\alpha_1^2 + \alpha_2^2)] \\ &= \frac{zk}{2k_B Tr^6} (\alpha_1 - \alpha_2)^2 \\ &> 0 \end{aligned}$$

¹Rubinstein and Colby (2003, p. 144) contains an alternate statement of the Hildebrand equation that directly includes v_0 . This problem could be equivalently solved using this statement.

as desired.

I assume that $z, k > 0$; unless we are in a gas, $z > 0$ is safe to assume, and I will have to take $k > 0$ for granted since I have no other information about it. I also assume $\alpha_1 \neq \alpha_2$; if they are equal, then the enthalpy of mixing will be zero (no greater forces than the ones already present) and mixing will be purely entropically driven. Lastly, I make all of the assumptions used in the derivation of the Flory χ parameter, e.g., mean field. \square

3. a) What is the critical value of χ required for high molecular mass polymers to dissolve in a solvent in all proportions?

Answer. Given high molecular mass polymers 1 and 2 with degrees of polymerization N_1 and N_2 , Q1e tells us that

$$\boxed{\chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}} \right)^2}$$

\square

- b) For a polystyrene-polybutadiene blend, explain under what temperature conditions you expect to find a homogeneously mixed system if the molecular weight of polystyrene is 10^5 g/mol and polybutadiene is 10^4 g/mol. The structures of these two polymers can be found in the literature/online. Describe these temperature conditions at all compositions — in other words, at what temperature can you guarantee a homogeneously mixed system for any composition? Assume that χ can be expressed as

$$\chi = \frac{A}{T}$$

where A is a constant you need to determine. Note that the solubility parameters for this system are given in Q2.

Answer. From Q2a, we know that a polystyrene-polybutadiene blend at room temperature has $\chi \approx 0.152$. Thus,

$$A = \chi T \approx (0.152)(298 \text{ K}) \approx 45 \text{ K}$$

The molecular weight of styrene is 104.15 g/mol and the molecular weight of butadiene is 54.09 g/mol. Thus, the degree of polymerization of each component is

$$N_{\text{PS}} \approx 960.$$

$$N_{\text{PB}} \approx 185$$

Therefore, the critical temperature T_c at and above which we can guarantee a homogeneously mixed system for any composition is

$$\begin{aligned} T_c &= \frac{A}{\chi_c} \\ &= \frac{2A}{\left(N_{\text{PS}}^{-1/2} + N_{\text{PB}}^{-1/2} \right)^2} \\ &= \frac{2(45 \text{ K})}{\left(960^{-1/2} + 185^{-1/2} \right)^2} \\ T_c &\approx 8041 \text{ K} \end{aligned}$$

\square

- c) Polymer solutions are not well described by the mean-field theory because the connectivity of the chain keeps monomers from being uniformly distributed in solution (particularly at low polymer concentrations). An empirical form that better relates χ to the Hildebrand solubility parameter in polymer solutions is widely used with an entropic part of χ of 0.34, as follows.

$$\chi = 0.34 + \frac{v_0}{k_B T} (\delta_A - \delta_B)^2$$

Using this formula and the following table, decide which solvents will dissolve poly(dimethyl siloxane), for which $\delta_{\text{PDMS}} = 14.9 \text{ MPa}^{1/2}$ and which will dissolve polystyrene ($\delta_{\text{PS}} = 18.7 \text{ MPa}^{1/2}$) at room temperature.

Solvent	<i>n</i> -Heptane	Cyclohexane	Benzene	Chloroform	Acetone
Molar volume (cm ³ /mol)	195.9	108.5	29.4	80.7	74.0
Solubility parameter (MPa ^{1/2})	15.1	16.8	18.6	19.0	20.3

Answer. From Q1e, $\chi_c \rightarrow 1/2^+$ for a solvent-polymer blend as $N_2 \rightarrow \infty$. Thus, if our calculated values of $\chi \leq 1/2$, we can be confident that mixing will occur in all proportions. Let's begin.

For a mixture of PDMS in *n*-heptane at room temperature, we have that

$$\begin{aligned} \chi &= 0.34 + \frac{V_m(\text{H}_2\text{P}_2\text{H})}{RT} (\delta_{\text{PDMS}} - \delta_{\text{H}_2\text{P}_2\text{H}})^2 \\ &= 0.34 + \frac{1.959 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (14.9 \text{ MPa}^{1/2} - 15.1 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2} \end{aligned}$$

and hence [PDMS dissolves in *n*-heptane.]

For a mixture of PS in *n*-heptane at room temperature, we have that

$$\begin{aligned} \chi &= 0.34 + \frac{V_m(\text{H}_2\text{P}_2\text{H})}{RT} (\delta_{\text{PS}} - \delta_{\text{H}_2\text{P}_2\text{H}})^2 \\ &= 0.34 + \frac{1.959 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (18.7 \text{ MPa}^{1/2} - 15.1 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2} \end{aligned}$$

and hence [PS dissolves in *n*-heptane.]

For a mixture of PDMS in cyclohexane at room temperature, we have that

$$\begin{aligned} \chi &= 0.34 + \frac{V_m(\text{C}_6\text{H}_{14})}{RT} (\delta_{\text{PDMS}} - \delta_{\text{C}_6\text{H}_{14}})^2 \\ &= 0.34 + \frac{1.085 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (14.9 \text{ MPa}^{1/2} - 16.8 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2} \end{aligned}$$

and hence [PDMS dissolves in cyclohexane.]

For a mixture of PS in cyclohexane at room temperature, we have that

$$\begin{aligned} \chi &= 0.34 + \frac{V_m(\text{C}_6\text{H}_{14})}{RT} (\delta_{\text{PS}} - \delta_{\text{C}_6\text{H}_{14}})^2 \\ &= 0.34 + \frac{1.085 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (18.7 \text{ MPa}^{1/2} - 16.8 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2} \end{aligned}$$

and hence [PS dissolves in cyclohexane.]

For a mixture of PDMS in benzene at room temperature, we have that

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{PhH})}{RT} (\delta_{\text{PDMS}} - \delta_{\text{PhH}})^2 \\ &= 0.34 + \frac{2.94 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (14.9 \text{ MPa}^{1/2} - 18.6 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2}\end{aligned}$$

and hence [PDMS dissolves in benzene.]

For a mixture of PS in benzene at room temperature, we have that

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{PhH})}{RT} (\delta_{\text{PS}} - \delta_{\text{PhH}})^2 \\ &= 0.34 + \frac{2.94 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (18.7 \text{ MPa}^{1/2} - 18.6 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2}\end{aligned}$$

and hence [PS dissolves in benzene.]

For a mixture of PDMS in chloroform at room temperature, we have that

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{CHCl}_3)}{RT} (\delta_{\text{PDMS}} - \delta_{\text{CHCl}_3})^2 \\ &= 0.34 + \frac{8.07 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (14.9 \text{ MPa}^{1/2} - 19.0 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2}\end{aligned}$$

and hence [PDMS dissolves in chloroform.]

For a mixture of PS in chloroform at room temperature, we have that

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{CHCl}_3)}{RT} (\delta_{\text{PS}} - \delta_{\text{CHCl}_3})^2 \\ &= 0.34 + \frac{8.07 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (18.7 \text{ MPa}^{1/2} - 19.0 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2}\end{aligned}$$

and hence [PS dissolves in chloroform.]

For a mixture of PDMS in acetone at room temperature, we have that

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{Ace})}{RT} (\delta_{\text{PDMS}} - \delta_{\text{Ace}})^2 \\ &= 0.34 + \frac{7.40 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (14.9 \text{ MPa}^{1/2} - 20.3 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2}\end{aligned}$$

and hence [PDMS dissolves in acetone.]

For a mixture of PS in acetone at room temperature, we have that

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{Ace})}{RT} (\delta_{\text{PS}} - \delta_{\text{Ace}})^2 \\ &= 0.34 + \frac{7.40 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (18.7 \text{ MPa}^{1/2} - 20.3 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2}\end{aligned}$$

and hence PS dissolves in acetone. □

4. The area per chain Σ of polymers attached to a surface or interface is an important quantity that influences the thickness of the polymer layer in any resulting morphologies. In general, when the area per chain of the polymer attached to an interface is small enough to induce elongation of the polymer away from that interface, we call this stretched morphology a **polymer brush**. Microphase separated diblock copolymers can be thought of as similar to polymer brushes, where each block is “attached” to the IMDS and elongates away from it.

- a) For a microphase-separated compositionally symmetric diblock copolymer, qualitatively explain the free energy contributions that determine the optimal elongation of polymer chains away from the IMDS.

Answer. For such a system, there will be an enthalpic and entropic contribution to the free energy functional. The entropic term deals with the fact that to maximize entropy, the homogeneous strands would like to entangle on both sides of the interface (entropy is minimized when the strands are perfectly straight). The enthalpic term deals with the fact that there is more interaction energy when everything is straight because the most alike monomers are closest to each other.

A series of variables contribute to both the entropic and enthalpic terms; among them are the temperature, segment length, number of steps, and Flory interaction parameter between the two species. □

- b) Consider a linear ABC terpolymer and a 3 arm ABC star terpolymer, each consisting of 33.3% of the respective A, B and C blocks. Where do you think the center of the star polymer will be pinned?

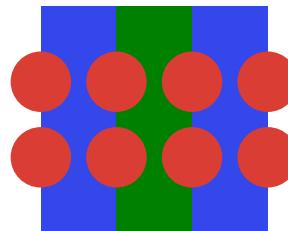
Answer. I think the morphology of choice will be parallel cylinders in an almost hexagonal grid, with each junction in the grid being the center of a star polymer. This would allow each cylinder to be composed of the like strands of three different molecules. □

Carefully draw a to-scale representation of the expected morphology in the melt state for each type of pure macromolecule for...

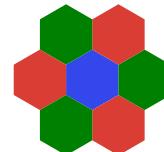
- i) A system where all the χ parameters are positive and equal and the degree of polymerization of each arm is sufficiently large so that microphase separation occurs;

Answer. A positive χ parameter likely corresponds to demixing and microphase separation, as the problem statement indicates.

For the ABC triblock copolymer, we expect cylinders of B in an alternating sea of A and C. This is because each strand is 66.6% the end segments, so these will constitute the majority of the material and alternate lamellarily, while the relatively smaller amount of the middle segment gathers in cylinders.



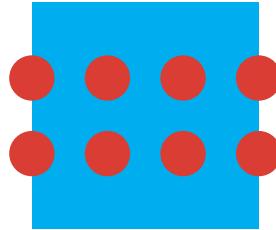
For the star polymer, as mentioned, we will form a kind of hexagonal lattice.



□

- ii) A system where $\chi_{AB} = \chi_{BC} > 0$ while χ_{AC} is negative.

Answer. What we essentially have here is a biphasic system, where the A and C components will form one phase and component B will form a different phase. Thus, from the perspective of the B chain, the A/C mixed phase will be at one end regardless of architecture. Thus, for both architectures, the expected morphology for a 33% distribution is cylinders, as follows. Note that the A/C blue/green mixed phase is colored cyan.



□

5. A common example of a polymer brush in real systems consists of homopolymers grafted to a solid surface. Think of this as hairs with a sticky end that can bind to a scalp. If each chain grafted to the surface gains in enthalpy $-\varepsilon$ by sticking to the surface...

- a) Describe what grafting density is necessary for a grafted polymer system to be considered a brush (i.e., when chains overlap and stretch away from surface due to excluded volume effects). Qualitatively, under what condition would brush formation be thermodynamically favorable? *Hint:* Think about overlap of polymer chains.

Answer. Brush formation would be thermodynamically favorable under the condition that the decrease in energy caused by the sticking enthalpy is greater than increase in entropy caused by not being constrained to a rigid surface. □

- b) Find the optimal grafting density in chains/area for a polymer brush system in terms of ε . Define any variables you use and remember the effect of steric (excluded volume) interactions.

Answer. From class, we have that

$$\Delta G = \Delta H + \Delta S = v\rho^2 D^2 H - \varepsilon + \frac{H^2}{Na^2} = \frac{vN^2}{D^2 H} - \varepsilon + \frac{H^2}{Na^2}$$

The optimal grafting density is obtained when the optimal height H^* is obtained, i.e., $\partial\Delta G/\partial H = 0$. Solving this constraint, we have

$$\begin{aligned} 0 &= \frac{\partial}{\partial H} \left(\frac{vN^2}{D^2 H} - \varepsilon + \frac{H^2}{Na^2} \right) \Big|_{H^*} \\ &= -\frac{vN^2}{D^2 (H^*)^2} + \frac{2H^*}{Na^2} \\ \frac{vN^3 a^2}{2D^2} &= (H^*)^3 \\ H^* &= \sqrt[3]{\frac{vN^3 a^2}{2D^2}} \end{aligned}$$

□

- c) What is the scaling of the brush height with degree of polymerization in the dense brush regime from part (b)?

Answer. Equal scaling: $H^* \propto N$. □